



Dielectric, nuclear magnetic resonance and x-ray diffraction study of cesium ammonium dihydrogen phosphate
by Steven Carl Louis Meschia

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:

This work represents the first investigation of mixed crystals of cesium ammonium dihydrogen phosphate, abbreviated CADP. Mixed crystals of CADP were grown from solutions with molar ratios of ammonium to cesium, x , of 0.10, 0.20 and 0.40. Analytical chemical analysis revealed that the respective molar ratios of ammonium to cesium incorporated into the crystals, x_a , were 0.057, 0.060 and 0.064. X-ray transmission scattering at room temperature showed that the lattice structure of these crystals was identical to that of the pure cesium dihydrogen phosphate (CDP) crystal: monoclinic with a space group of $P2_1/m$.

^{31}P nuclear magnetic resonance produced at least two distinct minima in the logarithm of the spin-lattice relaxation time versus temperature, corresponding to motion of the acid protons and hindered rotation of the ammonium ions. Good agreement with the measured relaxation rates was obtained by assuming liquid-like hydrogen motion and by considering only dipolar coupling between the phosphorus and hydrogen nuclei.

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The ferroelectric phase transition is analyzed in terms of the quasi-one-dimensional Ising Model.

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STUDY OF CESIUM AMMONIUM DIHYDROGEN PHOSPHATE

BY

STEVEN CARL LOUIS MESCHIA

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style and consistency, and is ready for submission to the College of Graduate Studies.

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Date Dec. 10, 1997

Credibility is a consequence of the method.

-CARL SAGAN, *A DEMON HAUNTED WORLD* (1996)

I dedicate this paper to my inordinately patient wife, Rosa María Nieto López, who encouraged me to complete my thesis after numerous self-imposed deadlines transpired.

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TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	ix
LIST OF FIGURES	x
ABSTRACT	xiii
 1. INTRODUCTION.....	 1
1.1. Motivation	1
1.2. Summary	2
1.3. Definitions.....	3
1.3.1. Material Classification	3
1.3.2. Phase Transitions.....	9
1.3.3. Theoretical Models.....	11
1.3.4. Mixtures	13
1.4. The Pure Parent Crystals	13
1.4.1. Cesium Dihydrogen Phosphate	13
1.4.2. Ammonium Dihydrogen Phosphate	24
1.5. Problem Statement	29
 2. CRYSTAL GROWTH	 30
2.1. Background	30
2.2. Method	30
2.3. Results	33
2.4. Discussion	33
 3. X - RAY DIFFRACTION.....	 34
3.1. Background	34
3.2. Method	35
3.3. Results	36
3.4. Discussion	37
 4. ANALYTICAL CHEMISTRY	 39
4.1. Background	39
4.2. Method	39
4.3. Results	39
4.4. Discussion	40
 5. NUCLEAR MAGNETIC RESONANCE.....	 41
5.1. Background	41

5.2. Method	43
5.3. Results	48
5.4. Discussion	52
6. DIELECTRIC MEASUREMENTS	57
6.1. Background	57
6.2. Method	58
6.2.1. Sample Preparation	58
6.2.2. Electrode Effect	58
6.2.3. Apparatus	59
6.2.4. Thermal Contact	62
6.2.5. Thermal Isolation	64
6.2.6. Temperature Sensor Accuracy	64
6.2.7. Temperature Range	65
6.2.8. Program	65
6.3. Results	65
6.3.1. CDP	66
6.3.2. CADP.10	66
6.3.3. CADP.20	67
6.3.4. CADP.40	70
6.3.5. DCADP.20	70
6.3.6. Pulverization	70
6.4. Discussion	107
6.4.1. Ferroelectric Anomaly	107
6.4.2. Anomalous Conduction	120
6.4.3. Ordinary Protonic Conductivity	124
6.4.4. Effect of Pulverization	128
7. CONCLUSION	133
7.1. Contributions	133
7.2. Future Work	135
BIBLIOGRAPHY	137
APPENDIX	140

LIST OF TABLES

1. CDP Bond Lengths and Angles.....	16
2. Principal Root-Mean-Square Atomic Displacements about Mean Positions in CDP and Angles from the Principal Axes.....	17
3. Crystal Lattice Dimensions and Angles of CADP.	37
4. Crystal Ammonium Concentration, x_A , Versus Solution Concentration Ammonium, x	40
5. Thermal-Electrical Conductivity Ratios of Common Engineering Materials.....	63
6. T_m Along the a Axis Versus Ammonium Solution Concentration, x	108
7. T_m Versus Axis for CADP.20.....	108
8. $J_{ }$ and $J_{\perp}$ for CADP.20 and CDP.	111
9. $T_m(b)$ for CADP.20 and DCADP.20.....	113
10. Summary of Dielectric Responses.	128

LIST OF FIGURES

1. CDP Crystal Structure. (From Ref. 21.).....	16
2. $\epsilon'_b(T)$ of CDP at 1 kHz.....	19
3. $\epsilon'_b(T)$ of CDP at High Frequencies.	19
4. Thermal Conductivity of CDP Along a , b and c Axes.....	22
5. Longitudinal 10 MHz Sound Velocity Along a , b and c Axes.	23
6. ADP Crystal Structure. ⁴⁴	25
7. Schematic of a Typical CADP Crystal for All Grown Concentrations.....	33
8. Schematic of Pulsed NMR Apparatus with Quadrature Detection.	44
9. Free Induction Decay in CADP.20 at $T = 326$ K.	49
10. Fourier-Transformed Free Induction Decay at $T = 326$ K in CADP.20.....	49
11. Fourier-Transformed, Phase-Adjusted, Baseline-Corrected FID at $T =$ 326 K in CADP.20.	50
12. Magnetization Versus Delay Between Pulse and Echo Formation at $T =$ 326 K in CADP.20.	50
13. Plot of $\ln(T_1)$ Versus Inverse Temperature	51
14. Model Showing Minimum Atomic Distances ($\text{\AA}$).	54
15. Model Showing Minimum Ammonium-Phosphorus Atomic Distances ($\text{\AA}$).....	55
16. Dielectric Apparatus Schematic.....	60
17. $\epsilon'_c(T)$ upon Cooling of CDP.....	72
18. $\epsilon''_c(T)$ upon Cooling of CDP.	73
19. $\epsilon'_c(T)$ upon Heating of CDP.....	74
20. $\epsilon''_c(T)$ upon Heating of CDP.....	75
21. $\epsilon'_c(T)$ upon Cooling of CADP.10.....	76
22. $\epsilon''_c(T)$ upon Cooling of CADP.10.	77
23. $\epsilon'_c(T)$ upon Heating of CADP.10.	78
24. $\epsilon''_c(T)$ upon Heating of CADP.10.....	79
25. $\epsilon'_a(T)$ upon Cooling of CADP.20.....	80
26. $\epsilon''_a(T)$ upon Cooling of CADP.20.	81

27. $\epsilon'_a(T)$ upon Heating of CADP.20.	82
28. $\epsilon''_a(T)$ upon Heating of CADP.20.	83
29. $\sigma'_a(T)$ upon Heating of CADP.20.	84
30. $\epsilon'_b(T)$ upon Cooling of CADP.20.	85
31. $\epsilon''_b(T)$ upon Cooling of CADP.20.	86
32. $\epsilon'_c(T)$ upon Cooling of CADP.20.	87
33. $\epsilon''_c(T)$ upon Cooling of CADP.20.	88
34. $\epsilon'_c(T)$ upon Heating of CADP.20.	89
35. $\epsilon''_c(T)$ upon Heating of CADP.20.	90
36. $\sigma'_c(T)$ upon Heating of CADP.20.	91
37. Magnified $\epsilon'_c(T)$ upon Heating of CADP.20.	92
38. Magnified $\epsilon''_c(T)$ upon Heating of CADP.20.	93
39. $\epsilon'_c(T)$ upon Cooling of CADP.40.	94
40. $\epsilon''_c(T)$ upon Cooling of CADP.40.	95
41. $\epsilon'_b(T)$ upon Cooling of DCADP.20.	96
42. $\epsilon''_b(T)$ upon Cooling of DCADP.20.	97
43. $\epsilon'_c(T)$ upon Cooling of DCADP.20.	98
44. $\epsilon''_c(T)$ upon Cooling of DCADP.20.	99
45. $\epsilon'_c(T)$ upon Heating of DCADP.20.	100
46. $\epsilon''_c(T)$ upon Heating of DCADP.20.	101
47. $\epsilon'(T)$ upon Cooling of CADP.20 Powder.	102
48. $\epsilon''(T)$ upon Cooling of CADP.20 Powder.	103
49. $\epsilon'(T)$ upon Heating of CADP.20 Powder.	104
50. $\epsilon''(T)$ upon Heating of CADP.20 Powder.	105
51. Magnified $\epsilon''(T)$ upon Cooling of CADP.20 Powder.	106
52. Quasi-One-Dimensional Ising Fit to $\epsilon'_b(T)$ for CADP.20.	112
53. T_m Versus Bias Field for CADP.20.	114
54. T_m Versus Bias Field for ϵ'_b in DCADP.20.	114
55. $\epsilon_b'(T)$ Peak Height Versus Electric Bias Field for CADP.20.	115

56. Quasi-One-Dimensional Ising Fit to $1/\epsilon'_b(T)$ for DCADP.20.....	116
57. $\epsilon''_c(f)$ Versus $\epsilon'_c(f)$ for CADP.20 upon Heating at $T = 250$ K.	118
58. E_A and σ_0 Versus $1/kT$	127
59. $\epsilon'_a(T)$ Upon Heating of DRADP.20.	131
60. $\epsilon''_b(f; T)$ Versus $\epsilon'_b(f; T)$ upon Cooling of CADP.20.	132
61. Front Panel of Dielectric Measurement Program.....	143
62. Frame 0 of Dielectric Measurement Program.....	144
63. Frame 1 of Dielectric Measurement Program.....	145
64. Subframe 0 of Frame 2 of Dielectric Measurement Program.....	146
65. Subframe 1 of Frame 2 of Dielectric Measurement Program.....	147
66. Subframe 2 of Frame 2 of Dielectric Measurement Program.....	148
67. Subframe 0 of Frame 3 of Dielectric Measurement Program.....	149
68. Subframe 1 of Frame 3 of Dielectric Measurement Program.....	150
69. Subframe 2 of Frame 3 of Dielectric Measurement Program.....	151
70. Subframe 3 of Frame 3 of Dielectric Measurement Program.....	152
71. "Dielectric Permittivity" Diagram.....	153
72. "Rename if Duplicate" Diagram.....	153

ABSTRACT

This work represents the first investigation of mixed crystals of cesium ammonium dihydrogen phosphate, abbreviated CADP. Mixed crystals of CADP were grown from solutions with molar ratios of ammonium to cesium, x , of 0.10, 0.20 and 0.40. Analytical chemical analysis revealed that the respective molar ratios of ammonium to cesium incorporated into the crystals, x_A , were 0.057, 0.060 and 0.064. X-ray transmission scattering at room temperature showed that the lattice structure of these crystals was identical to that of the pure cesium dihydrogen phosphate (CDP) crystal: monoclinic with a space group of $P2_1/m$.

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The ferroelectric phase transition is analyzed in terms of the quasi-one-dimensional Ising Model.

1. INTRODUCTION

1.1. MOTIVATION

Phase transitions are important characteristics of many diverse physical systems because of the abrupt changes in some of the associated physical properties. Ferroelectrics provide a simple example for phase transitions, in general, and are technologically interesting because of their strong coupling of electrical fields with mechanical displacements, thermal fluctuations and optical transmission. Because members of the chemical family of potassium dihydrogen phosphate, abbreviated KDP, possess simple structures that exhibit ferroelectric behavior, they are consummate ferroelectrics for basic scientific investigation: At atmospheric pressure and sufficiently low temperatures, KDP, rubidium dihydrogen phosphate (RDP) and cesium dihydrogen phosphate (CDP) and the corresponding arsenates (KH_2AsO_4 , RbH_2AsO_4 and CsH_2AsO_4) all become ferroelectric, whereas ammonium dihydrogen phosphate (ADP) becomes antiferroelectric. No (anti-) ferroelectric phase transitions have been observed in the remaining chemical isomorphs, sodium dihydrogen phosphate and lithium dihydrogen phosphate. It is widely accepted that the displacement of the hydrogen atoms is largely responsible for the interesting dielectric behavior in this family.

One of the most powerful methods for understanding transitional behavior consists of mixing isomorphs that have different preferred orderings. It is thus interesting to mix varying concentrations of ferroelectric and antiferroelectric members of the KDP family of chemical isomorphs in order to observe what phases or metastable states are

avored in various temperature-concentration regions. In such ferroelectric-antiferroelectric mixtures, many distinct polar states have been observed, including temporal and spatial mixtures of these two phases, a paraelectric phase and a distinct glass phase.

The mixed crystals of cesium ammonium dihydrogen phosphate, $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$, abbreviated CADPx, investigated in this work are especially interesting because they are the only known quasi-one-dimensional crystals of the KDP chemical family of ferroelectrics. Although, in order to simplify the physical modeling, mixed three-dimensional systems have sometimes been approximated as one-dimensional systems, this work will demonstrate that CADP exhibits strikingly different behavior from its three-dimensional brethren.

1.2. SUMMARY

The introduction will first define key terms used in the text. This section will also include a review of the behavior of each of the parent isomorphs of CADP: CDP and ADP.

The next section will describe the background, procedure, equipment and results for each of the experimental techniques used: crystal growth, x-ray transmission analysis, chemical analysis, nuclear magnetic resonance (NMR) and dielectric permittivity measurements. The section on crystal growth will describe how the crystals were grown from slow evaporation. The section on x-ray analysis will present the cell dimensions, crystal structure, orientation information and ammonium concentration. The section on

NMR will complement the dielectric measurements because they are nuclei specific and determine motional rates in a much higher frequency range. The dielectric measurements will determine the macroscopic response of the crystal to external electric fields. These measurements will help to identify phase transitions and motional rates of charged particles in the crystal.

A theoretical section will interpret the results according to quasi-one-dimensional Ising model. It will also include comparisons with the three-dimensionally ordered KDP isomorphs, including the chemically closest relative of CADP to have been studied, namely CDA.

Finally, the main contributions of this work to the field of phase transitions will be presented.

1.3. DEFINITIONS

1.3.1. Material Classification

A *dielectric* is any material having a very low electrical conductivity, say, below 10^{-6} S m^{-1} .

In addition to other terms, the Gibbs free energy, G , may be expanded in terms of the applied electrical and mechanical strains, P and x , respectively:

$$G(x, P) = \frac{1}{2} \sum \chi_{ij} P_i P_j + \frac{1}{3} \sum \omega_{ijk} P_i P_j P_k + \frac{1}{2} \sum c_{ijkl} x_{ij} x_{kl} +$$

Equation 1

$$\sum a_{ijk} x_{ik} P_k + \frac{1}{2} \sum q_{ijkl} x_{ik} P_k P_l + \dots,$$

where the summations are performed over all possible combinations of the subscripts from 1 to 3, where the subscripts represent the three spatial dimensions.¹ In this expansion χ_{ij} is called the reciprocal susceptibility, c_{ijkl} the elastic tensor, a_{ijk} the piezoelectric tensor, q_{ijkl} the electrostrictive tensor and P is referred to as the electrical polarization. For centrosymmetric crystals, odd powers of P vanish. Therefore, the piezoelectric tensor must be zero. Since q_{ijkl} is the coefficient of an even power of the polarization, it is nonzero for all crystals.

On the basis of symmetry considerations, all noncentrosymmetric dielectrics may have a nonzero a_{ijk} , except the cubic 432 point group. Of these twenty piezoelectric classes, ten have a unique *polar* axis, i.e., an axis which has different properties on either end.

In normal polar dielectrics, the polarization values which can be measured upon application of experimentally attainable fields are extremely small. Consequently, the polarization has a negligible effect on their physical properties, such as elastic (piezoelectric), optical (optoelectric) and thermal (pyroelectric) behavior. However, a class of polar dielectrics, known as *ferroelectrics*, exhibit polarization values which are several orders of magnitude higher than those of other polar dielectrics. The name *ferroelectric* arises from the analogy with a *ferromagnet*. Just as a ferromagnet exhibits a spontaneous magnetization and magnetic hysteresis effects, a *ferroelectric* shows spontaneous electrical polarization and electric hysteresis effects. This behavior is evidenced by hysteresis in the dielectric displacement versus externally applied electric field. An *antiferroelectric* is the analogous antipolar dielectric.

A *ferroelectric* differs most significantly from a ferromagnet in that a macroscopic external polarization is not usually apparent in a ferroelectric. There are two reasons for this: (1) The intrinsic electric dipole moment of polar materials is quickly neutralized by mobile charged particles that migrate to the surface from either internal conduction or from the ambient atmosphere. (2) The surface depolarization energy U_E is much larger in ferroelectrics than in ferromagnets, which usually results in *domains*, homogeneously polarized regions whose direction of polarization differs from the directions of polarization of the adjacent regions.² Domains may form in any material either because of imperfections or because they increase the entropy of the sample. However, domains usually form in finite ferroelectrics because of a surface energy U_E which tends to depolarize the crystal: For a spherical particle of volume V and polarization P with a single domain, the depolarizing energy U_E is given by Equation 2.

$$U_E = \frac{P^2 V}{6\epsilon_0}, \quad \text{Equation 2}$$

while, in the Landau approximation, the competing energy of transition U_Q favoring a single domain is given by Equation 3.¹ Here, T_c is the transition temperature and C is the Curie-Weiss constant.

$$U_Q = -\frac{1}{2\epsilon_0 C} T_c P_{sat}^2 V, \quad \text{Equation 3}$$

where P_{sat} is the saturation polarization.

It is possible to compensate for the depolarizing surface energy U_E by, for example, placing the crystal in an electrically conductive medium. If, for a single crystal

at a given temperature T , it is energetically favorable for all of the domains to align in the same direction, the crystal is said to possess a *spontaneous polarization* P_s . All polar materials possess a *spontaneous polarization*, P_s , which, in general, is a function of temperature. Therefore, all of these polar materials will produce a voltage along their polar axis upon a change in temperature. For this reason, polar dielectrics are often referred to as *pyroelectrics*.

A *ferroelectric* is defined as a pyroelectric for which the direction of P_s can be switched by applying a nondestructive electric field. Usually, the crystal becomes both pyroelectric and ferroelectric below a critical temperature, T_c , known as the *Curie point*.

Since polar materials cannot sustain monopolar charges for more than several minutes, it is convenient to consider instead the first moment of charge distribution, the *dipole*. In the interaction between any two dipoles, there are only two minima for the dipolar contribution to the free energy of a polar dielectric corresponding to parallel and antiparallel orientation of the dipoles. This can be seen by inspecting the Hamiltonian for the interaction of two dipole vectors $\vec{\mu}_1$ and $\vec{\mu}_2$ separated by a vector $\vec{r}$:³

$$H = \frac{-3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} + \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3}. \quad \text{Equation 4}$$

A global minimum occurs when $\vec{\mu}_1$, $\vec{\mu}_2$ and $\vec{r}$ are all parallel. However, in any two or three dimensional lattice it is not possible to have all of the dipoles parallel to the adjoining vector $\vec{r}$. If the chains of parallel dipoles approach each other in the other dimensions, then $\vec{r}$ may be nearly perpendicular to $\vec{\mu}_1$ and $\vec{\mu}_2$. In this case the minimum occurs when the dipoles are antiparallel. Which condition is favorable depends on the

particulars of the lattice. For many polar crystals the minimum energy corresponds to having all dipoles pointed in the same direction. However, in an *antipolar* crystal the minimum energy corresponds to having adjacent dipoles with alternating polarity. Sometimes the interaction between more than two dipoles becomes important, resulting in more complicated patterns of alternation of the dipoles. If the ratio of the alternation of the direction of the dipolar polarization to the unit lattice dimension in the direction of the polarization alternation can be expressed exactly by a rational number, then the phase is said to be *commensurate*. If the ratio is an irrational number, the phase is said to be *incommensurate*.

Because of the term $T \cdot S$ in the Gibbs free energy, G , where T is temperature and S is entropy, at sufficiently high temperatures, even in a crystal with negative U_0 , the minimum in G will correspond to complete randomness in the orientation of the dipoles. In analogy with paramagnetism, the nonpolar state above T_c is referred to as the *paraelectric* phase.¹

Some of the KDP isomorphs undergo a nonpolar transition to another phase called the *superionic conductor*. Superionic conductivity is defined by ionic conductivities of more than $10^{-3} \Omega^{-1} \text{ cm}^{-1}$. As the temperature is increased, this phase is preceded by a large, faster-than-exponential increase in the imaginary part of the permittivity. The prototypical superionic conductor is silver iodide.⁴

Materials containing competing interactions, such as mixtures of ferroelectrics and antiferroelectrics, may have *frustration*, a probabilistic distribution of dipolar interactions with variance that is larger than the mean.⁵ A novel state of matter, called the

dipole glass, occurs in such frustrated systems. This state of matter may either be just a non-ergodic and metastable state or a bona fide phase. This state is characterized by a frozen randomness in the orientation of the microscopic polarizations. If protons are the relevant modulators of polarization, then the state is referred to as a *proton glass*. Dipole glass behavior results from frustration and a random distribution of competing interactions.⁶ A dipole glass is characterized by its multiple valley structure in energy configuration space: a practically infinite array of structurally distinct configurations with nearly identical energies, separated by large potential barriers. This state is characterized by the following experimental properties:⁷

- A broad, dispersive (frequency-dependent) cusp in the real part of the dielectric permittivity $\epsilon'(\omega, \tau)$ at T_c that shifts to lower temperatures and increases in magnitude with decreasing frequency in the audio range.
- The imaginary part of the dielectric permittivity $\epsilon''(\omega, \tau)$ shows a relatively sharp maximum T_f^* slightly below T_f , defined as the freezing temperature. The distribution of ϵ'' versus ϵ' is broad and asymmetric: $\epsilon''(\omega, \tau)$ is almost independent of frequency over several decades. The frequency dependence of T_f^* can often be described by a Vogel-Fulcher formula.
- When cooling without applying an external bias field E_B , there is no macroscopic spontaneous or sublattice polarization below T_f , indicating the absence of long-range order.
- By cooling with a small external bias field E_B , a remanent polarization is observed below T_f that decreases logarithmically with time after switching off the field and

depends critically on cooling rate. However, if E_B is switched on below T_f , then the remanent polarization is smaller and decreases more rapidly. This shows the irreversibility of the system below T_f .

- The specific heat does not present the usual sharp anomaly which characterizes most *phase transitions*.

1.3.2. Phase Transitions

A *phase transition* can be investigated by examining the Gibbs free energy, G , of the system. The G is a function of the intensive parameter $= T, \vec{E}, \vec{H}, u, s$ and extensive parameter $\vec{P}$ and $\vec{M}$:

$$G = G(T, \vec{E}, \vec{H}, \dots) = u - T \cdot s - \vec{E} \cdot \vec{P} - \vec{H} \cdot \vec{M} + \dots, \quad \text{Equation 5}$$

where T is temperature and $\vec{E}$ and $\vec{H}$ are the electric and magnetic fields, respectively, u is the internal energy per unit volume, s is the entropy per unit volume, $\vec{P}$ is the electric polarization and $\vec{M}$ is the magnetization. The equilibrium state of a phase is obtained by simultaneously minimizing $G(T, \vec{E}, \vec{H}, \dots)$ with respect to the extensive variables, f_i :

$$\begin{aligned} \frac{\partial G(T, \vec{E}, \vec{H}, \dots)}{\partial f_i} &= 0, \quad \forall f_i \\ \frac{\partial^2 G(T, \vec{E}, \vec{H}, \dots)}{\partial f_i \partial f_j} &= 0, \quad \forall f_i, f_j \end{aligned} \quad \text{Equation 6}$$

With the sole exception of Bose-Einstein condensation, the thermodynamic functions of noninteracting systems are both smooth and continuous.⁸

Interparticle interactions in the class of systems exhibiting phase transitions cannot be removed by a transformation of the coordinate system of the problem;

accordingly, the energy levels of the system are not simply related to those of the interacting constituents. Rather, one often finds a strong, cooperative interaction at a critical point in the relevant f_i . If the relevant parameter is temperature, then the critical point T_c is called the *transition temperature or critical temperature*. Usually a rearrangement of the physical system occurs at a critical point. A decrease in the entropy S will, by definition, lead to an increase in order, implying a decrease in symmetry.

Typically, phase transitions are characterized by analytic discontinuities in the first or second derivatives of the relevant parameter. A *phase transition* is called a *first order* or *second order* transition depending on whether the discontinuity in the thermodynamic function, i.e., G , is in the first or second derivative with respect to the relevant parameter.⁹ In practice, however, the order of a phase transition may be obscured by crystal imperfections and impurities.

In a first order phase transition there is a discontinuity in the entropy, $S = -\partial G/\partial T$, and a divergence in the specific heat, $C_p = -T\partial^2 G/\partial T^2$. At T_c multiple phases may coexist at equilibrium.¹⁰ Because of this coexistence, thermal hysteresis also occurs. The dependence of T_c on the extensive parameters of state x_i and their corresponding intrinsic parameters f_i is described by the Clausius-Clapeyron equation:

$$\frac{\partial T_c}{\partial f_i} = \frac{\Delta x_i}{\Delta S} \quad \text{Equation 7}$$

In a second order phase transition the dependence of the free enthalpy G on the temperature is continuous at T_c . There is no heat of transition Q and no coexistence of phases at the critical point. Since both phases are identical at T_c , the group of symmetry

of the low temperature phase must be a subset of the group of symmetry of the high temperature phase. The second order phase transition exhibits a characteristic behavior around T_c that is characterized by *scaling relations* and *power laws*; these exponents are independent of the microscopic details of the interaction, but depend instead on global parameters such as the range of the interactions and the dimensionality of both the system and the order parameter.¹¹

1.3.3. Theoretical Models

There are several successful approaches to the general theory of phase transitions. The theories that have been most successful are the microscopic *Ising Model*, the macroscopic, phenomenological *Landau theory* and renormalization group theory. The Ising model considers quantum-mechanical interactions between nearest-neighboring spins and long-range interactions with the mean field produced by all of the spins. The Landau theory is a macroscopic theory of phase transitions based on the concept of the order parameter, η , which permits a qualitative and occasionally quantitative description of phase transitions.¹² η is the physical quantity that is responsible for breaking the symmetry as the sample undergoes a transition in a low-temperature phase.

The microscopic theory of structural phase transitions in polar materials is based on the model Hamiltonian, H , given in Equation 8, where p_k represents the polarization of the k^{th} nucleus, J_{ij} is the coupling constant between the i^{th} and j^{th} nuclei and E is the external electric field.

$$H = \sum_j \left\{ \sum_{i, i > j} J_{ij} p_i p_j \right\} + E \sum_j p_j + \text{anisotropy terms}, \quad \text{Equation 8}$$

Here the interaction term is assumed to depend only on the separation $r_i - r_j$ and has translational symmetry. The predictions for the rate of decay of the order parameter P (Equation 9), the static susceptibility χ (Equation 10) and the correlation length ξ (Equation 11) as the temperature T approaches the critical temperature T_c are given below.

$$P \equiv \begin{cases} (T_c - T)^\beta & T < T_c \\ 0 & T > T_c \end{cases}, \quad \text{Equation 9}$$

$$\chi = \frac{\partial P}{\partial E} \equiv |T - T_c|^{-\gamma}, \quad \text{Equation 10}$$

$$\xi = \begin{cases} \infty & T < T_c \\ (T - T_c)^{-\nu} & T > T_c \end{cases} \quad \text{Equation 11}$$

(for Ising-like models $\xi = (T - T_c)^{-\nu}$ for $T < T_c$, as well), and

$$P(t) = P(0)e^{-\alpha t} \quad T > T_c, \quad \text{Equation 12}$$

where $\alpha \sim (T - T_c)^z$.⁵ Here z is a critical exponent that may change as T_c is approached. The transition temperature T_c and the proportionality constants depend on the strength of the interaction, while the critical indices β , γ and ν depend only on the dimensionality of the solid and of the order parameter. This universality is a consequence of the uniformity of the interaction, $J_{ij} = J(r_i - r_j)$, which, in the case of the Ising model, is assumed to be short-range and independent of p .

1.3.4. Mixtures

KH_2PO_4 , RbH_2PO_4 , CsH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ are considered to be *isomorphs*. The term *isomorphs* was coined in 1819 by Mitcherlich who, by studying KDP, KDA (KH_2AsO_4) and ADP, generalized the knowledge of mixtures.¹³ *Isomorphs* are characterized by their ability to form *mixed* systems. This ability to form mixtures was used extensively by Mendeleev in order to help form the periodic table of the elements.¹³

A *mixed* material is a material in which there are two or more *components*, where a *component* is a constituent of a material such that its composition, at least in one aggregate state, does not depend on the concentration of the other parts. A mixture is, therefore, distinct from a *chemical compound*, in which the ratio of constituents must be fixed. There is no essential difference in the number or types of defects between an ordered binary crystal and a single component crystal: the density of *dislocations* is the same; the number of *vacancies* increases insignificantly, if at all.¹³ Theory and experiment show that in an ordered atomic crystal, the fraction of vacancies close to the melting point is 10^{-3} to 10^{-4} , and decreases rapidly as temperature decreases.¹³

1.4. THE PURE PARENT CRYSTALS

1.4.1. Cesium Dihydrogen Phosphate

Paraelectric Phase At ambient temperature and pressure CDP is paraelectric, belonging to the monoclinic space group $\text{P2}_1/\text{m}$.^{14,15,16} The “/m” designates an invariance upon reflection through a mirror plane perpendicular to the principal rotation axis. The 2_1 designates an invariance upon rotation by $2\pi/2$ coupled with a translation of $1/2$ of a unit

translation along the rotation axis. The P (primitive) denotes that there is only one Bravais lattice point per unit cell. The crystal structure of CDP is shown in Figure 1.*²⁰ Hydrogen bonding links the phosphate groups into sheets in the c - b plane. Since there is no hydrogen bonding along the a axis, the crystals cleave very easily perpendicular to that axis. The hydrogens, shown as H(1) and H(2) in Figure 1, are referred to as "acid" hydrogens in order to distinguish them from the hydrogens contained in the ammonium groups in CADP. In contrast to KDP, in which the O(1)-H(1)...O(2) and O(3)-H(2)...O(3)' bonds are equivalent, as seen from Table 1,¹⁷ these bonds have very different lengths in CDP. Table 1 also shows that the phosphate groups are somewhat distorted from regular tetrahedra. Table 2 summarizes the root-mean-square displacements of the atoms in CDP from their equilibrium positions, and the angles, ϕ , of these displacements from the principal axes a , b and c . As seen from Table 2, the longest axes of the thermal vibration ellipsoid of the oxygen atoms in the phosphate groups are perpendicular to the directions of corresponding P-O bonds, corresponding to librational motion.¹⁸

High-resolution magic-angle-spinning NMR confirms the high anisotropy in CDP with a shielding anisotropy $\Delta\sigma \sim 120$ ppm.¹⁹ Neutron scattering studies also have shown extreme anisotropy in the correlations between the order parameter fluctuations.²⁰

NQR studies have shown an ^{17}O EFG tensor that is practically independent of temperature above the ferroelectric transition temperature, T_c , and have shown that the

* In general, there is no well established protocol for assigning the a and c axes. However, the assignment

supposedly paraelectric phase tensor actually corresponds to the average of two "ferroelectric" ones corresponding to the close and far sites in the acid proton bond.²¹ This is incompatible with a displacive type of transition in which the EFG tensor would be strongly temperature dependent above T_c . In other words, the O(3)-H(2)...O(3)' protons move in a double well potential above T_c and freeze into one of two possible states below T_c . Such behavior is only compatible with a dynamic order-disorder model of the transition as seen in PbHPO_4 and KH_2PO_4 . The O-H(1)...O bonds, by contrast, remain ordered above the transition temperature T_c . Therefore, they do not contribute to the ferroelectric behavior in CDP. This is evidenced by the flat NQR line both above and below T_c . The persistence of correlations along the O(3)-H(2)...O(3)' bonds well above T_c suggests that the phase transition is one-dimensional in character since three-dimensional systems should show a discrete transition from an uncorrelated state to a correlated state below T_c .²²

Dielectric measurements confirm the quasi-one-dimensional character of CDP far from T_c , but indicate that the transition is dominated by three-dimensional correlations within 3 K of T_c upon either heating or cooling.²³

of the axes of CDP in most of our references has been consistent with our assignments.

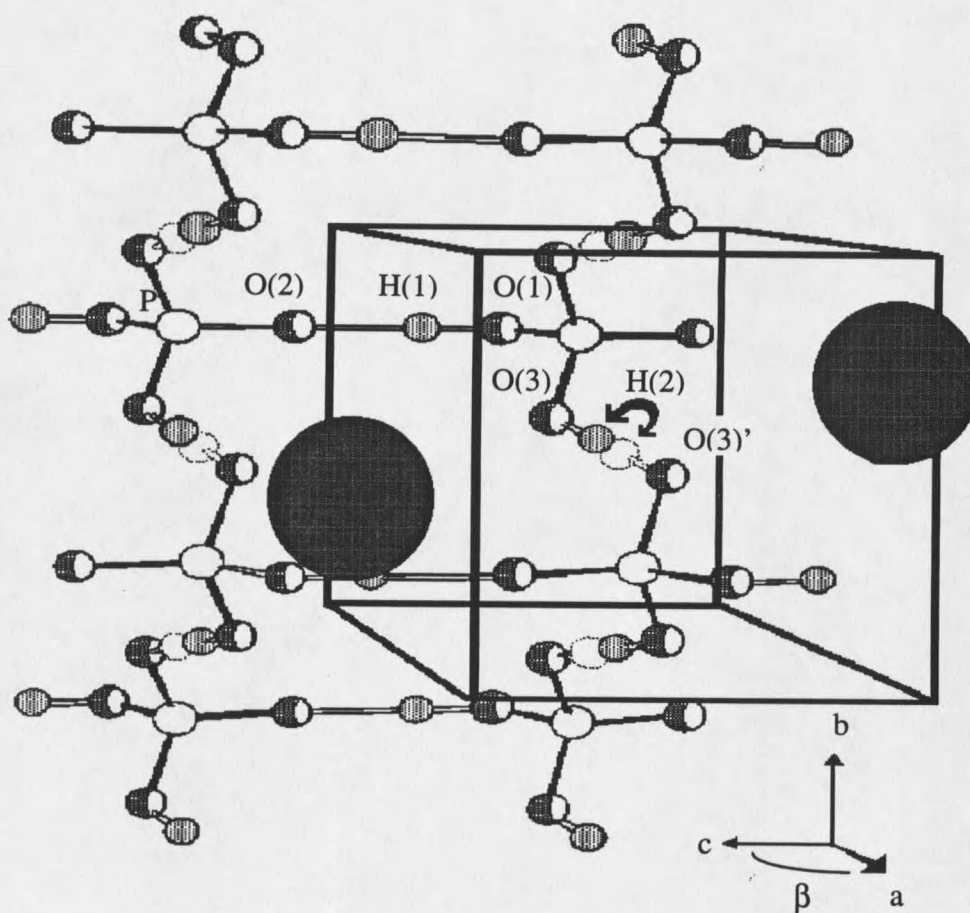


Figure 1. CDP Crystal Structure. (From Ref. 21.)

Atom #1	Atom #2	Bonded	Distance (nm)	Reference
O(1)	H(1)	yes	0.0995(7)	17
O(2)	H(1)	no	0.1530(7)	17
O(1)	O(2)	no	0.2521(7)	17
O(3)	H(2)	yes	0.100(2)	17
O(3')	H(2)	no	0.146(2)	17
O(3)	O(3')	no	0.246(1)	17
H(2)	H(2')	yes	0.48(4)	17
P	O(3)	yes	0.149	16
P	O(4)	yes	0.153	16
P	O(1)	yes	0.161	16
Bonds	Angle			
O(1)-H(1)...O(2)	173.2(5)			4
O(3)-H(2)...O(3')	174.(4)			4

Table 1. CDP Bond Lengths and Angles.

Atom	R.M.S. Displacement	ϕ_a (degrees)	ϕ_b (degrees)	ϕ_c (degrees)
Cs	0.18	5	90	115
	0.16	90	0	90
	0.15	85	90	23
P	0.16	90	0	90
	0.14	152	90	101
	0.10	118	90	11
O(1)	0.19	90	0	90
	0.15	143	90	110
	0.11	53	90	160
O(2)	0.25	90	0	90
	0.21	162	90	90
	0.10	108	90	0
O(3)	0.25	63	124	58
	0.17	150	116	62
	0.15	101	45	45
H(1)	0.14	-	-	-
H(2)	0.23	-	-	-

Table 2. Principal Root-Mean-Square Atomic Displacements about Mean Positions in CDP and Angles from the Principal Axes.

Ferroelectric Phase Transition The O-H(1)...O bonds, aligned along the b axis, have a center of inversion about their midpoints and are thought to be responsible for the ferroelectric phase at ambient pressure and $T_c = 154$ K,¹⁷ which, except for a lack of mirror symmetry, is structurally identical to the paraelectric phase.^{24,25} The crystal, losing its mirror plane of symmetry, is monoclinic with group symmetry $P2_1$. A fit of the specific heat to the Landau theory shows that this phase transition is of the second order with a critical exponent of zero (a logarithmic divergence and a finite discontinuity).²⁶ Upon cooling through T_c the acid hydrogens along the b axis no longer possess sufficient thermal energy to "hop" between the two possible lattice sites with equal probability. As the hydrogen atoms condense, they distort the O(1)-H(1)...O(2) potential for neighboring

hydrogens, making it energetically favorable for all of the hydrogens to be displaced in the same direction along the b axis chain. Although the principal displacement at T_c is that of the acid hydrogens, there is also an appreciable displacement of phosphorus relative to its neighboring oxygens.¹⁶

At T_c CDP exhibits very large anomalies in heat capacity²⁶ and in many of the physical properties that have been measured along the b axis: dielectric permittivity,^{24,26} thermal conductivity and others. Raman scattering studies, however, have not detected any soft mode at T_c .²⁷

The real part of the dielectric permittivity along the b axis as a function of temperature T , $\epsilon'_b(T)$, around T_c is shown in Figure 2. The curve represents data acquired with a 1 kHz alternating electric field with an amplitude of 1 V cm^{-1} .¹⁵ $\epsilon'_b(T)$ at radio frequencies is shown in Figure 2. In this frequency regime only a single dielectric relaxation is observed with a characteristic time τ , which increases in the vicinity of T_c to an extrapolated value of $\tau = 1 \times 10^{-9} \text{ s}$ at T_c .

A paraelectric-ferroelectric-antiferroelectric triple point exists at a pressure of 3.3 kbar and a temperature of 135 K²⁸. DCDP also has such a triple point, occurring at a considerably higher pressure of 6 kbar.²⁹ In the pressure-induced AFE phase in both CDP and DCDP the structure doubles along the a axis due to antiferroelectric stacking of FE ordered b - c planes.³⁰

Neutron scattering studies reveal that both CDP and its deuterated analog, DCDP, have long correlation lengths near T_c . The correlation length in DCDP reaches a maximum of almost 60 nm along the b axis at T_c or more than 180 PO_4 groups, and drops

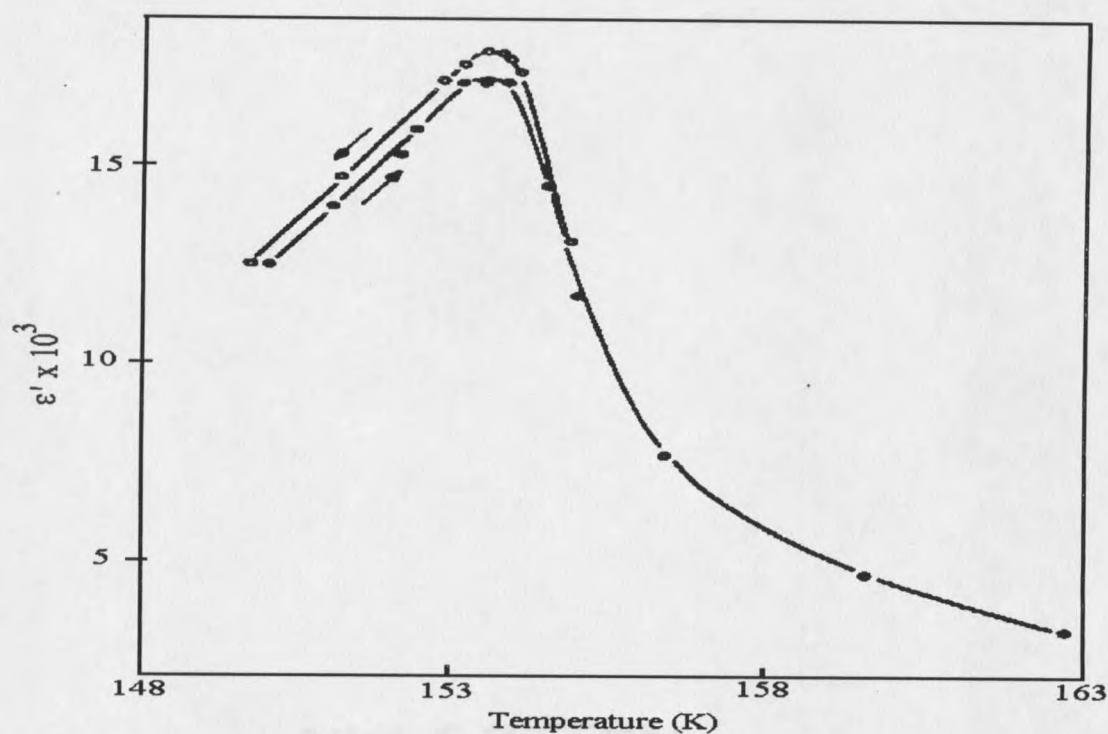


Figure 2. $\epsilon'_b(T)$ of CDP at 1 kHz.

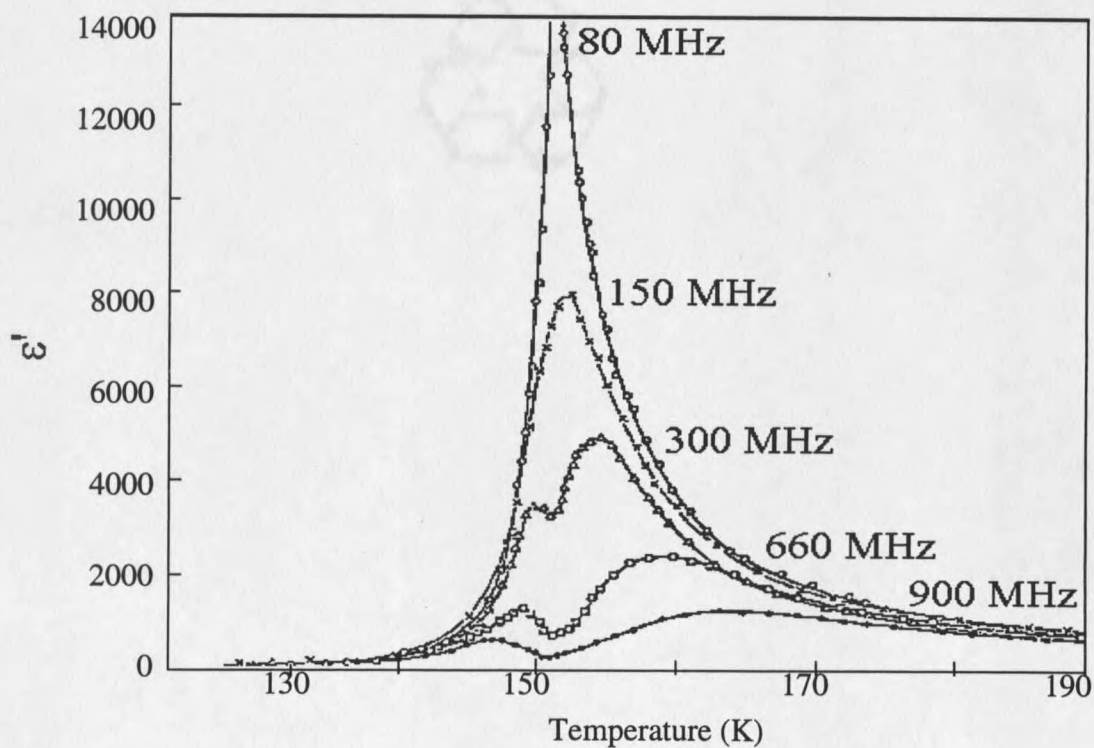


Figure 3. $\epsilon'_b(T)$ of CDP at High Frequencies.

to about 40 nm at 315 K.¹⁶ Such long-range correlations are typical of one-dimensional ordering, which, in the case of CDP, results because the hydrogens bond molecular-ionic groups with very strong local interactions between the protons and the molecular electronic wave functions.¹⁶ The interactions between hydrogens along the *b* axis are one hundred times larger than correlations along the *a* axis and still larger than correlations along the *c* axis.³¹

In contrast to most other ferroelectrics, the dielectric permittivity in CDP cannot be well fit by a Curie-Weiss law. Much better agreement with experiment is obtained with a quasi-one-dimensional Ising model. This model yields the following dependence of the permittivity ϵ' on temperature T :

$$\epsilon'(0) = \epsilon'_\infty + \frac{A}{\exp(-\frac{2J_{\parallel}}{kT}) - \frac{J_{\perp}}{kT}}, \quad A \equiv \frac{n\mu^2}{k_B T}, \quad \text{Equation 13}$$

where ϵ'_∞ is the limiting value of the permittivity at infinite frequency, μ is the dipole moment, n is the number of dipoles per unit volume, k_B is the Boltzmann constant and $J_{\parallel}$ and $J_{\perp}$ are the intra- and inter-chain coupling constants respectively.³² The temperature dependence of the permittivity of CDP in the range of $25 \text{ K} < T - T_c < 200 \text{ K}$ supports the pseudo-one-dimensional nature of the phase transition. However, significant deviations from Equation 13 occur for $T - T_c < 20 \text{ K}$. Dielectric dispersion in both CDP and DCDP is well described by monodispersive relaxation with a characteristic time on the order of $\tau = (1.8 \times 10^{-9} \text{ s K}) / (T - T_c)$.³³

The single-particle dipolar reorientation time is much shorter ($\tau_0 = 1.7 \times 10^{-14}$ s) than that in KH_2PO_4 .³⁴ The dielectric dispersion data in CDP show order parameter relaxation rates in the range of $10^7 - 10^9$ Hz, whereas in KH_2PO_4 the corresponding rates are much higher (10^{11} - 10^{12}).³⁴ Such low relaxation rates are characteristic of one-dimensional systems.

T_c increases from about 160 K in CDP to 264 K in deuterated CDP, DCDP.¹⁵ This remarkable effect of deuteration on T_c has been used to argue that hydrogens play an essential role in the ferroelectric phase transition. The quasi-one-dimensional model does not consistently explain the effects of deuteration: $J_{||}$ decreases by a factor of 2 upon deuteration, but since $J_{||}$ is proportional to μ^2 , P_s should decrease by about 30%, rather than the moderate increase found upon deuteration.

Adiabatic heat capacity studies reveal anomalies in the heat capacities of both CDP and DCDP at T_c : upon heating the heat capacities reach a peak value and then decrease precipitously as the paraelectric phase is reached, with respective magnitudes of $\Delta C_E = 4.5 \pm 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta C_E = 4.9 \pm 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$.²⁶ From the logarithmic divergence of the heat capacity it was determined that the ferroelectric phase transitions in CDP and DCDP are of the second order and that their critical exponents for the specific heat are zero.²⁶

In dielectric¹⁵ measurements around T_c no anomalies other than ordinary protonic conductivity have been observed along either the a and c axes. However, anomalies along all three axes have been observed around T_c both in the sound velocity³⁵, V , and in the thermal conductivity, λ .³⁶ A graph of thermal conductivity versus temperature for CDP is

shown in Figure 4. The anomalies in the ultrasound velocity, V , which is shown in Figure 5, attenuation, α , and energy relaxation time, τ_E , exhibit the usual logarithmic

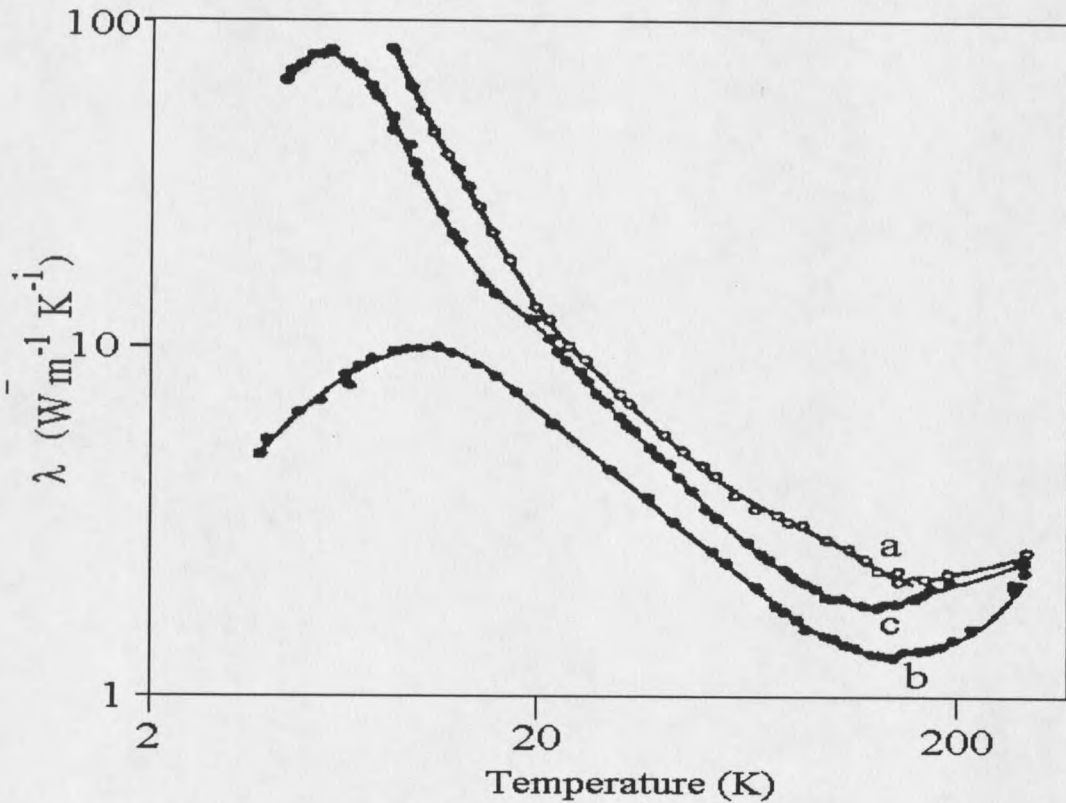


Figure 4. Thermal Conductivity of CDP Along a , b and c Axes.

singularities characteristic of ferroelectric phase transitions: $\Delta V \sim \log(T-T_0)$, $\Delta\alpha^{1/2} \sim \log(T-T_0)$ and $\tau_E \sim (T-T_0)^{-1}$.³⁵ These results, combined with the logarithmic singularity of the heat capacity,³⁷ strongly suggest that the dipole-dipole interaction dominates in the critical anomaly of V in CDP.³⁸ The results in the ultrasound velocity V are considerably more isotropic perhaps because the longitudinal fluctuation of the polarization is suppressed along the b axis, smearing the attenuation of the ultrasound.³⁹ Ultrasound

velocity and attenuation measurements at a frequency of 10 MHz indicated an energy relaxation time³⁷ $\tau_E \cong 1.1 \times 10^{-10}$ s and a polarization relaxation time⁴⁰ $\tau_p \cong 9 \times 10^{-10}$ s.

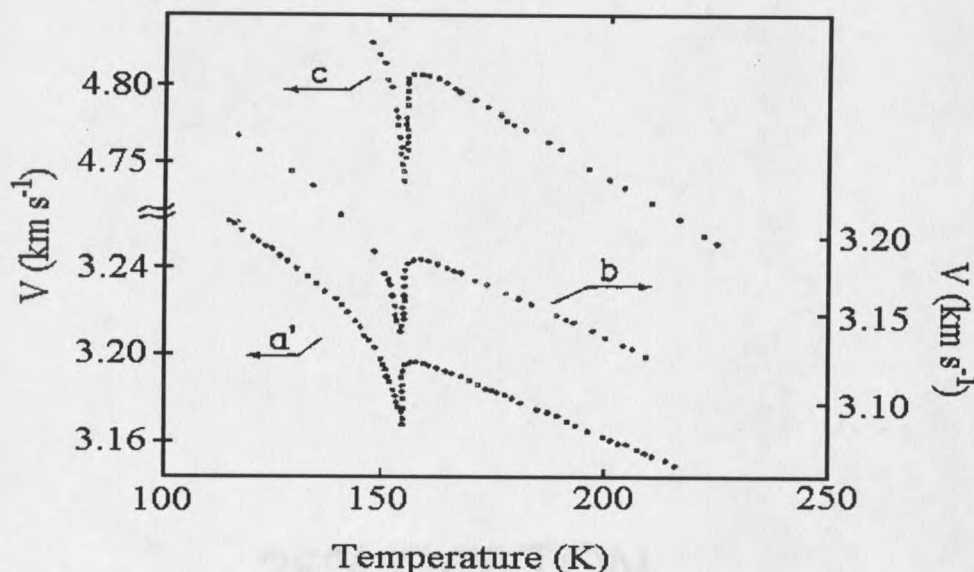


Figure 5. Longitudinal 10 MHz Sound Velocity Along *a*, *b* and *c* Axes.

Ferroelastic Phase As the temperature of the paraelectric phase is raised above 373 K, CDP becomes ferroelastic, but maintains the same point group.⁴¹ The appearance of ferroelasticity suggests the existence of a higher-symmetry prototypic phase, which, in this case, would presumably be orthorhombic.

Superionic Phase On heating to $T = 504$ K, CDP undergoes a first-order, reconstructive phase transition from a monoclinic paraelectric to an apparently cubic superionic conductor.⁴² At the transition the conductivity abruptly increases by a factor of 10^3 to 10^4 . The transition is strongly hysteretic, with CDP returning to the paraelectric state at 482 K on cooling.⁴² In the superionic phase, single domain samples can be seen to become multi-granular, by observing the phase under a polarizing microscope.⁴³

1.4.2. Ammonium Dihydrogen Phosphate

Paraelectric Phase Above a critical transition into an antiferroelectric phase at $T_c = 148$ K, $\text{NH}_4\text{H}_2\text{PO}_4$, ADP, is paraelectric with space group identical to KDP: ADP is a tetragonal paraelectric of the space group $I\bar{4}2d$.⁴⁴ A schematic of the crystal structure in the paraelectric phase of ADP is shown in Figure 6.

Antiferroelectric Phase The transition at T_c produces a discontinuous, first-order drop in the real and imaginary parts of the dielectric permittivity, ϵ .⁴⁵ The antiferroelectric order may be either along the a or b axis. This instability in the direction of ordering results in pronounced thermal hysteresis in T_c and, as different domains in the crystal distort in different directions, large internal stresses, which frequently shatter the crystal.⁴⁶

The structure of ADP in the antiferroelectric phase is D_2^4 with space group $P2_12_12_1$.⁴⁷ In cooling through T_c , the phosphorus and nitrogen ions are displaced along the b axis relative to the oxygen framework. At T_c both the phosphate and ammonium ions become distorted.⁴⁸ In addition, the a and b axes are increased in length by 0.002 nm and 0.004 nm respectively.^{49, 50}

Deuteration dramatically increases T_c to a value, averaged over heating and cooling, of 245 K.⁵¹

Under hydrostatic pressure, ADP behaves similarly to KDP with T_c decreasing as a function of increasing pressure, eventually becoming zero.⁵² This was interpreted in terms of increased tunneling as pressure reduces the hydrogen bond length and the barrier between its minima, but may be more simply interpreted as a classical decrease in the

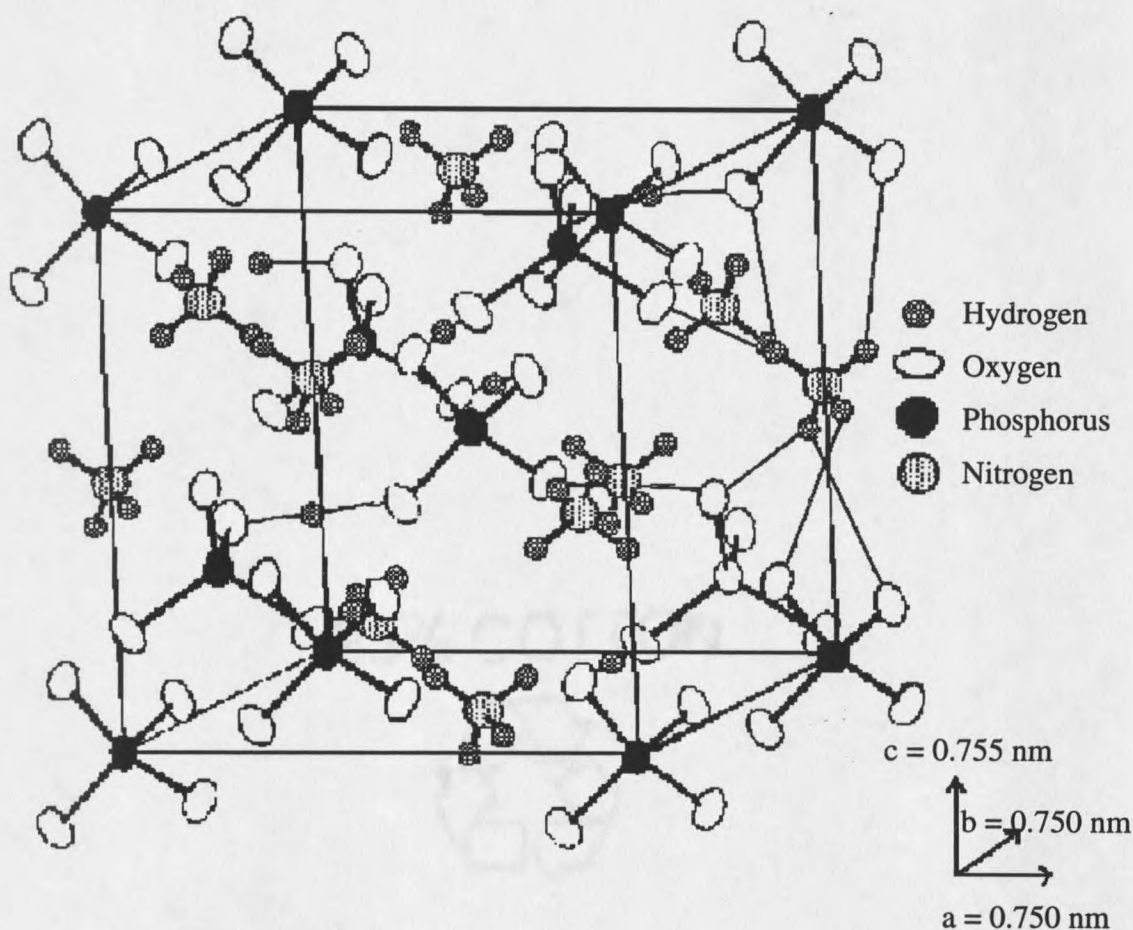


Figure 6. ADP Crystal Structure.⁴⁴

hydrogen O-H...O barrier height resulting from increasing overlap of the O-H and O...H electrostatic potentials.

Low-frequency Raman spectra of ADP show that in the paraelectric phase, there are both B_2 - and E-symmetry lattice modes, just as in KDP.⁵³ In KDP it is the B_2 mode that is soft and overdamped and precipitates the transition to the ferroelectric state. However, in ADP the antiferroelectric transition occurs before either the B_2 or E zone-

center modes approach their condensation points. An ordered phase in ADP should, according to the proton-lattice formalism, be produced by the condensation of an antiferroelectric mode at the zone boundary along the c^* axis, where c^* is the reciprocal lattice vector in the c direction. Such a mode has been observed for deuterated ADP by quasi-elastic neutron scattering.⁵⁴ This scattering confirms the existence of a soft mode at this point and can be understood in terms of an overdamped mode with roughly temperature-independent damping constant and frequency. This indicates that low-frequency excitations are concentrated along the c axis and that the antiferroelectric fluctuations are mainly in the a - b -plane. Proton-lattice coupling is believed to be responsible for the soft mode. This contrasts with KDP where the quasi-elastic scattering occurs in planes along the c axis and polarization fluctuates along the c axis.

High-Temperature Phase Transition In addition to the antiferroelectric phase transition, sharp increases in the conductivity have been measured in ADP at $T_h = 433$ K and in its deuterated analog, DADP, at $T_h = 414.7$ K, and were ascribed to structural phase transitions.^{55,56} These phase transitions are marked by rapid increases upon heating in the real part of the dielectric permittivity, ϵ' , along the a and c axes over a temperature range of about 40 K centered about T_h , followed by a plateau in the response. The plateau values of ϵ' along the c axis are 64 and 125 for ADP and DADP, respectively.⁵⁶ The corresponding plateau values of ϵ' along the a axis are 67 and 202.⁵⁶ The increase in temperature of T_h upon deuteration may be understood in terms of an additional thermal energy required in order to produce free rotation in the heavier deuterated ammonium groups. T_h is considerably hysteretic: along both axes T_h occurs approximately 20 K

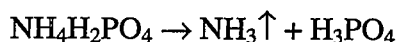
lower upon cooling than upon heating.⁵⁶ It is believed that T_h is related to the transitions occurring in many other ammonium-containing crystals, viz., NH_4Cl , NH_4Br , LiNH_4SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, and that it results from the onset of free rotation of the NH_4^+ ions.⁵⁶ Although a phase transition above T_c also occurs in KDP, it differs fundamentally in nature, decreasing in temperature upon deuteration.⁵⁷ Some authors believe the increase in ϵ' results from the contribution to the polarizability of the freely rotating NH_4^+ groups. However, the ammonium ion is practically rotationally symmetric; its rotation should not have an appreciable direct effect on ϵ' . Instead, others propose that this free rotation contributes hydrogen atoms by allowing the NH_4^+ groups to approach the phosphate groups closely enough to donate protons to the more electronegative phosphate groups.⁶²

Direct Conduction Debate remains on the precise nature of the electrical conduction mechanism in ADP.⁵⁸ Although several groups have observed a discontinuity in the slope of the logarithm of conductivity versus inverse temperature, there is some disagreement regarding the conductivity mechanism, the temperature at which this discontinuity occurs and the values of the associated activation energies.^{56,59,55,56,60} Others did not observe any discontinuity.⁶¹ However, experiments on single crystals of ADP employing guard rings convincingly showed the discontinuity to be a result of surface conductivity.⁶² These measurements showed pure thermally-activated behavior; with a conductivity, σ_T , given by Equation 14.

$$\sigma_T = \sigma_0 \exp(-h / k_B T), \quad \text{Equation 14}$$

where σ_0 is $0.88 \pm 0.14 \Omega^{-1} \text{ cm}^{-1}$ parallel to the c axis and $1.23 \pm 0.15 \Omega^{-1} \text{ cm}^{-1}$ perpendicular to the c axis, and h is $0.65 \pm 0.01 \text{ eV}$ parallel to the c axis and $0.68 \pm 0.01 \text{ eV}$ perpendicular to the c axis, k_B is Boltzmann's constant and T is temperature.⁶²

Surface conduction in ADP may be understood in terms of thermal dissociation: When subjected to temperatures above 313 K, a small fraction of ADP partially dissociates into ammonia gas and phosphoric acid.⁶²



This leaves a thin film of phosphoric acid on the surface, allowing surface conduction which, if not compensated by a guard ring, may be misinterpreted as bulk conduction. However, it also results in higher protonic conductivity by providing protons for conductivity and charge deficient NH_3 lattice sites into which protons may move. In addition to protonic conductivity in ADP, transient ionic current measurements find evidence for conduction by oxygen atoms as well.⁶³ The calculated mobility for oxygen, μ_{O} , is $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and for that of hydrogen, μ_{H} , is $3.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶³

The complete process by which oxygen and hydrogen are transported through the lattice was discovered by comparing the relative intensities of the infrared spectrum in the original, unbiased ADP sample with spectra taken from near the electrodes of biased samples:⁶³ As in KDP, the H_2PO_4^- unit in ADP rotates about the center of the PO_4^- tetrahedra. This rotation results in a geometrically unstable configuration of two adjacent hydroxyl groups, O-H-O-H. This structure dissociates forming a P-O-P bond along with two "free" protons and one "free" oxygen.

1.5. PROBLEM STATEMENT

We investigated, by studying mixed crystals of CADP_x in the region of small x , the nature of the conductivity mechanism, the influence of mixing on the ferroelectric phase transition in CDP, and the extent to which the quasi-one-dimensional Ising model may still apply to this system.

2. CRYSTAL GROWTH

2.1. BACKGROUND

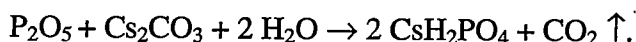
We cannot *a priori* expect that a solution with a molar fraction of ammonium relative to cesium, x , will have an equal molar fraction of ammonium relative to cesium incorporated into the crystal, x_A . In fact, in all multicomponent systems the concentration and microstructure of the crystals depends both on extrinsic growth parameters such as temperature, pressure and solution acidity, and on the particular free energies of the components.⁶⁴ In order for a thermodynamically stable mixture of two components, with free energies given by f_A and f_B , to occur, the free energy, f , must contain a negative term, Δm , corresponding to the free energy of mixing. Since such a term is not guaranteed, it may be impossible to form stable mixtures of some components under particular conditions. If we let x represent the concentration of component B , then the expression for f of a stable mixture of components A and B is given by Equation 15.

$$F = (1-x)f_A + xf_B + \Delta m \quad \text{Equation 15}$$

Since we restrict the study to atmospheric pressure, then by Gibbs' phase rule the phase diagram is two-dimensional (temperature and concentration), and the single-phase system occupies a limited area of the temperature-concentration plot.

2.2. METHOD

CDP was formed by combining equal molar amounts of cesium carbonate, Cs_2CO_3 , and phosphorus pentoxide, P_2O_5 , as shown by the following chemical reaction:



Because P_2O_5 (molecular weight = 141.943) reacts violently with water, it was added very slowly to a beaker containing several times the amount of purified water necessary for the reaction. To the resulting solution of concentrated phosphoric acid, the molar equivalent of Cs_2CO_3 was added (molecular weight = 325.83). Additional Cs_2CO_3 was added until the pH of the solution was 7.0 ± 0.2 , as determined by litmus paper.

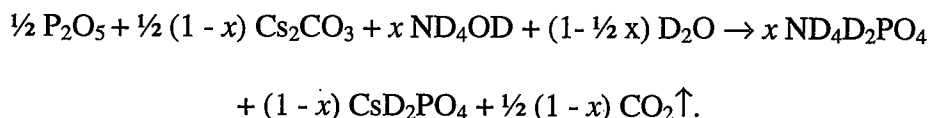
The solution was stirred for several minutes in order to ensure that the chemicals completely reacted. The excess water was slowly evaporated at 30°C for several hours. The resulting solute was pulverized and placed in the desiccator for several more hours in order to desiccate the powder. An analogous procedure was performed with ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, instead of cesium carbonate in order to form ADP. Each of the powders was desiccated and pulverized until the powders no longer clumped. In order to form CADP, $1 - x$ moles of desiccated powder of CDP were then combined with x moles of desiccated ADP for the molar fractions $x = 0.1, 0.2$ and 0.4 , and placed in separate flat-bottomed beakers.

These powder mixtures of CDP and ADP were then redissolved in purified water. The resulting solutions were mixed at room temperature with magnetic stirrers for over eight hours.[†]

[†] This is usually sufficient time for complete randomness of the constituents on the atomic scale, but does not necessarily mean either that the resulting crystal does not have random clustering of ammonium ions or that the concentration of ammonium ions relative to cesium ions necessarily equals that of the solution. In fact, in the next section, we will find that the concentration of ammonium in the crystal was about one eighth of the concentration in the solution.

The solutions were then almost entirely covered with glass lids and allowed to slowly evaporate at $23\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ over a period of months. In order to prevent twinning, the largest untwinned "seed" crystals with well defined habit were occasionally removed from the solution, followed by redissolution of the smaller crystal seeds and replacement of the seed crystals. This was complicated by the fact that the index of refraction of the crystals almost exactly matched that of the solution, rendering the crystals nearly invisible. For each of the concentrations, this method produced several transparent crystals measuring approximately 100 mm^3 .

A deuterated crystal of CADP with ammonium fraction $x = 0.2$, abbreviated DCADP.20, was also grown. In this case, the deuterated analog of ammonium carbonate is not readily available, so DCADP was formed by the following reaction instead:



In order to prevent excessive heating of the solution, many times more D_2O was used than was needed for the reaction.

Because the hydrogens in atmospheric water can readily exchange with deuterons in the crystal, the growth of the deuterated crystals had to occur in an atmosphere devoid of such water, which still allowing for evaporation. Such an atmosphere was achieved by placing the samples in a chamber that was sealed except for two $\frac{1}{4}$ inch tubes, one connected to a tank of inert gas (Ar) and a outlet connected through an oil-filled beaker, in order to prevent the back-flow of ambient air. The inert gas was allowed to slowly flow over the sample.

2.3. RESULTS

All samples required several months in order attain sizes of $\sim 100 \text{ mm}^3$. The crystal were transparent and had no visible defects or signs of twinning.

The CADPx crystals grew with the c axis in the vertical direction. A schematic of the shape of a typical CADPx crystal is shown in Figure 7.

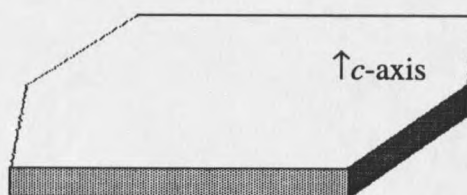


Figure 7. Schematic of a Typical CADP Crystal for All Grown Concentrations.

Typical DCADPx crystals had a similar ratio of dimensions in the a , b and c directions, but differed from CADP in that the a - b plane was nearly rectangular instead of quasi-hexagonal.

2.4. DISCUSSION

The shape in which the crystals grew does not necessarily correspond to the natural habit of the crystals, since the bottom of the container imposed a strong boundary condition on the growth of the crystal. In order to determine the natural crystal habit, the crystals must either be suspended in the solution or be neutrally buoyant.

3. X - RAY DIFFRACTION

3.1. BACKGROUND

X-ray and neutron diffraction are common techniques for obtaining crystal structure. X-ray crystallography is dependent on the particular *phasing model* chosen : crystallographic data consist only of the relative magnitude of the structure factors and not their relative phases.⁶⁵ It is useful to define a structure factor $f = \sum_{j=1} g_j(\vec{K}) e^{i\vec{K} \cdot \vec{d}_j}$, where $\vec{K}$ is the difference between the incident and reflected wave vectors and $g_j(\vec{K})$ is the atomic form factor, determined by the internal structure of the ion that occupies position d_j in the lattice. $g_j(\vec{K})$ is treated as the Fourier transform of the electronic charge distribution of the corresponding ion. The structure factor represents the extent to which interference from ions within the basis can diminish the intensity of the reflected peak associated with the reciprocal lattice vector $\vec{K}$. In general, a particular set of structure factor magnitudes does not uniquely determine a crystal structure or electron distribution. However, by making several reasonable assumptions about the nature of the electron distribution, the crystal structure can be uniquely determined: the interatomic distances must be both within reasonable limits and somewhat spherically distributed about the lattice positions. The process of structure determination employed is as follows: direct calculation of initial phases and deduction of an atomic model from a Fourier map. An expansion of the squares of the structure factors is made and the residuals, R , calculated in order to yield a confidence level.

An expansion of the difference, Δf , between an initial guess of the structure factors, $|f_c|$, and the observed structure factor, $|f_0|$, is made. The R is given by:

$$R = \frac{\sum |\Delta f|^2}{\sum |f_0|^2}. \quad \text{Equation 16}$$

If the wavelength of the beam is close to the absorption edge of the scattering atoms, as is the case with the cesium atoms, an absorption pattern characteristic of that atom, with parts $\Delta f'$ and $\Delta f''$, will arise. $\Delta f'$ is independent of the particulars of the crystal lattice and can be simply subtracted from the spectra. The other component $\Delta f''$ has a more complex, but smaller effect. However, the effect of $\Delta f''$ may be eliminated by interpolating the tabulated values corresponding to the $\sin(\theta)/\lambda$ employed.

The most common difficulty that arises in lattice assignment involves lattices that can be indexed as centered cells.⁶⁵ Small intensity reflections cannot be ignored; all of the intensity data should be used weighted by their uncertainties.⁶⁶

3.2. METHOD

X-ray transmission required the samples to be cut to less than one millimeter per side. This was accomplished by mounting them in modeling clay and pulling a wet cotton thread slowly across. For identification purposes, small samples of the CADP crystals were prepared such that each of the three axes had significantly different dimensions. From these $\sim 1 \text{ mm}^3$ samples, unit cell parameters and crystallographic orientation of CADP were obtained using a Siemens (Nicolet) R3m diffractometer with a Siemens P4 upgrade. Once the orientation was obtained, smaller, semi-spherical samples

were made in order to reduce the effect of the extinction coefficients on the transmission spectrum.

Ellipsoidal, spherical and fixed refinements of the thermal parameters were tried for the ratio of the cesium to ammonium thermal parameters versus ammonium concentration in order to produce the most self-consistent results.

3.3. RESULTS

Because the anisotropic brittleness of the crystals made it difficult to produce spherical samples by conventional grinding methods and because of the high crystal quality, the extinction coefficients in $CADP_x$ were atypically large.

The most self-consistent results were obtained after fixing the ratio of the ammonium to cesium thermal parameters using published values for the cesium thermal parameters in pure CDP.¹⁸ The lattice dimensions for CADP crystals with ammonium concentrations in solution of $x = 0.1, 0.2$ and 0.4 are shown in Table 3.

The measured cell dimensions do not differ from the most-recently published values for the crystal structure of CDP when possible systematic errors from extinction coefficients are considered: All three crystals were monoclinic with two formula units per unit cell. The space group was uniquely determined to be $P2_1/m$. In Table 3, a , b and c are the dimensions of the crystallographic axes, and β is the angle of the monoclinic cell as shown in Figure 1.

X-ray analysis was also used to try to determine the concentration of ammonium substitution in the crystal. This was possible because ammonium and cesium ions reflect

x-rays very differently. For all three crystal compositions (with solution concentrations of $x = 0.1$, $x = 0.2$ and $x = 0.4$) a much smaller concentration of ammonium was present in the crystals than in the solutions from which they were grown: all of the crystals were found to have $x = 0.05 \pm 0.05$, with the error in the concentrations being estimated as twice the deviation between the measured values between two samples with the same nominal concentration.

x	a (Å)	b (Å)	c (Å)	β (deg)	Ref.
0.00	7.90065(8)	6.36890(9)	4.87254(12)	107.742(9)	25
0.10	7.896(29)	6.3851(11)	4.876(05)	107.61(07)	-
0.20	7.903(55)	6.384(84)	4.883(73)	107.58(95)	-
0.20	7.893(67)	6.383(46)	4.876(13)	107.56(06)	-
0.40	7.8896(11)	6.3847(16)	4.874(56)	107.51(77)	-
0.40	7.888(57)	6.384(26)	4.872(93)	107.52(77)	-

Table 3. Crystal Lattice Dimensions and Angles of CADP.

3.4. DISCUSSION

The high anisotropy of the extinction coefficients and the sharpness of the diffraction spectra, indicated high crystal quality *of the crystalline portion of the sample*. However, because amorphous materials scatter x-rays isotropically, it is difficult to accurately determine by x-ray diffraction whether amorphous regions coexist with regions of high crystal quality. Therefore, it could not be ruled out that the crystals may have contained small occlusions of the solvent from which they were grown. In such a case, during the pulverization process, the crystals would have been mostly likely to break along surfaces containing the occlusions. Since it is know that a significant amount of

ammonia gas can evolve from the related crystal, ADP, it is plausible that the required pulverization process results in an erroneously low value of the ammonium concentration in the bulk of the crystal.

Large extinction coefficients meant that errors in their values could appear in the refinement of the thermal parameters, leading to model-dependent lattice parameters. The accuracy of the lattice parameters is, therefore, somewhat overstated by a least-squares estimation of the error. Therefore, the lattice structure and space group of CADP were not significantly different from the values reported for CDP.²⁵

The result that all of the samples incorporated less than ten percent of ammonium was somewhat surprising, considering that cesium is fourteen percent larger than ammonium. Because the x-ray diffraction measurements were not sufficiently precise to yield mutually exclusive values for the concentrations of the ammonium ions in the samples, more precise analytical chemical techniques were needed.

4. ANALYTICAL CHEMISTRY

4.1. BACKGROUND

Analytical chemistry is an accurate method for determining bulk concentrations, but requires either partial or total destruction of the sample.

4.2. METHOD

Samples were cut from the edges of the CADP crystals used for dielectric measurements. A typical sample weighed only 0.4 g.

The weight fractions of nitrogen in the CADP crystals, f , was determined using colorimetry and the macroscopic Kjeldahl method.⁶⁷

If we let W_X represent the formula weight of nucleus X , then the laboratory results were converted into terms of actual molar fraction of ammonium, x_A , by means of Equation 17.

$$x_A = \frac{(2 W_H + W_P + 4 W_o) f + W_{Cs} f}{W_{Cs} f - f W_N - 4 f W_H + W_N} \quad \text{Equation 17}$$

4.3. RESULTS

Table 4 shows x_A for the crystals of CADP grown from solutions with ammonium concentrations x .

x	x_A
0.100 ± 0.001	0.057 ± 0.002
0.200 ± 0.002	0.060 ± 0.002
0.400 ± 0.004	0.064 ± 0.003

Table 4. Crystal Ammonium Concentration, x_A , Versus Solution Concentration Ammonium, x

4.4. DISCUSSION

The analytical results are consistent with the results obtained by x-ray analysis: x-ray diffraction analysis determined that the molar concentration of ammonium in the sample was less than ten percent, whereas analytical chemical techniques determined an ammonium concentration near six percent. The analytical chemical techniques cannot account for possible inclusions of ammonium-rich solution, so the true concentration in the crystal could be lower. The x-ray diffraction method measures only the concentration in the crystal

Both techniques have conclusively shown that, for all values of x for which CADPx was grown, x is greater than x_A and that the disparity between x and x_A is larger than in other KDP isomorphs. For example, deuterated rubidium ammonium dihydrogen arsenate, DRADAx, with $x = 0.7$ yielded $x_A = 0.6$. We believe that the larger disparity between x and x_A in CADPx is due to the larger mismatch in atomic radii between Cs ($r(\text{Cs}) = 0.167 \text{ nm}^{68}$) and NH_4 ($r(\text{NH}_4) = 0.147 \text{ nm}^{69}$) than between Rb ($r(\text{Rb}) = 0.148 \text{ nm}$) and NH_4 : Rubidium is nearly exactly the same size as ammonium, whereas cesium is fourteen percent larger than ammonium.

5. NUCLEAR MAGNETIC RESONANCE

5.1. BACKGROUND

Low-resolution nuclear magnetic resonance (NMR) is useful for determining the rates of motional processes that couple to the particular nucleus of interest. Rates for thermally activated processes are determined via the theory of Bloembergen, Purcell and Pound (BPP),⁷⁰ in which a minimum in the plot of the logarithm of T_1 , the *spin-lattice relaxation time*, versus inverse temperature occurs when a particular motional frequency is equal to that of the resonant frequency of the nucleus in the static magnetic field. Process rates at other temperatures may be extrapolated by assuming that the process continues to be thermally activated; i.e., that the characteristic time, τ , of the motion is given by $\tau = \tau_0 \exp(E_a/kT)$.

When atoms are placed in a constant magnetic field, H_0 , of a few Tesla at temperatures much above 0° K, the nuclear magnetic moments ("spins") will remain nearly randomly oriented with respect to the externally applied magnetic field. The NMR signal results from the small excess of spins which are aligned with the external field. If this excess is eliminated, for instance by applying a " $\pi/2$ pulse", the excess builds up again with a time constant T_1 . Finite values of T_1 result from a transfer of energy between the spins and the lattice vibrations, referred to as the "spin bath" or "lattice". In order for energy to be transferred it is both necessary and sufficient that there be non-zero terms in the Hamiltonian involving states of the aligned spins.

In CADP we expect a dispersion of ^{31}P T_1 times because of the different types of fluctuating magnetic environments at the phosphorus atoms, resulting from differing numbers of neighboring ammonium ions. From any given phosphorus atom in CADP there are six approximately equidistant sites at which either a cesium or ammonium could be situated. Because of the large magnetic moment of the proton relative to that of any other nucleus, it is fair to assume that the magnetic environment inside CADP is almost entirely governed by the magnetic moments of the protons. The magnetic field from a dipole decreases as the inverse cube of the distance from the center of the dipole, suggesting that only the magnetic field changes caused by motions of the nearest neighbors will have significant contribution to T_1 . In addition to the six sites which may be occupied by ammonium ions, there are four hydrogens which are bonded to the four oxygens in a phosphate group. However, at any instant there are not more than ten hydrogen atoms which are close enough to a given phosphorus nucleus that can have a significant effect on the value of T_1 .

The radius of an ionically bonded cesium atom is 0.167 nm. The bond length between phosphorus and oxygen is 0.149 for the P-O(3) bond, 0.153 in the P-O(4) bond and 0.161 in P-O(1) bond in CDP.¹⁶ From x-ray diffraction, we know that the bond lengths are nearly the same as in CDP. In CDP, there are two different types of O-H...O hydrogen bonds: those ordered bonds which link phosphate groups along the c axis and those which form zigzagging chains along the ferroelectric b axis and are disordered above $T_c = 156$ K. The O-H...O bonds forming chains along the c axis have a length 0.2562 nm and those along forming chains along the b axis have a length of 0.246 nm.⁷¹

Knowing the distances of the hydrogen nuclei from the phosphorus nuclei, the correlation times for the interbond and intrabond motions and the amplitude vectors for these motions, one can determine the expected value of T_1 as a function of temperature.

A Hamiltonian describing the coupling of a particle and its environment can be written as a sum of Hamiltonians over all of the independent interactions. In this case, the Hamiltonian is a sum of many terms, including the Zeeman H_Z , magnetic dipolar H_d and chemical shift interactions H_s : $H = H_d + H_s + H_Z$.⁷¹ In most low-resolution NMR experiments on spin $I = 1/2$ nuclei such as ^{31}P , the dipolar contribution to the total Hamiltonian dominates the other contributions. For $I \geq 1$, electric quadrupolar interactions are likely to dominate.

5.2. METHOD

A schematic of the instrumentation used in our NMR experiment is shown in Figure 8.

^{31}P nuclear magnetic resonance requires extremely precise tuning in order to obtain a recognizable signal: the signal was tuned to within 10 Hz of the resonant frequency of the ^{31}P nuclei for our particular static magnetic field, H_0 : $\nu_0 = 28,189,500$ Hz. If we define γ as the gyromagnetic ratio of ^{31}P , then the resonant frequency is given by

$$\nu_0 = \frac{|\gamma| H_0}{2\pi} \quad \text{Equation 18}$$

All naturally occurring phosphorus is of the ^{31}P isotope, which has a γ equal to $10.8394 \cdot 10^7 \text{ T}^{-1} \text{ s}^{-1}$.⁷² H_0 was set in order to maximize the ν_0 of the phosphorus, which was limited by the bandwidth of the Matec 625 preamplifier, $\sim 29 \text{ MHz}$. The current necessary to achieve this was calculated according to the formula given in the manual for the superconducting magnet from Cryomagnetics, Inc.: $I = H_0/0.06016 \text{ T/A} = 71.2 \text{ A}$ for a target ν_0 of 28 MHz.

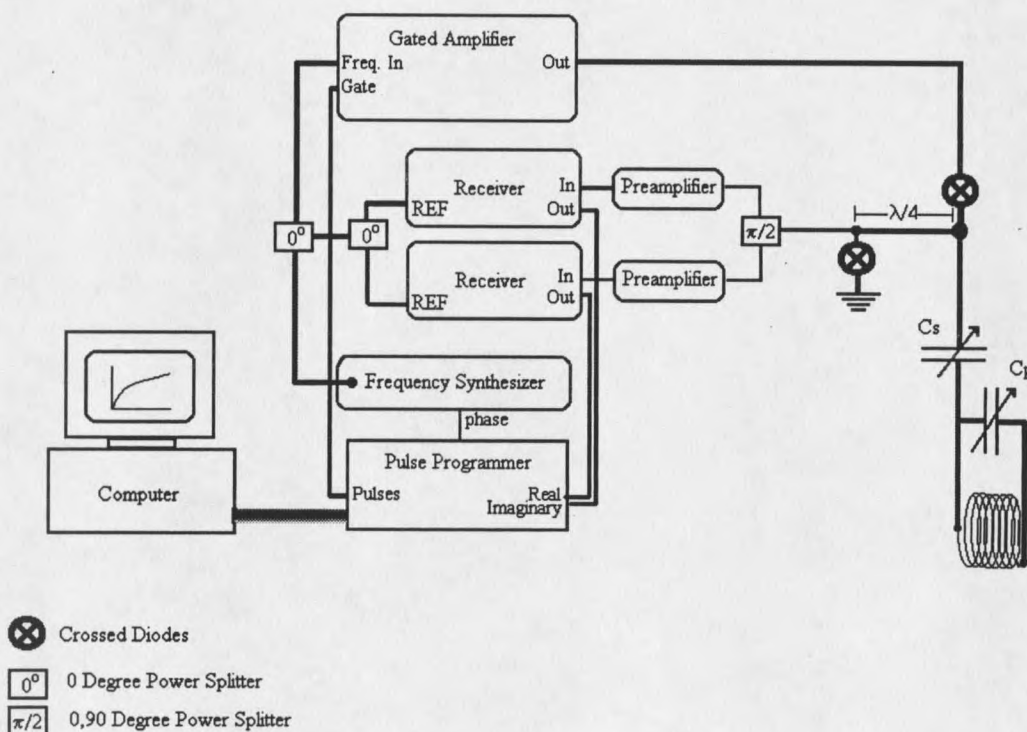


Figure 8. Schematic of Pulsed NMR Apparatus with Quadrature Detection.

Electronics NMR employs a method of increasing the signal-to-noise ratio (SNR) known as lock-in amplification, without which the signal would be undetectable. The noise in the electronics used in NMR, as in most sensitive electronics, is dominated by

the thermal noise intrinsic to the instruments and the connecting cables. In general, any material with an electrical resistance R at a temperature T will produce a minimum noise voltage $V_n = (4 k_B T R \Delta f_n)^{1/2}$, where k_B is Boltzmann's constant and Δf_n is the frequency bandwidth observed. Therefore, if a signal has a well defined spectral width Δf_s , then the SNR will be maximized for $\Delta f_n \cong \Delta f_s$. In our case, Δf_s was limited by the inhomogeneity of H_0 to a full-width-half-maximum of $\Delta f_s = 20$ kHz. For $\nu_0 = 28$ MHz, lock-in amplification improves the SNR by a factor of $(28000/20)^{1/2} \cong 37.4$ over frequency indiscriminate amplification.

Not only does the signal have a definite frequency, but also a definite phase relation to the applied radio-frequency (RF) pulse. This can be exploited to further improve the SNR because the phase of the noise is uncorrelated with the phase of the signal. Depending on the phase resolution δ we can obtain an additional improvement in the SNR of $\cos(\delta)/(2 \delta)$. Phase sensitive amplification is accomplished by using a *double balanced mixer* where the IF (intermediate frequency) port is set to the reference frequency and the signal is sent to the RF port. A *double balanced mixer* is a device which produces an output that contains signals at the sum and difference frequencies of the input RF and IF signals: $A = (A_{RF} + A_{IF}) \cos[(\omega_{RF} - \omega_{IF})T - (\phi_{RF} - \phi_{IF})] + \dots$ If the frequency of the signal ω_{RF} equals that of the reference ω_{IF} , then the amplitude of the leading order term is proportional to the cosine of the difference in phases of the signal and reference: $A = A_{RF} \cos(\phi_{RF} - \phi_{IF})$.

The addition of phase control to the NMR apparatus enabled elaborate cycles of phases, which dramatically improved the signal-to-noise ratio, reduced systematic errors, eliminated spurious mirror reflections about the resonant frequency and enabled the signal to be recovered from a much larger ringing of the resonant cavity. A variety of phase sequences were employed depending on the particular problems encountered in a given temperature range. However, all of the pulse sequences employed at least *zero-order* and *first-order* phase cycles. The *zero-order* phase cycle consists of zero degree pulses alternating with 180 degree pulses. This eliminates the peak at the resonance in the frequency domain, because the response is inverted with the pulse, while the offset is equal and opposite. The first-order phase cycle consists of the following sequence of phase angles in degrees: 0, 90, 180, 270. This cycle, when coupled with quadrature detection, eliminates the mirror-reflected peak in the Fourier-transformed signal, corresponding to a rotation of the magnetization in the direction opposite to the real rotation.

For a measurement of the spin-lattice relaxation time T_1 , we employed the following measurement sequence: a train of $\pi/2$ pulses (3.8 μs), which ensured that the magnetization began at zero, a variable delay τ , another $\pi/2$ pulse, a π pulse (7.7 $\mu\text{s}^\dagger$), a moderate delay (30 μs) in order to allow for the decay of the coil ringing, a measurement and a relatively long (6 s) recovery period. In each sequence the π pulses are in phase

[†] Notice that the π pulse is not exactly twice the duration of the $\pi/2$ pulse; the π and $\pi/2$ pulses are defined such that the magnetization is zero and maximal, respectively.

both with each other and with the acquisition, and ninety degrees out of phase with the $\pi/2$ pulse. The rationale behind using an additional π pulse rather than simply measuring the signal after the second $\pi/2$ pulse is that this allows an additional time for the resonant coil ringing to decay, during which the magnetization may rephase. This technique is commonly known as *spin-echo*.⁷³

This process yielded a set of *free induction decays*, FIDs, for the various delays, T , where FID is an exponential decay of the magnetization with time constant $T_2^* = (T_2^{-1} + (\gamma H_0)^{-1})^{-1}$, where T_2 is the spin-spin or transverse relaxation time. This set of FIDs was manipulated with MacNMR software from Tecmag, Inc. of Houston, Texas in order to produce well-defined maxima, whose amplitude could be compared: The FIDs were filtered by multiplying by a decaying exponential function in order to reduce high-frequency noise, Fourier-transformed into the frequency domain and phase and baseline corrected until the signals were upright and symmetric and the responses far from the signals appeared flat.

The amplitudes of the pulses, M , which are proportional to the net magnetization, were then plotted as a function of τ . The data could not be fit to the standard function, $M = M_0(1 - \exp(-T/T_{11}))$. However, we obtained quite good fits by adding two additional free parameters, T_{12} and M_{02} , as shown in Equation 19.

$$M = M_{01}(1 - \exp(-T/T_{11})) + M_{02}(1 - \exp(-T/T_{12})) \quad \text{Equation 19}$$

This modification physically corresponds to having a set of phosphorus nuclei in a second nuclear environment. Although we could have justified more physical parameters on the basis of the presumed structure, we did not have sufficient data to adequately restrict more free parameters.

This process was repeated at several temperatures in order to obtain a function of T_{11} and T_{12} versus temperature.

These results were used in conjunction with BPP theory in order to determine the frequencies of proton motion.

Sample Preparation In order to maximize the fill-factor of the probe, we pulverized several small crystals of CADP.20 into a powder with an average diameter of about one micron and then stuffed the dry powder into the Macor ceramic form for the resonant coil. The resonant coil was then closed with a polytetrafluoroethylene plug.

5.3. RESULTS

A typical measurement ($T = 326$ K) of a free induction decay is shown in Figure 9. The rapidly increasing part of the signal results from the recovery of the receiver from saturation. The slowly varying part corresponds to the decay of the magnetization of the sample.[§]

[§] Note that the characteristic exponential decay time of this process is not the intrinsic spin-spin relaxation time T_2 , but rather, T_2^* , which results predominantly from the inhomogeneity of the magnetic field.

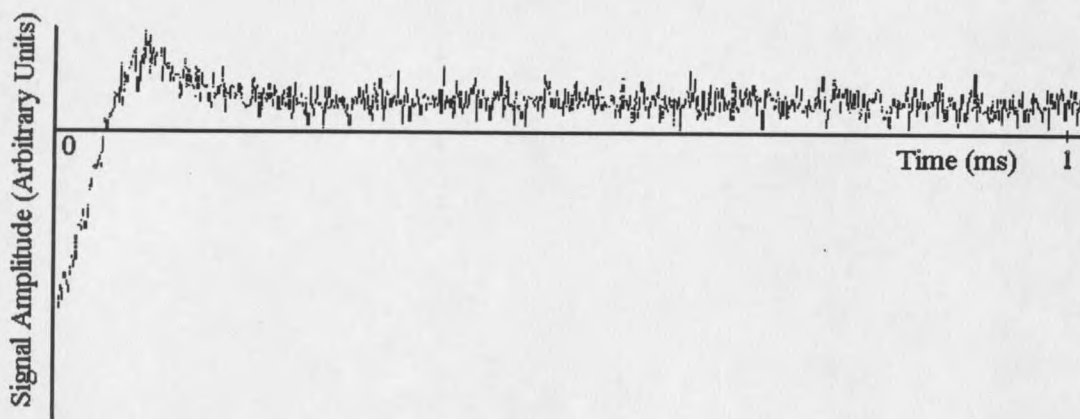


Figure 9. Free Induction Decay in CADP.20 at $T = 326$ K.

A Fourier transform converts the signal into the frequency domain as seen in Figure 10. When this result is manipulated as detailed in the Section 5.2, Figure 11 is obtained. A plot of the maximum amplitude of a set of these spectra as a function of pulse delay τ is shown in Figure 12. The circles represent data values. The squares points represent a best fit to the double exponential function shown in Equation 19.

The logarithm of the fit parameters T_{11} and T_{12} obtained by this process were then plotted as a function of inverse temperature as shown in Figure 13.

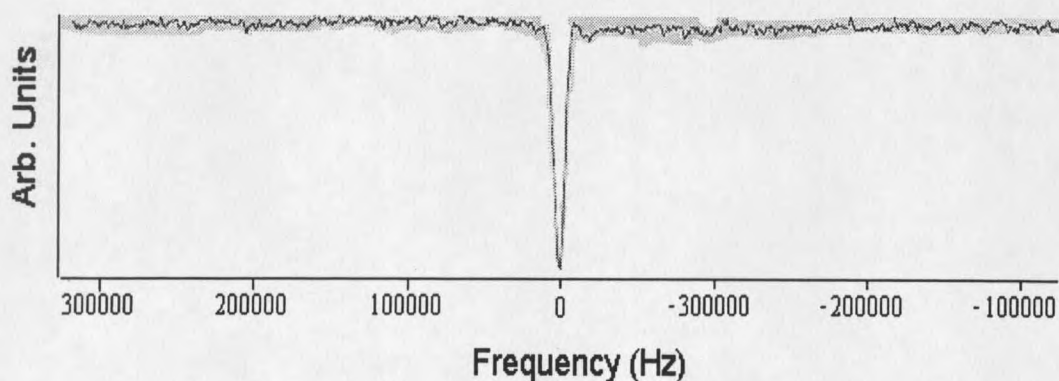


Figure 10. Fourier-Transformed Free Induction Decay at $T = 326$ K in CADP.20.

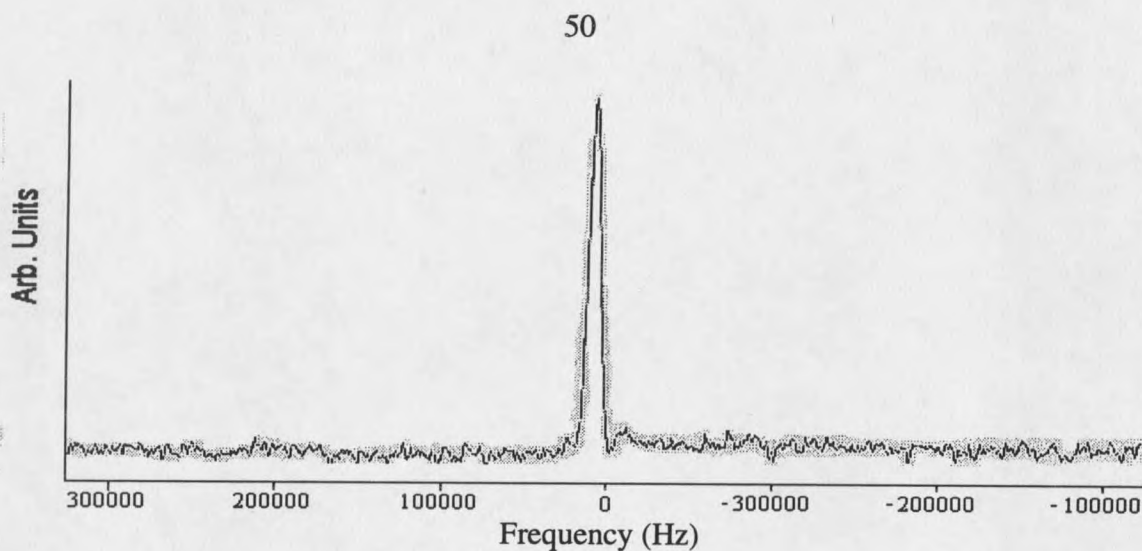


Figure 11. Fourier-Transformed, Phase-Adjusted, Baseline-Corrected FID at $T = 326$ K in CADP.20.

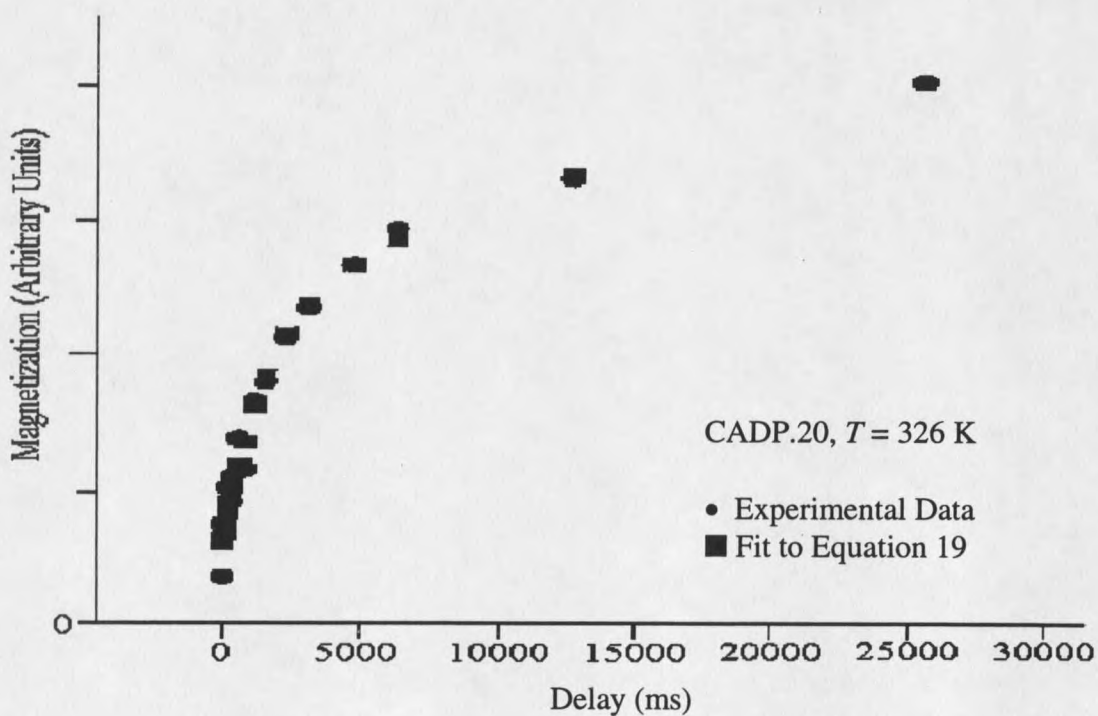


Figure 12. Magnetization Versus Delay Between Pulse and Echo Formation at $T = 326$ K in CADP.20.

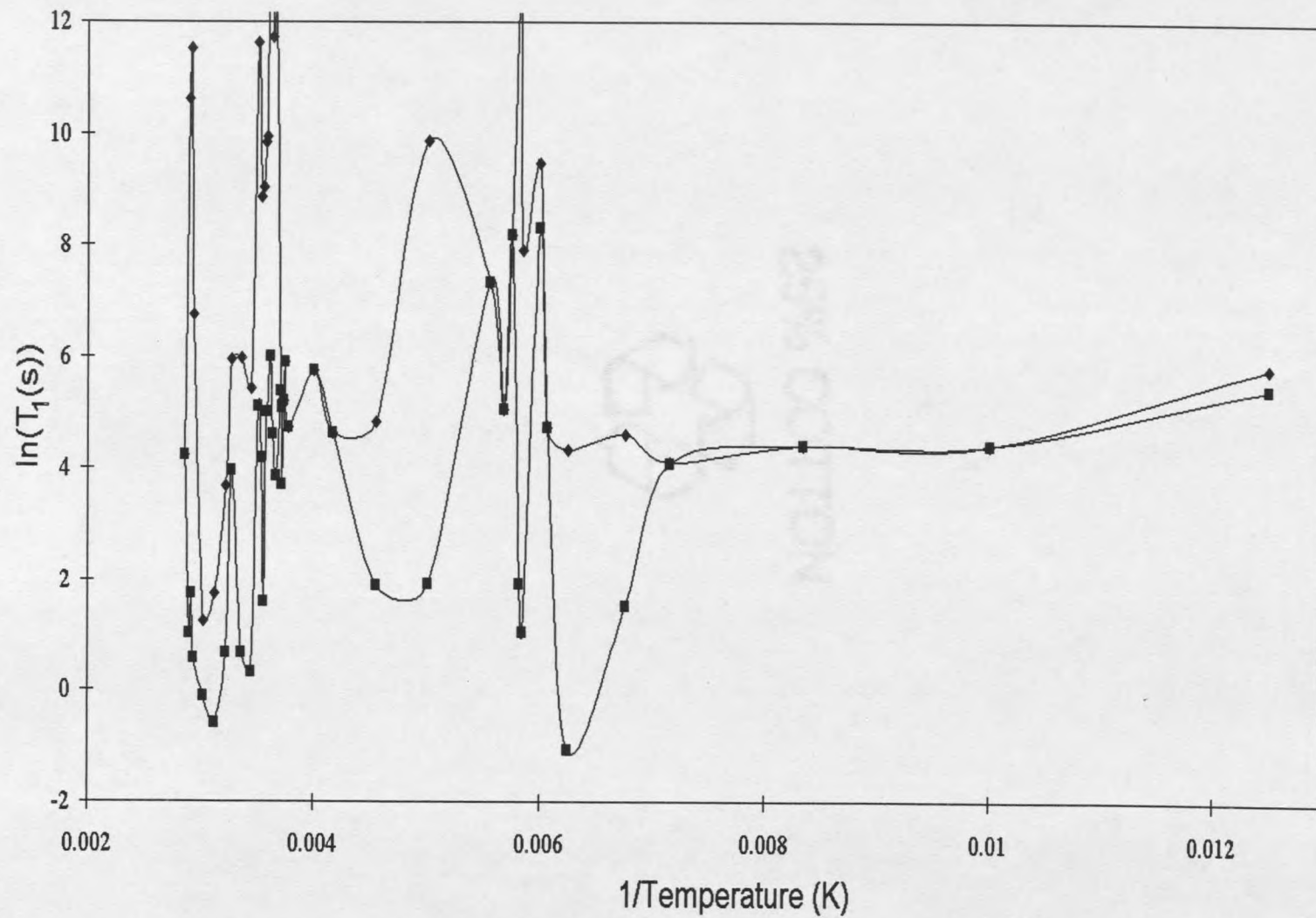


Figure 13. Plot of $\ln(T_1)$ Versus Inverse Temperature

5.4. DISCUSSION

The fact that there were multiple relaxation processes complicated the analysis of the data because we could not assume that the physical process corresponding to the lower T_1 at one temperature necessarily remains lower at all temperatures. Instead, in interpolating separate curves through the data, we sought to maximize the continuity of each of the T_1 curves.

While even minute amounts of paramagnetic impurities can often provide the dominant relaxation mechanism, the relatively long relaxation times and the agreement with theoretical relaxation times suggest that the level of paramagnetic impurities in the sample was small and that the primary mechanism for ^{31}P T_1 relaxation in our sample was dipolar coupling between hydrogen and phosphorus nuclei in the lattice.

In the case of the ammonium nuclei, reorientation arises from the rotation of the ammonium groups about their lattice positions. In the case of the conduction protons, reorientation arises from hopping between lattice sites. In addition, we will only consider the dipolar contribution to the relaxation time. With these liquid-like assumptions, the T_1 relaxation time for nuclei (1) resulting from the interaction between nuclei (1) and (2) with gyromagnetic ratios of γ_1 and γ_2 and resonant frequencies of ω_1 and ω_2 , respectively, is given by⁷²

$$T_1 = \frac{160 \pi^2 r^6}{\mu_0 \hbar^2 \gamma_1^2 \gamma_2^2 (\tau / (1 + (\omega_1 - \omega_2)^2 \tau^2) + 3 \tau / (1 + \omega_1^2 \tau^2) + 6 \tau / (1 + (\omega_1 + \omega_2)^2 \tau^2))} ,$$

Equation 20

where $\hbar$ is Planck's constant, μ_0 is the permeability of the vacuum and τ is the relaxation time of the nuclear motion.

The dominant dipolar interaction with phosphorus in CADP occurs with ^1H because it has a much larger gyromagnetic ratio ($\gamma(^1\text{H}) = 26.752156$) than any other nucleus, except for the exceedingly rare radioactive ^3H nucleus, and because the average positions of several hydrogens are closer than those of the other dipolar nuclei present in the crystal, i.e., ^{133}Cs ($\gamma_{\text{Cs}} = 3.533253$) and ^{31}P .

At all temperatures, hydrogen is the more mobile nuclear species, implying that the relaxation time τ is characteristic of a specific motion of the hydrogen. For a static NMR field H_0 giving a resonant frequency of 28 MHz for ^{31}P , we obtain $T_1(\text{min}) = 8.89 \cdot 10^{-57} \text{ m}^{-6} \text{ s } r^6$. Since the diameter of ammonium ($r = 0.148 \pm 0.001 \text{ nm}^{69}$) is less than that of cesium ($r = 0.167 \pm 0.001 \text{ nm}^{68}$), for the small concentrations of ammonium incorporated into the lattice, the ammonium ions should experience little hindrance to rotation.

Bond distances were calculated on a personal computer using a software program called Shelxtl by G. M. Sheldrick of Siemens Analytical Instruments of Madison, Wisconsin. A picture of bond distances between the acid protons and the phosphate groups is shown in Figure 14. The minimum acid hydrogen-phosphorus bond distance of 0.2603 nm calculated by Symstat yields a T_1 value of 2.77 s at the minimum.

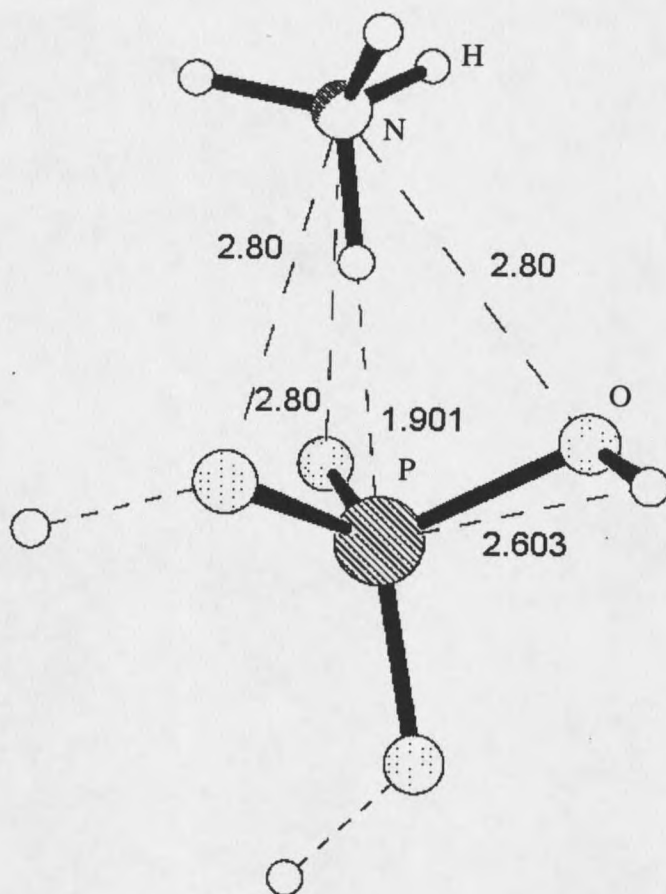


Figure 14. Model Showing Minimum Atomic Distances (Å).

Figure 15 shows the result of the Simstat lattice refinement for an ammonium group at a cesium lattice site. The numbers in the figure correspond to bond lengths in Angstroms. The minimum distance between a hydrogen atom from an ammonium group and a phosphorus atom was calculated by the software to be 0.2402 nm, corresponding to a T_1 of 1.71 s.

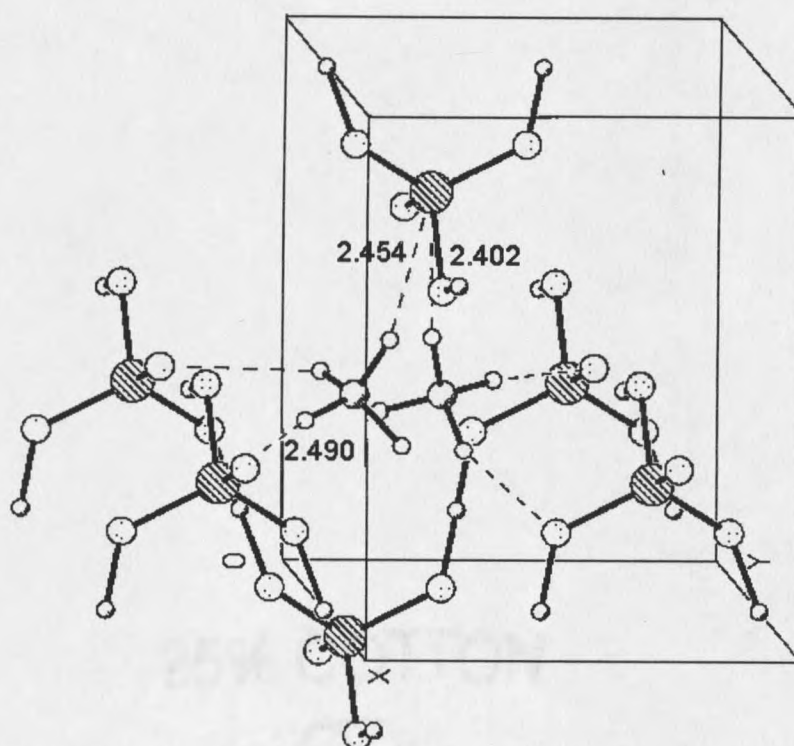


Figure 15. Model Showing Minimum Ammonium-Phosphorus Atomic Distances (Å).

Figure 13 shows a plot of the natural logarithm of T_1 versus inverse temperature. Assuming that the concentration of paramagnetic impurities was negligible and that other mechanisms were small, we tentatively associate the minimum in Figure 13 at $T = 154$ K with ammonium hindered rotation and the minimum at $T = 328$ K with hydrogen interbond motion. The values of T_1 associated with these minima, $T_1 = 0.61$ and $T_1 = 0.90$ s, are about one third of the values of the relaxation times as calculated by the minimum bond distances, $T_1 = 1.71$ s and $T_1 = 2.77$ s, suggesting either that the liquid-like assumption is in need of refinement or that contributions to the relaxation time from other P...H couplings are significant.

By minimizing T_I as a function of temperature, the frequency of the processes at these minima, f , is determined to be 38.9 MHz. Expecting that the effect of the small intrabond proton displacements is too small to detect by ^{31}P relaxation and assuming an activated process with activation energy, E_A , the relaxation times, τ , of the motions at arbitrary temperatures can be calculated from $\tau = \tau_0 \exp(E_A / k T)$. Setting the energy of motion equal to the thermal energy at the minimum, we obtain

$$E_A = k_B T \ln(k T / h f), \quad \text{Equation 21}$$

where k_B is Boltzmann's constant and h is Planck's constant. This equation yields theoretical values of $E_A = 0.35$ eV at $T = 328$ K, and $E_A = 0.16$ eV at $T = 162$ K.

These values agree reasonably with the E_A as determined from the slope of the curves of $\ln(T_I)$ versus inverse temperature near the minima: $E_A = 0.46$ eV for the acid relaxation at $T = 328$ K, and $E_A = 0.19$ eV for the ammonium relaxation at $T = 162$ K. Since intrabond motion has little effect on T_I , the process near $T = 328$ K most probably corresponds to an actual mobility between the lattice sites associated with protonic electrical conductivity. Indeed, the activation energy of 0.46 eV is at the lower end of the activation energies found from the dielectric results presented in the following chapter.

The $T_I(T)$ relaxation results for CADP.20 powder are considerably more complicated than those obtained for ^{133}Cs in CDP, which only exhibits an anomaly at T_c and maybe be characterized by a single relaxation time.⁷⁴ The second relaxation time must, therefore, be associated with a feature of CADP that is not present in CDP, namely the presence of randomly distributed ammonium ions.

6. DIELECTRIC MEASUREMENTS

6.1. BACKGROUND

Dielectric measurements involve measurement of the complex permittivity, ϵ^{**} .

For many materials, such as inert gases, polymers and metals, ϵ may be treated as constant. However, many materials have values of ϵ' which depend on temperature, pressure, frequency, external bias, history and other factors. The complex permittivity ϵ and permeability μ are defined such that Maxwell's Equations governing the electric field $\vec{E}$ and magnetic field $\vec{H}$ in the presence of a charge density ρ assume their simplest forms:

$$\nabla \times \vec{H} = \epsilon_0 \epsilon \frac{\partial \vec{E}}{\partial t}, \quad \nabla \times \vec{E} = -\mu_0 \mu \frac{\partial \vec{H}}{\partial t},$$

Equation 22

$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0 \epsilon} \quad \text{and} \quad \nabla \cdot \vec{H} = 0.$$

Because even moderate external fields may induce nonlinear polarization, in general, ϵ and μ depend on the magnitude of the externally-applied fields. In order to simplify matters, we will take the conventional tactic of defining ϵ and μ by their values in the limit of vanishing external fields.

** In some treatments, what we call "permittivity" is instead called "relative permittivity", ϵ_R , and "permittivity" ϵ is defined as the product of ϵ_R with the permittivity of the vacuum, ϵ_0 . Similarly, we will abbreviate "relative susceptibility" as "susceptibility" and define the electrical susceptibility χ as $\chi = \epsilon - 1$ in MKSA units or $\chi = (\epsilon - 1)/4\pi$ in Gaussian units.

6.2. METHOD

6.2.1. Sample Preparation

Once the crystallographic axes of the samples had been determined by Laue x-ray scattering, faces parallel to the axes were cut and polished by mounting the crystals in modeling clay and pulling an H₂O- or D₂O-saturated cotton thread across the samples.

Opposite faces along the axis of interest were coated with silver paint from Structure Probe International (SPI, Inc.) of West Chester, Pennsylvania.^{††} After the paint had dried, 0.1 mm x 4 cm copper wires were attached by paint onto the electroded surfaces. These wires were then soldered to the coaxial posts of the dielectric measurement apparatus.

In addition to the crystalline samples, a sample of pulverized CADP.20 was prepared by crushing several small crystals of CADP.20 and then compressing the powder just enough so that it adhered together. The sample that was prepared in this way had a consistency of chalk and a mean particle size of ~1 μm . This sample was cut and painted by the methods detailed above for the crystals.

6.2.2. Electrode Effect

One sample of CADP.20 was also electroded on opposite faces along the *a* axis with evaporated gold in order to check for any artifacts that may have resulted from use

^{††} The conductivity of silver paint from Ted Pella, Inc. deteriorates quickly. Silver paste from SPI, Inc. is not vacuum-compatible because it out-gasses and hardens.

of the paint or from residual water vapor. In coating the sample with gold, the sample was placed in a vacuum of 10^{-4} mm of Hg and the surface was heated for several minutes under intense infrared radiation before being coated. This ensured complete dessication. Electrodes were attached by the method mentioned in Section 6.2.1.

Because the measurement of $\epsilon'_a(T)$ for the sample prepared in this way did not significantly differ from the $\epsilon'_a(T)$ for the sample prepared with painted electrodes, all subsequent measurements employed painted electrodes because of the relative simplicity of the technique.

6.2.3. Apparatus

Schematic The apparatus used for dielectric measurements consists of a personal computer, a temperature controller, an impedance analyzer, a helium compressor and a vacuum and a temperature sensor. A schematic of the apparatus is shown in Figure 16.

Inside the vacuum, the sample is supported by a copper disk, whose function is both to thermally contact and to protect a LakeShore DT-470-CU-13 silicon diode temperature sensor. A small channel was milled on the bottom side of the disk for the mechanically fragile leads of the sensor. The disk was machined to within half a millimeter of the sides of the sensor and polished to within 0.05 mm of the top of the sensor. In order to further improve thermal contact, the remaining gap was filled with a mixture of Al_2O_3 and vacuum-compatible silicone grease.

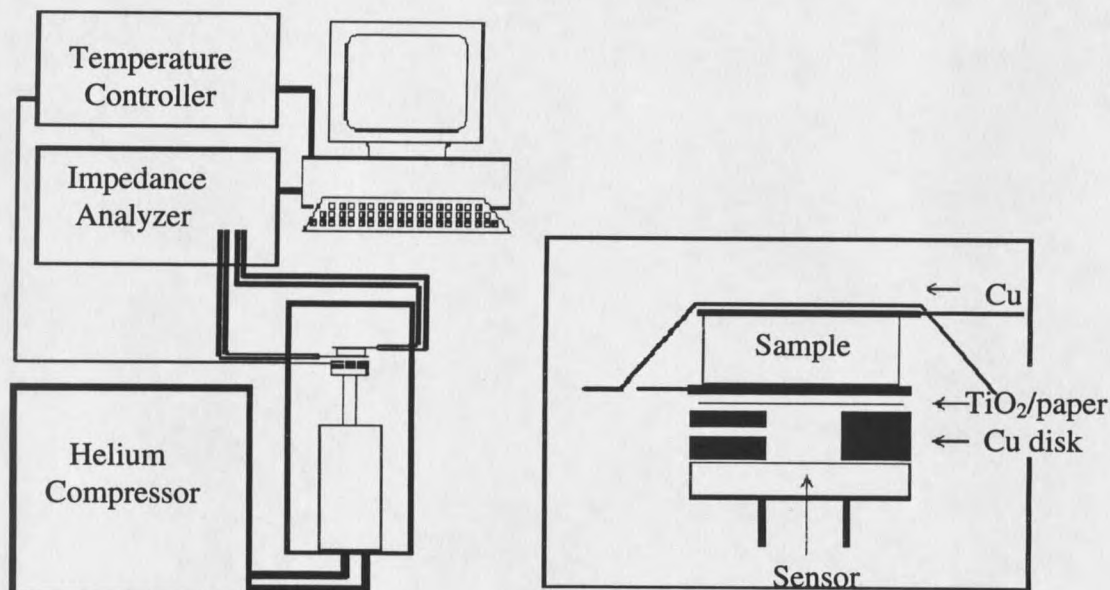


Figure 16. Dielectric Apparatus Schematic.

Just below the copper disk was wrapped a nichrome wire, whose purpose was to heat the sample to the appropriate temperature. The LakeShore 330 temperature controller regulated current flowing through the wire.

Electronics The dielectric impedance analyzer was a QuadTech 7600A RLC meter.^{††} The QuadTech 7600A could measure ϵ for a quasi-continuum of frequencies between 10 Hz and 2 MHz.

The measurements of electrical impedance employed four electrically-shielded coaxial leads: one for a sinusoidally-varying current source, another for a low-impedance return path for the current, and the remaining two for monitoring the voltage across the sample. This arrangement compensates for the contact resistance *variations* at the sample

and the non-zero impedance, $Z = 50 \Omega$, of the lead wires. All of the cable shields were connected together and grounded at the entrance of the cryostat. The leads were of equal length and tightly intertwined in order to reduce inductive coupling with external noise sources, by eliminating the effective magnetic loop created by the lead wires.

All of the shields were connected at the sample side. In order to compensate for small variations in the lead geometry and internal calibration between runs, both analyzers were trimmed both in short and open circuit, using internally automated procedures.

The QuadTech 7600A claimed a minimum accuracy of $|\Delta C/C| \cong 0.0005$ for the value of the capacitance for the measurement mode used. The signal was averaged twice, decreasing $|\Delta C/C|$ by a factor of $2^{1/2}$.^{§§} An alleged accuracy of 0.0005 for the dissipation factor, D , yielded a minimum accuracy for our sample ($D > 0.01$) of $|\Delta D/D| \cong 0.05$. The relative accuracy of the area, A , and thickness, d , of the sample were both about 0.01. The systematic accuracy of the measurement of the real and imaginary parts of the permittivity, ϵ' and ϵ'' , respectively, were calculated via Equation 23 and Equation 24, yielding total relative errors of one and five percent.

Another estimate of the stochastic error of the signals in some region may be obtained by taking a ratio of the local scatter of the data to their median value. Such an

**** A Wayne-Kerr 6245 Precision Component Analyzer that had been used previously had a lower signal-to noise ratio for a given measurement rate.

estimate yields stochastic errors of much less than one percent for ϵ' near the transitions and errors in ϵ'' as high as ten percent far from any anomalies.

$$\left| \frac{\Delta \epsilon'}{\epsilon'} \right| \cong \sqrt{\left(\frac{\Delta C}{C} \right)^2 + \left(\frac{\Delta d}{d} \right)^2 + \left(\frac{\Delta A}{A} \right)^2} \cong 0.0141 \quad \text{Equation 23}$$

$$\left| \frac{\Delta \epsilon''}{\epsilon''} \right| \cong \sqrt{\left(\frac{\Delta C}{C} \right)^2 + \left(\frac{\Delta d}{d} \right)^2 + \left(\frac{\Delta A}{A} \right)^2 + \left(\frac{\Delta D}{D} \right)^2} \cong 0.0520 \quad \text{Equation 24}$$

Bias Voltage In order to measure the effect of an external electric bias on the behavior of the dielectric response, a Power Designs 5015D linear power supply was ported into the rear of the QuadTech 7600A. The Power Designs 5015D claimed a regulation level of better than 0.005% and a ripple level of less than 1 mV peak-to-peak. The leads from the power supply to the impedance meter were tightly twisted, but unshielded. Since the meter on the device was uncalibrated, a BK Precision 388A multimeter, with an accuracy of 0.5%, was used to set the voltages.

6.2.4. Thermal Contact

Electrical conductors provide excellent thermal contact over a wide temperature range. However, the dielectric measurement technique required that both of the sample electrodes be electrically insulated. Therefore, good thermal contact between the temperature sensor, compressor and sample necessitated a dielectric with a good ratio of

^{§§} Noise levels that are uncorrelated with the desired signal can be reduced to any desired level by increasing the number of signal averages n ; the improvement in the signal to noise ratio, SNR , is proportional to $n^{1/2}$.

thermal to electrical conductivity. As seen from Table 5, which rates several common engineering materials based on the ratio of their thermal conductivity, σ_T , to electrical conductivity, σ_E , dioxides and fluoropolymers have excellent ratios of these conductivities.

Material	σ_T/σ_E (Ω W K ⁻¹)	σ_T (W m ⁻¹ K ⁻¹)
Polytetrafluoroethylene (PTFE)	$2.5 \cdot 10^{16}$	0.25
Titanium Dioxide	$2.5 \cdot 10^{16}$	0.21
Fluorinated Ethylene Propylene	$2.1 \cdot 10^{16}$	2.5
Silicon Dioxide	$1.5 \cdot 10^{16}$	1.5
Beryllium Oxide	$2.7 \cdot 10^{14}$	270
Aluminum Nitride	$1.8 \cdot 10^{14}$	180
Alumina	$3.0 \cdot 10^{13}$	30
Copper	$4.0 \cdot 10^{-7}$	237

Table 5. Thermal-Electrical Conductivity Ratios of Common Engineering Materials.⁷⁵

At first polytetrafluoroethylene was chosen as a sample support, leaving the area-to-thickness ratio to be optimized. Any improvement in the thermal contact by increasing the area-to-thickness ratio of the contacting surfaces necessarily comes at the expense of decreasing electrical isolation. While the impedance of the sample was comparable to that of the dielectric separating the sample electrodes and the metal support, apparently both component analyzers could compensate for very low impedance shunts without introducing significant amount of noise: systematically decreasing the insulating support thickness from more than 1 cm to 20 μ m resulted in no noticeable change in the signal, but much better thermal contact.

PTFE required a separate adhesive in order to provide intimate contact with the sample. Therefore we used a 20 μ m-thick layer of acid-free tissue paper impregnated with a mixture of titanium dioxide (for improved thermal conductivity) and silicone

vacuum grease (for adhesion) as a dielectric support instead. In order to provide pressure, PTFE tape was wrapped around the top of the sample.

6.2.5. Thermal Isolation

Accurate temperature measurements required that the sample not only have good thermal contact with the sensor and temperature-controlled surface, but also that it be thermally isolated from uncontrolled heat sinks/sources. Thermal isolation of most of the sample was achieved by placing it in a vacuum with a radiation shield cooled to $T = 10$ K surrounding it. Although the measurement leads provided a path for thermal conduction, all leads were thermally anchored to the temperature-controlled copper disk by wrapping them twice around brass bolts affixed to the disk and adhering them with a mixture of TiO_2 and thermoplastic adhesive.***

6.2.6. Temperature Sensor Accuracy

The error of the calibrated DT-470-Cu-13 temperature sensor is, according to the manufacturer, less than 20 mK down to $T = 30$ K, and within 2 mK below $T = 30$ K. In our apparatus, the dielectric behavior of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ was measured and several dielectric anomalies between 320 K and 10 K were reproduced and found to agree in temperature with the published values to within one degree.

Such agreement does not guarantee that the thermal contact will be sufficient, without an exact knowledge of the thermal characteristics of a particular sample. We

*** It was found that most epoxies and cyanoacrylates dissolved the polyimide insulation of the sensor wires.

used the fact that the difference between the temperatures at which a particular anomaly occurs during heating and cooling, Δ , should be independent of the rate of heating and cooling, R , if Δ is intrinsic (good thermal contact), and that Δ should be proportional to R , if Δ is extrinsic (poor thermal contact) in order to determine the quality of the thermal contact: Whenever there was evidence of hysteresis, the measurements on CADP were repeated both at $R^{-1} = 100 \text{ s K}^{-1}$ and at $R^{-1} = 200 \text{ s K}^{-1}$.

6.2.7. Temperature Range

Because a small amount of ammonium gas is known to evolve from ADP above 313 K, none of the samples used were studied above $T = 320 \text{ K}$. None of the samples were cooled below $T = 10 \text{ K}$ because the apparatus was unable to cool below that temperature.

6.2.8. Program

A program, "Dielectrica", was written in the graphical programming language, LabView from National Instruments, in order to automate the collection of dielectric permittivity data as a function of temperature and frequency. The details of the program are shown in the Appendix.

6.3. RESULTS

Typical measurement errors of temperature were $\pm 2 \text{ K}$, resulting mainly from extrinsic thermal hysteresis arising from the finite thermal conductivity of the sample and its support. The measurements of T_c were reproducible to within 1 K between runs with

the same sample, but considerably less reproducible between samples, $T_c \cong \pm 5$ K. Because ϵ'' is typically greater than ϵ' for the features above 240 K, these anomalies will be referred to as “conductive”, while the cusp-like anomalies below 180 K will be referred to as “ferroelectric”, for reasons that will become clear in the next section.

6.3.1. CDP

c axis Because the literature does not show any results along any axis other than the b axis for CDP, for comparison with CADP, we present the real and imaginary parts of $\epsilon_c(T)$ upon cooling of CDP in Figure 17 and Figure 18, respectively. The real and imaginary parts of $\epsilon_c(T)$ upon heating of CADP.10 are shown in Figure 19 and Figure 20, respectively. As can be seen by comparing Figure 19 with Figure 17 and Figure 20 with Figure 18, no significant thermal hysteresis is found in CDP along this axis.

6.3.2. CADP.10

The real and imaginary parts of $\epsilon_c(T)$ upon cooling of CADP.10 are shown in Figure 21 and Figure 22, respectively. The analogous results for heating are shown in Figure 23 and Figure 24, respectively.

Unlike CDP, there is significant thermal hysteresis in the dielectric response of CADP.10 above $T = 200$ K. For example, $\epsilon''(T = 295 \text{ K}, f = 100 \text{ Hz}) = 4$ upon cooling, as shown in Figure 22, and $\epsilon''(T = 295 \text{ K}, f = 100 \text{ Hz}) = 270$ upon heating, as shown in Figure 24. As in CDP, no response associated with the ferroelectric phase transition is seen along the a axis in CADP.10. A conductivity anomaly is seen at $T_n = 262$ K with an $\epsilon'_c(T = T_n, f = 100 \text{ Hz})$ of only 14.5, as shown in Figure 21.

6.3.3. CADP.20

a axis The real and imaginary parts of $\epsilon_a(T)$ upon cooling of CADP.20 are shown in Figure 25 and Figure 26, respectively. The analogous results for heating are shown in Figure 27 and Figure 28, respectively. Figure 29 shows the real part of the electrical conductivity, $\sigma'_a(T)$ which was obtained from $\epsilon''(T)$ via the relation

$$\sigma' = 2 \pi \epsilon'' \epsilon_0 f, \quad \text{Equation 25}$$

where ϵ_0 is the permittivity of the vacuum and f is the measurement frequency.

As along the other two axes, there were both ferroelectric and conductive anomalies in the dielectric response along the *a* axis. As was the case along the *c* axis, the exact response of the conductive anomaly appeared to be sensitively dependent on the thermal history of the sample, since it was never exactly reproducible between thermal cycles. However, upon cooling, both the ferroelectric and conductive anomalies along the *a* axis were considerably smaller than those along the *c* axis: One can see from Figure 25 that ϵ'_a is barely perceptible above the background and is considerable broadened, and that the conductive anomaly crests at $T_n = 319$ K, with $\epsilon''_a(T = T_n, f = 31.62 \text{ Hz})$ of only 29.

As seen from Figure 28, the magnitude of the conductive anomaly upon heating, $\epsilon''_a(T = T_n, f = 31.62 \text{ Hz}) = 1.4 \cdot 10^6$, is several orders of magnitude larger than upon cooling.

b axis The temperature and frequency dependence of the real and imaginary parts of $\epsilon_b(T)$ upon cooling of CADP.20 are shown in Figure 30 and Figure 31, respectively. The results for heating CADP.20 along the *a* axis are similar.

Although the concentration of ammonium ions incorporated into the crystal is small ($\sim 5\%$), the behavior of CADP.20 differs significantly from that in pure CDP:

- The maximum value of $\epsilon'_b(T)$, ~ 9000 , is significantly smaller than that in the pure system, ~ 17000 .
- $T_m(\text{CADP.20}) = 160 \pm 1$ K, whereas $T_m(\text{CDP}) = 154 \pm 2$ K.
- As seen in Figure 31, CDP only exhibits ordinary protonic conductivity between T_c and the superionic transition temperature, T_h .

c axis The dielectric response along the *c* axis in CADP.20 upon cooling, shown in Figure 32 to Figure 35, significantly differs from the responses along the corresponding axis in CDP: The pure compound exhibits no dielectric anomalies along this axis, whereas the mixed system exhibits at least two distinct anomalies: a ferroelectric anomaly, and a “conductive” anomaly seen only in the heating runs.

As shown in Figure 32, upon cooling along the *c* axis in CADP.20, the maximum in $\epsilon'_c(T, f = 1 \text{ kHz})$ occurs at $T_m = 170 \text{ K} \pm 2 \text{ K}$ and, as shown in Figure 33, the protonic conductivity appears at $T \cong 300 \text{ K}$. $\epsilon'_c(T_m)$ does not exhibit a significant amount of thermal hysteresis: the hysteresis in the value of T_m is within experimental error resulting from extrinsic hysteresis ($\pm 1 \text{ K}$).

Figure 34 and Figure 35 for heating runs show a huge conductivity anomaly with a sudden onset at $T = 255 \text{ K}$. In Figure 35 this anomaly swamps the relatively small

protonic conductivity seen in Figure 33 above $T = 300$ K. This conductive anomaly reaches a maximum value at $T = T_n$ of $\epsilon''_c(T_n = 289 \text{ K}, f = 10 \text{ Hz}) = 2.5 \times 10^4$. Upon three sequential thermal cycles between 320 K and 50 K, the conductive anomaly systematically increased: on the first cycle $\epsilon''_c(T_n, f = 31.6 \text{ Hz}) = 9.0 \cdot 10^1$, on the second cycle $\epsilon''_c(T_n, f = 31.6 \text{ Hz}) = 4.1 \cdot 10^3$ and on the third cycle $\epsilon''_c(T_n, f = 31.6 \text{ Hz}) = 9.8 \cdot 10^4$.

After the third thermal cycle, a cycle with a bias field, $E = 20 \text{ kV m}^{-1}$, was performed. The effect of this field on the ferroelectric anomaly was to reduce $\epsilon''_c(T_m, f = 1 \text{ kHz})$ from 200 to 130 and to shift T_m from 170 K to 145 K. However, the effect on the conductive anomaly was much more dramatic: $\epsilon''_c(T_n, f = 31.6 \text{ Hz})$ was reduced from $9.8 \cdot 10^4$ on the previous thermal cycle to a value of less than 5. A subsequent cycle without a bias field showed a partial recovery in $\epsilon''_c(T_n, f = 31.6 \text{ Hz})$ to a value of 2.3×10^3 . In the next cycle, CADP.20 was cooled only to 200 K before reheating to 320 K. This time there was only a small slowly varying anomaly that seemed to peak at $\epsilon''_c(T_n = 318 \text{ K}, f = 31.6 \text{ Hz}) = 27$. The dielectric behavior was similar to that which occurred when an external electric bias was applied.

Figure 29 shows the real part of the electrical conductivity, $\sigma'_c(T)$, along the c axis upon heating. One may see that here, as along the a axis, the conductivity in the region of the anomalous conductivity is not monotonically related to frequency.

6.3.4. CADP.40

The real and imaginary parts of $\epsilon_c(T)$ for CADP.40 are shown in Figure 39 and Figure 40, respectively.

6.3.5. DCADP.20

b axis The real and imaginary parts of $\epsilon_b(T)$ upon cooling DCADP.20 are shown in Figure 41 and Figure 42, respectively. The analogous results for heating do not differ significantly from these results. The effect of deuteration is, as in DCDP, to dramatically increase $\epsilon'_b(T_m)$. Indeed, both CADP.20 and DCADP.20 have T_m 's along the b axis that are considerably higher than in their ammonium-free counterparts, CDP and DCDP.

c axis The real and imaginary parts of $\epsilon_c(T)$ upon cooling of DCADP.20 are shown in Figure 43 and Figure 44, respectively.

The $\epsilon'_c(T)$ and $\epsilon''_c(T)$ upon heating of DCADP.20 are shown in Figure 45 and Figure 46, respectively. Unlike CADP.20, no ferroelectric anomaly was observed along this axis in DCADP.20.

The conductive anomaly, which was not evident upon cooling, occurs at about the same temperature as in CADP.20, i.e., $\epsilon''_c(T_n = 257)$.

6.3.6. Pulverization

The powder sample was less than one percent air by volume. The real and imaginary parts of $\epsilon(T)$ upon cooling of pulverized CADP.20 are shown in Figure 47 and Figure 48, respectively. The analogous results for heating are shown in Figure 49 and Figure 50, respectively.

Comparison between the permittivity for the three axes in crystalline CADP.20 and the permittivity for the powder shown in Figure 49 indicates that the dielectric results for pulverized CADP.20 differ considerably from the angularly averaged results for the

three axes: The ferroelectric transition in powdered CADP.20 is barely evident even in the magnified view of Figure 51 and seems to occur at a lower temperature and to be more diffuse than the transitions along any of the axes in crystalline CADP.20. This is consistent with the fact that T_c decreases in ferroelectrics in general as the crystal size decreases.

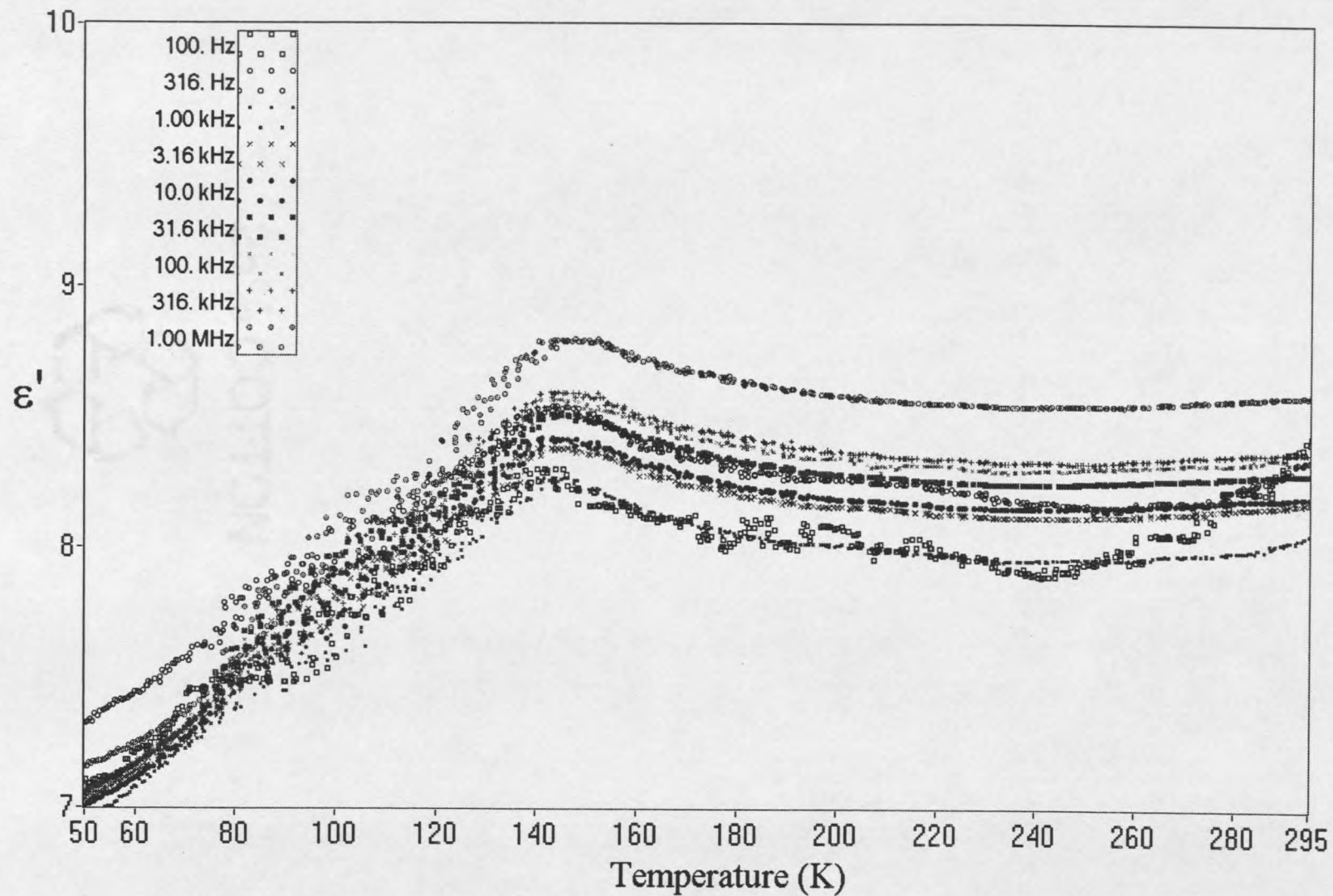


Figure 17. $\epsilon'_c(T)$ upon Cooling of CDP.

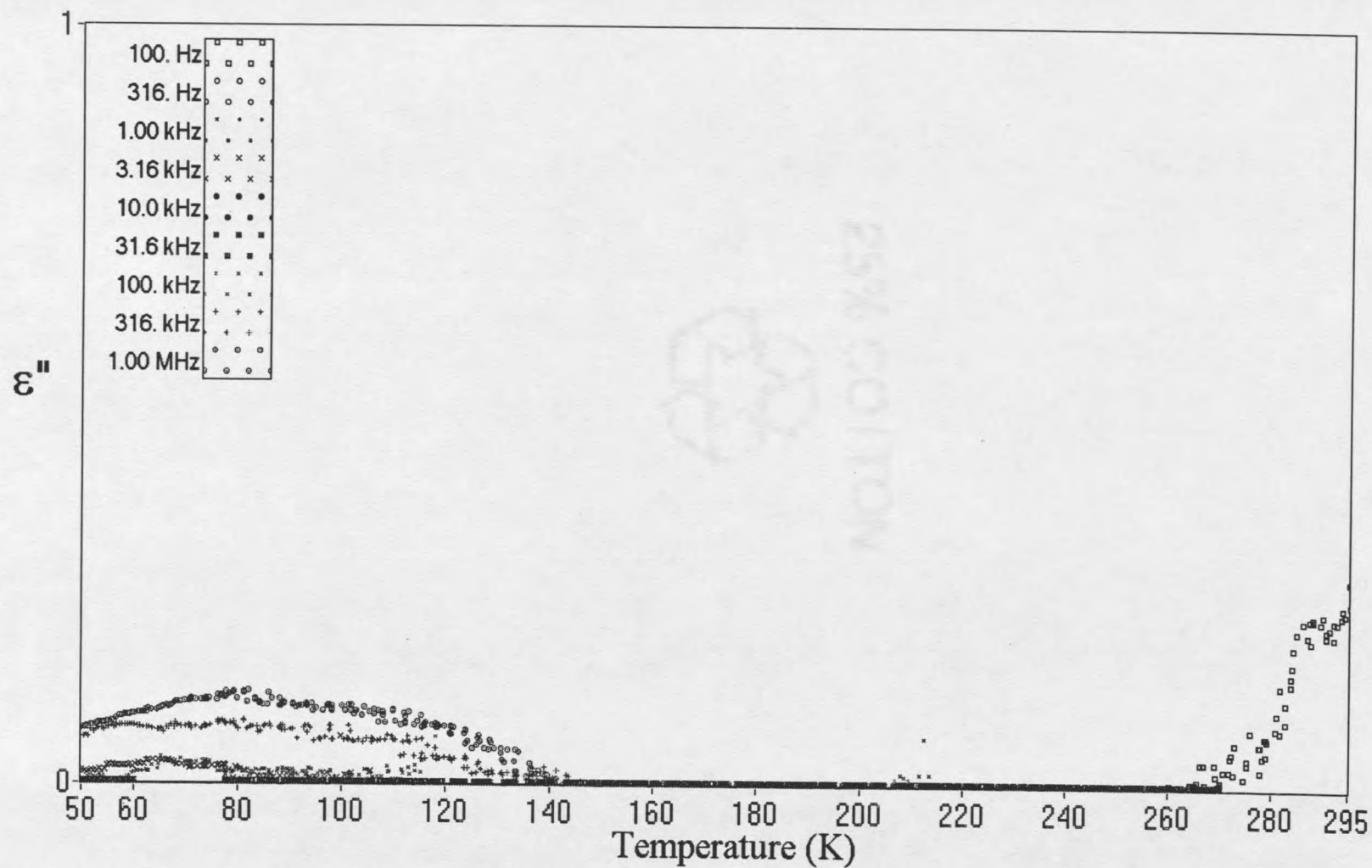


Figure 18. $\epsilon''_c(T)$ upon Cooling of CDP.

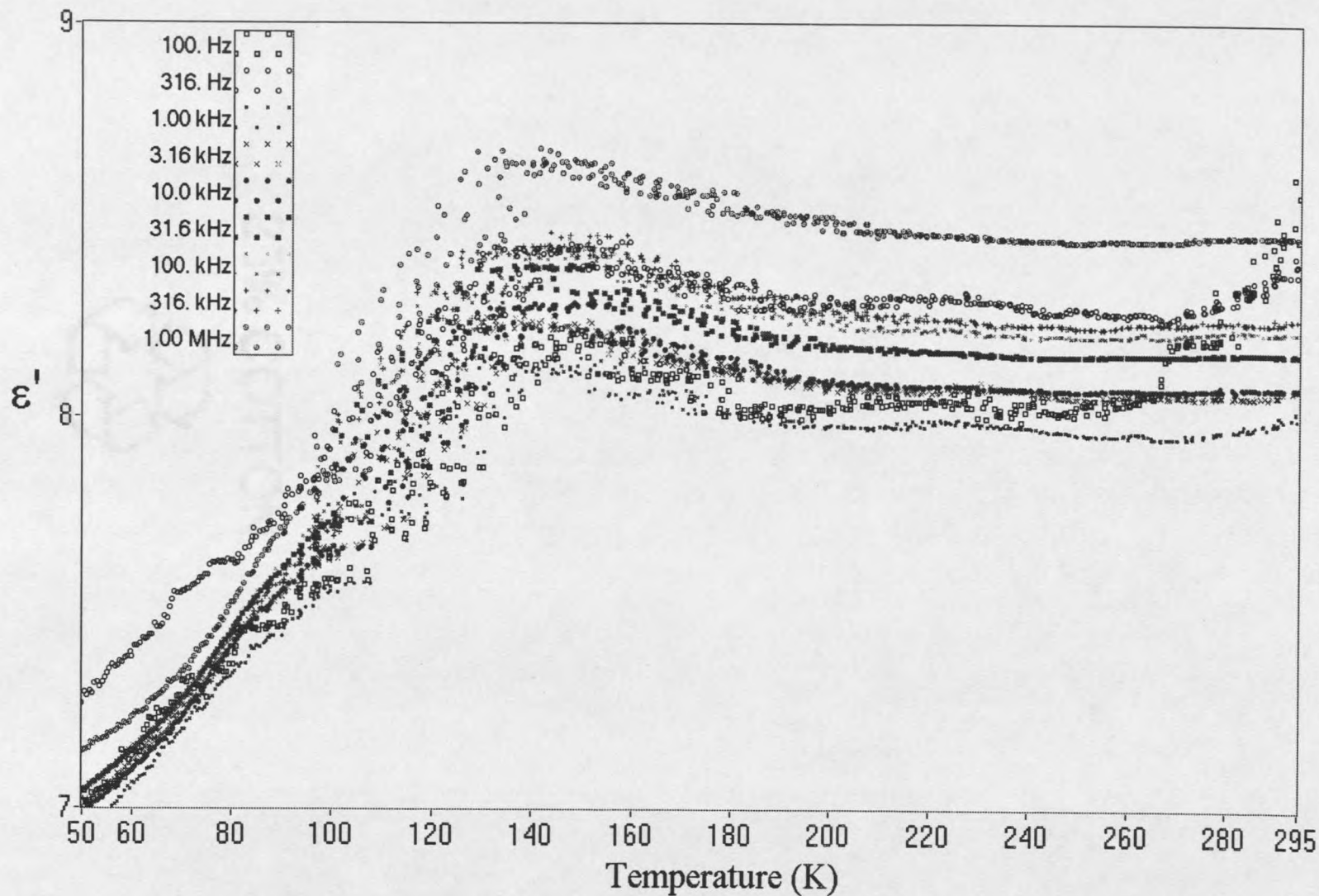


Figure 19. $\epsilon'_c(T)$ upon Heating of CDP.

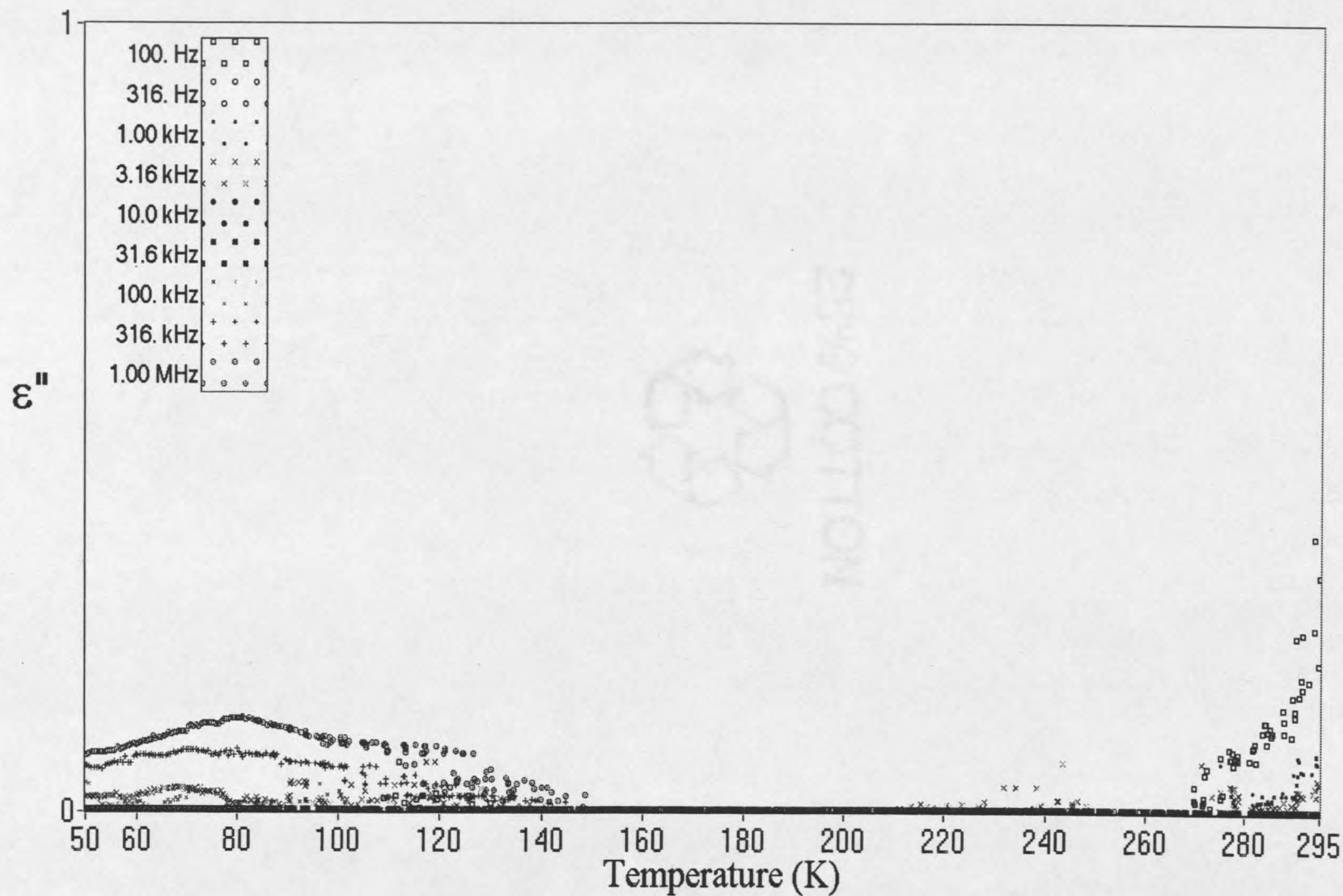


Figure 20. $\epsilon''_c(T)$ upon Heating of CDP.

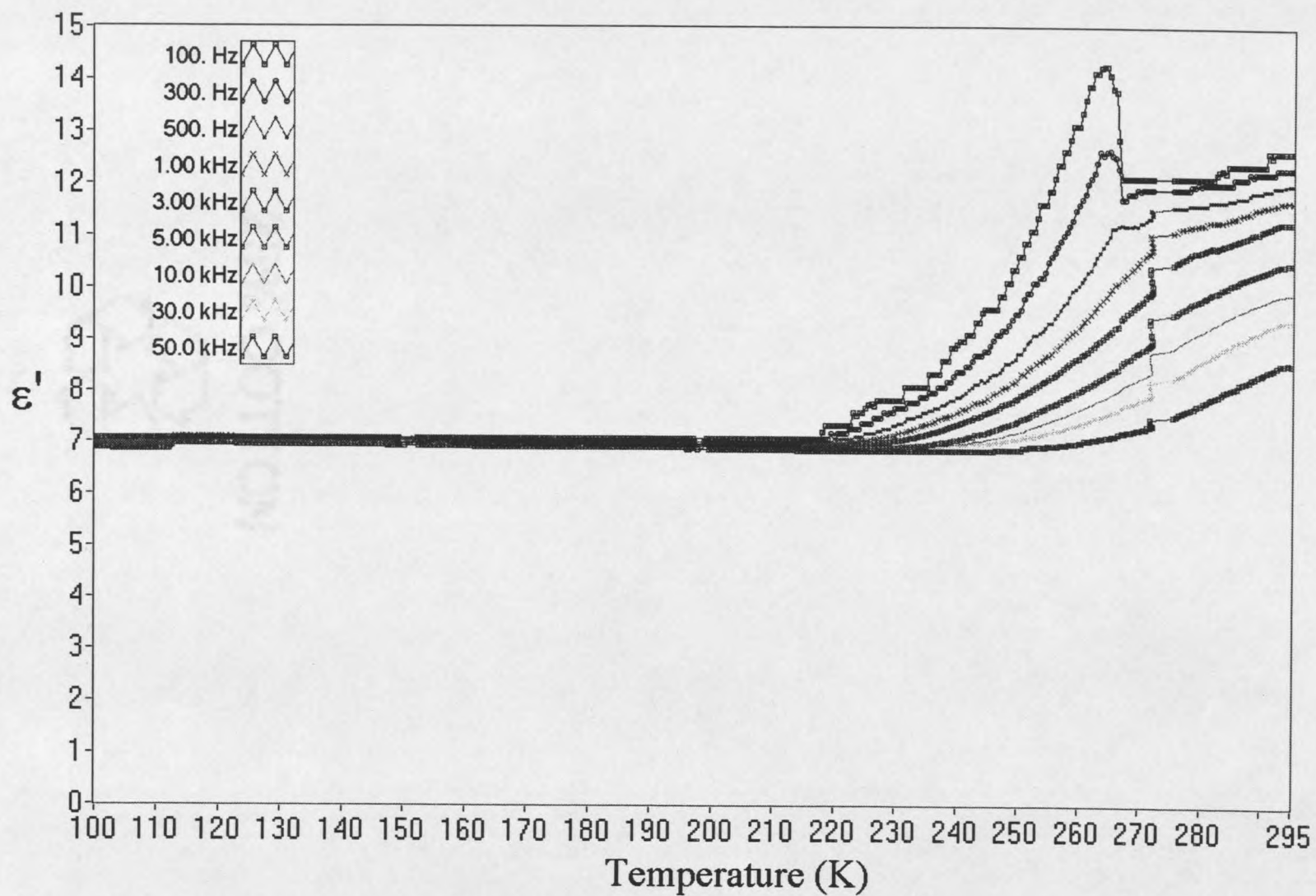


Figure 21. $\epsilon'_c(T)$ upon Cooling of CADP.10.

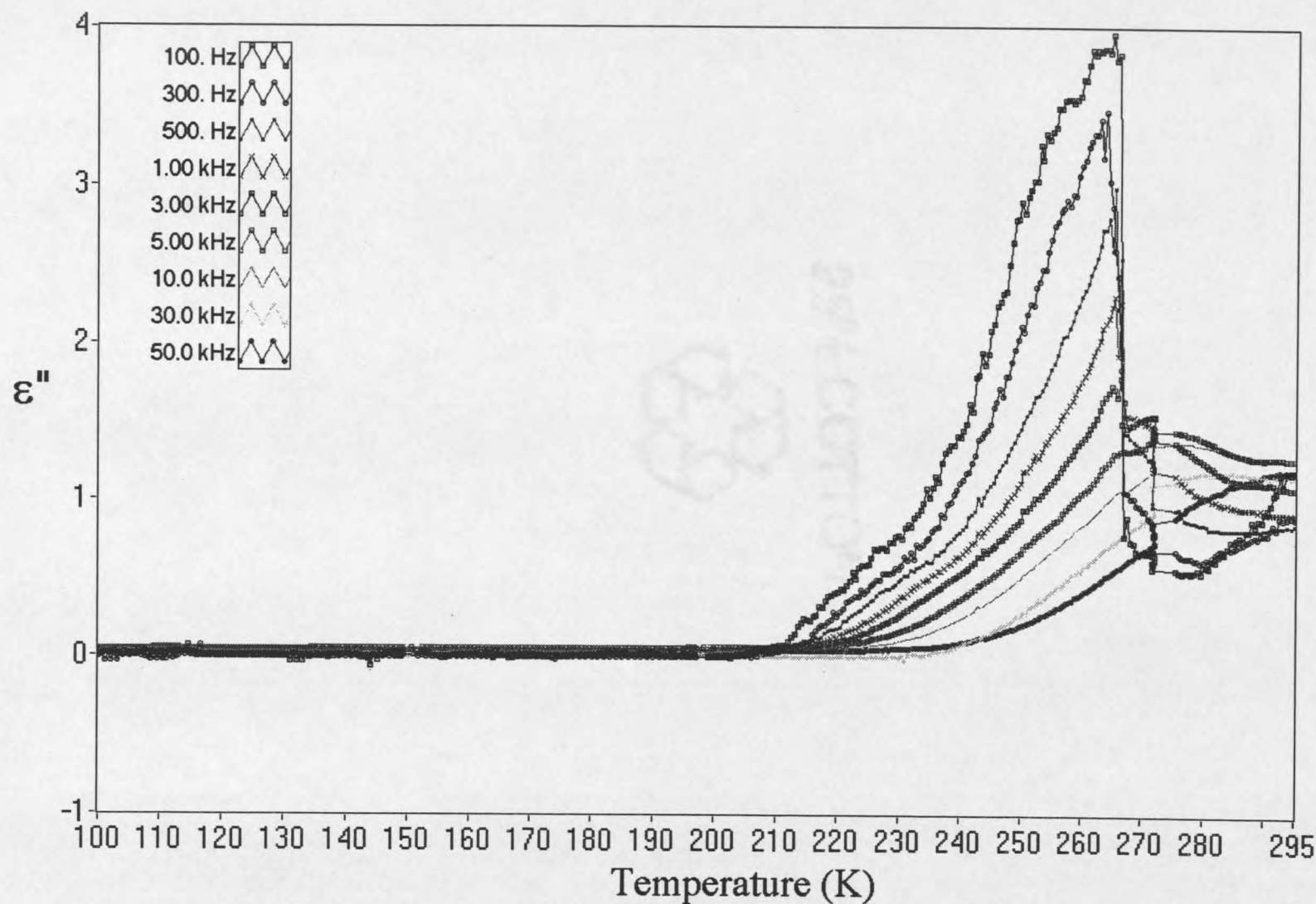


Figure 22. $\epsilon''_c(T)$ upon Cooling of CADP.10.

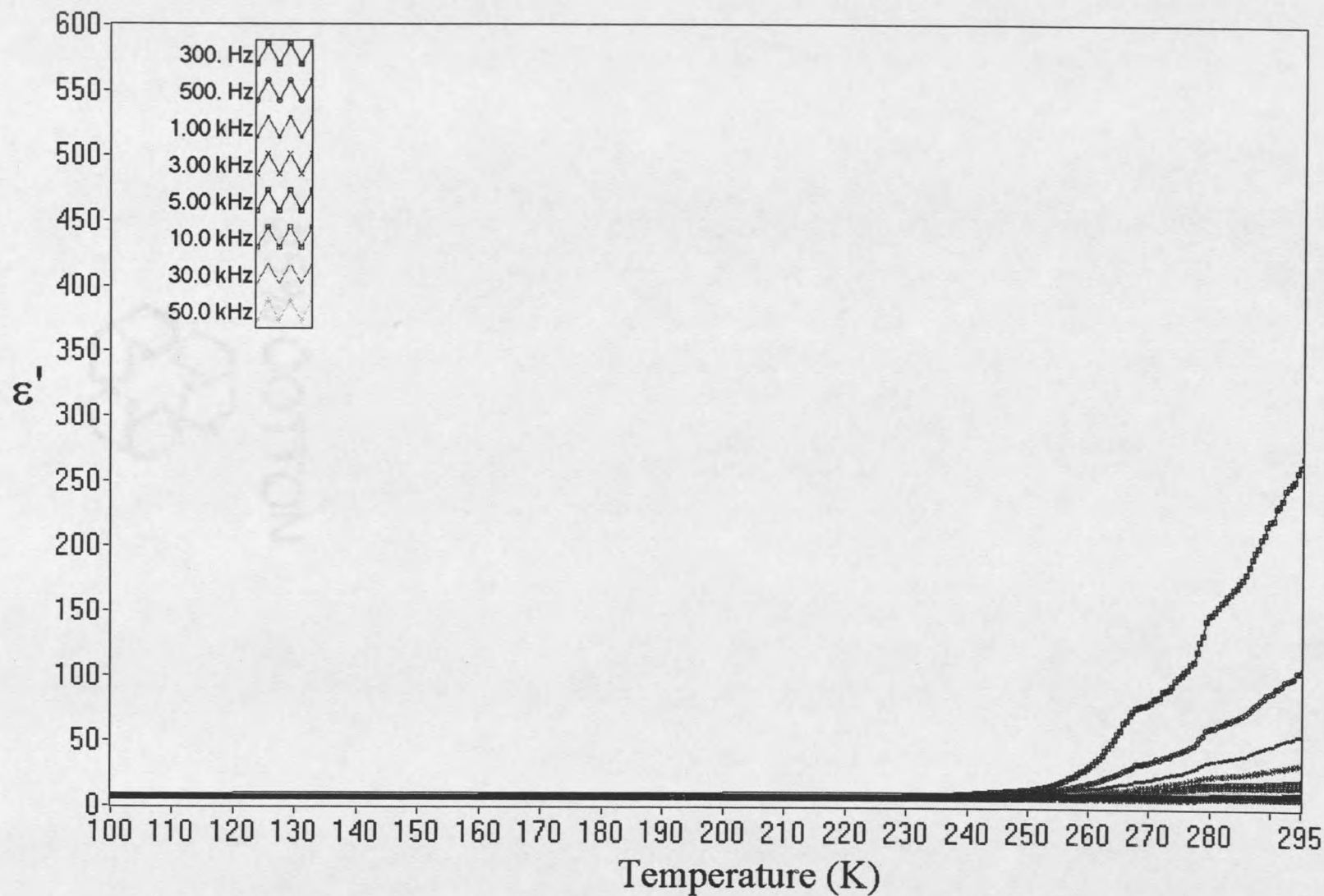


Figure 23. $\epsilon'_c(T)$ upon Heating of CADP.10.

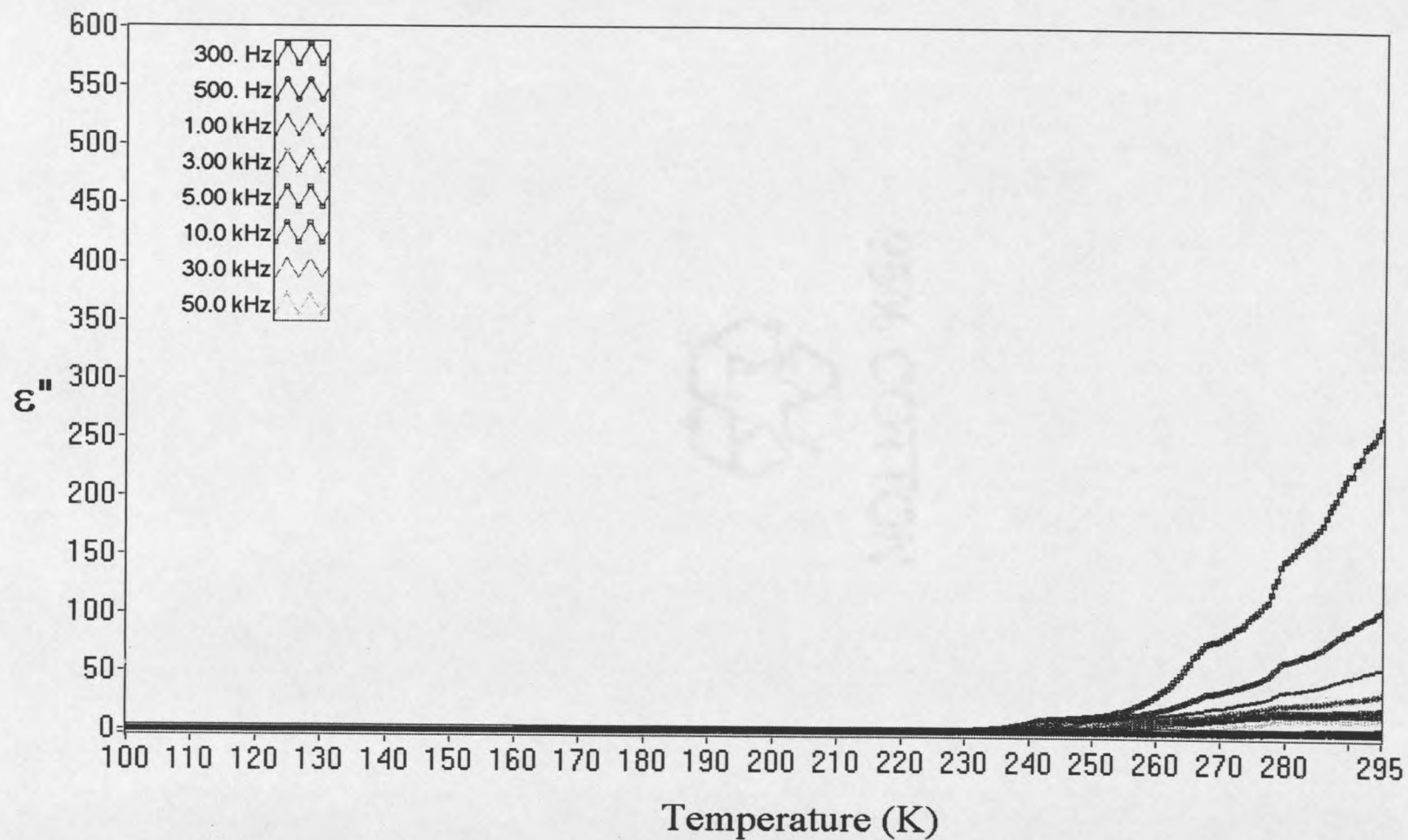


Figure 24. $\epsilon''_c(T)$ upon Heating of CADP.10.

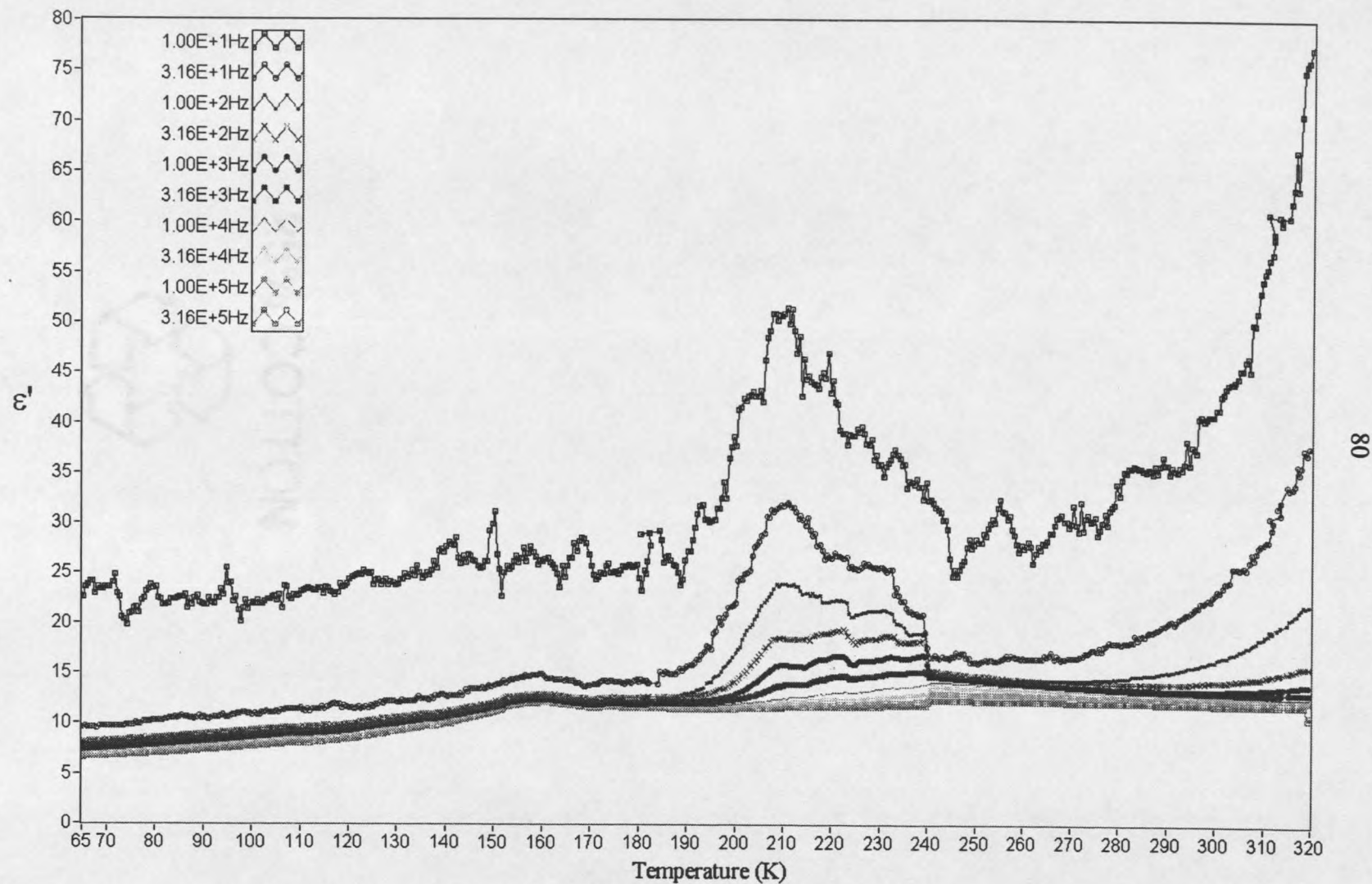


Figure 25. $\epsilon'_a(T)$ upon Cooling of CADP.20.

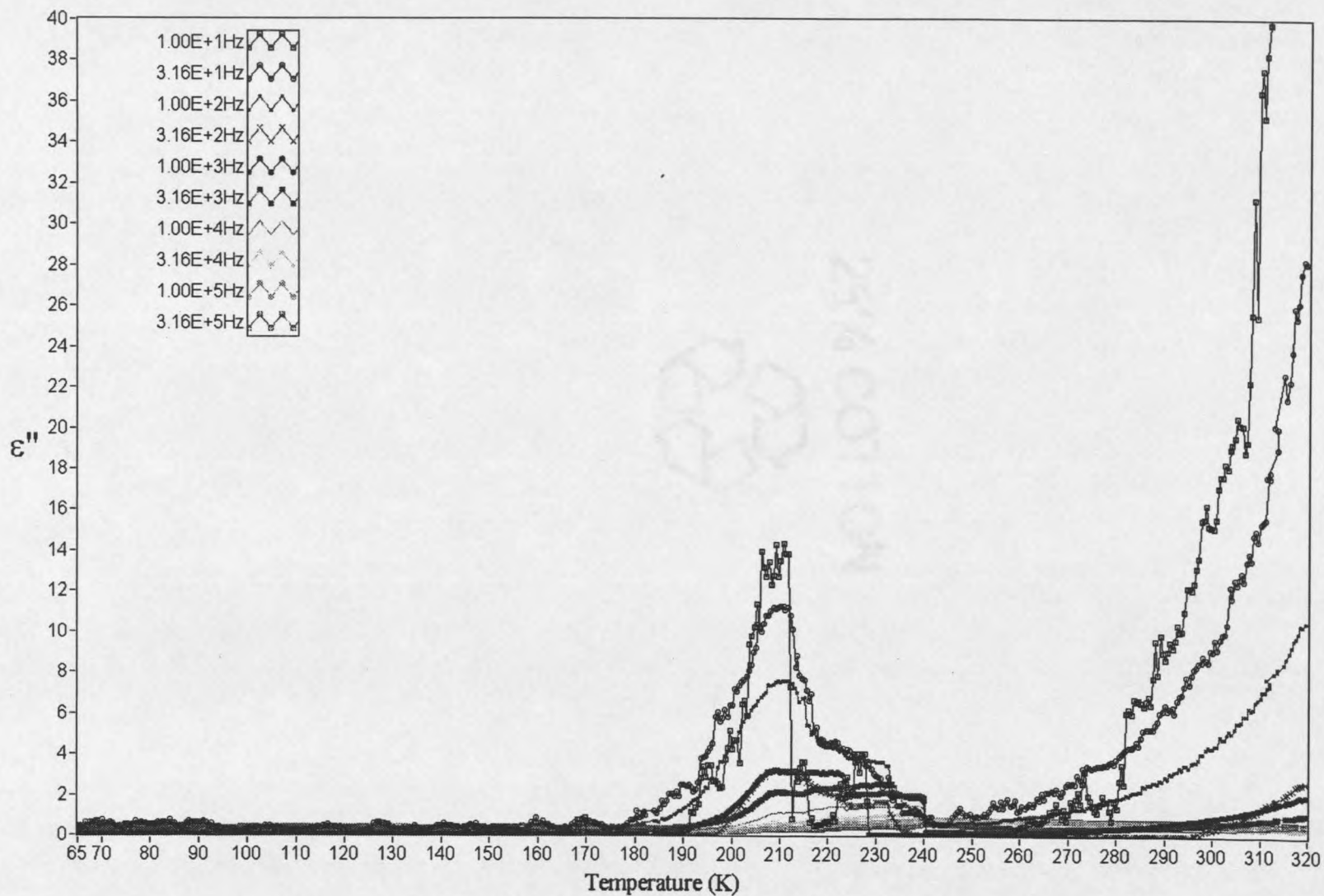


Figure 26. $\epsilon''_a(T)$ upon Cooling of CADP.20.

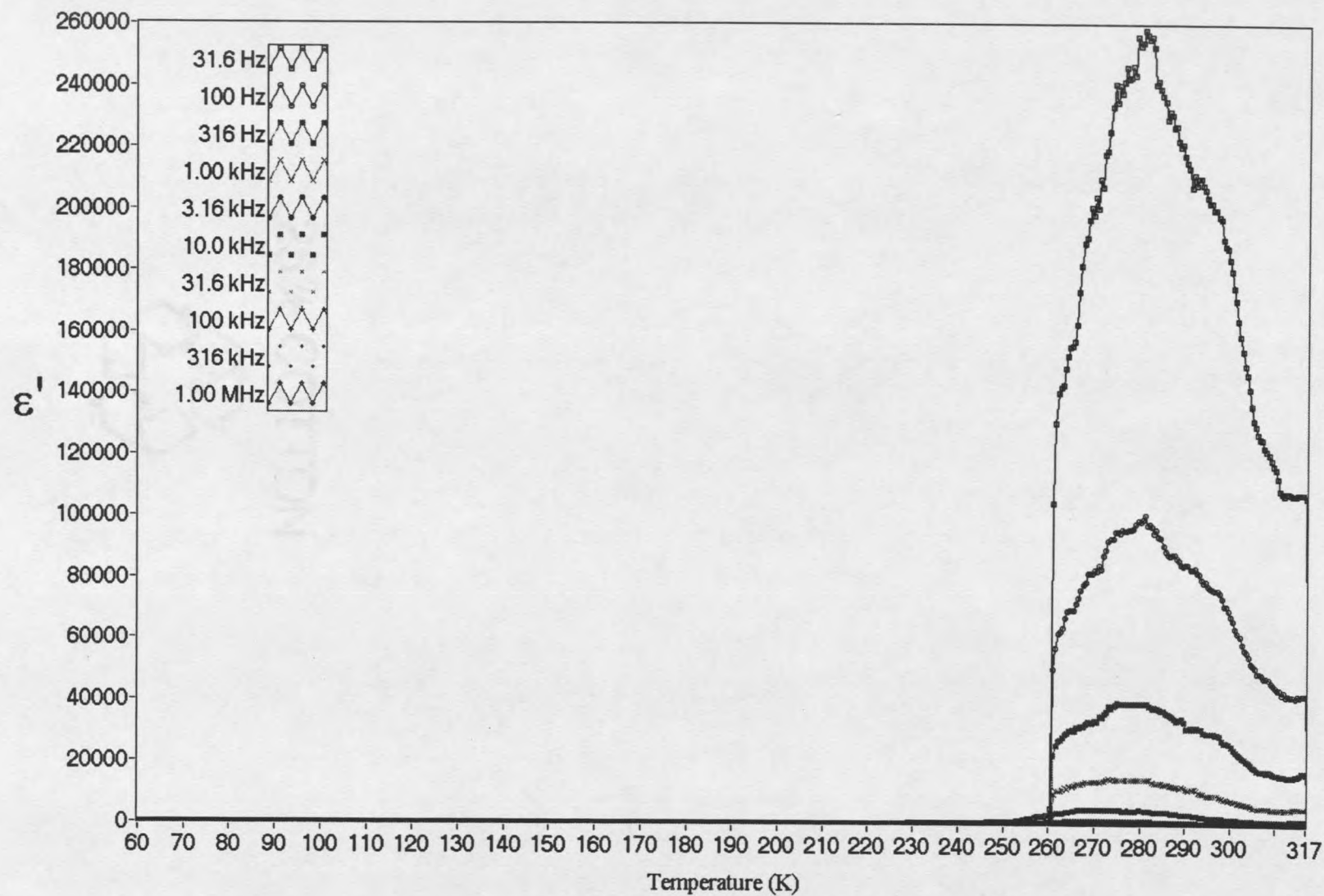


Figure 27. $\epsilon'_a(T)$ upon Heating of CADP.20.

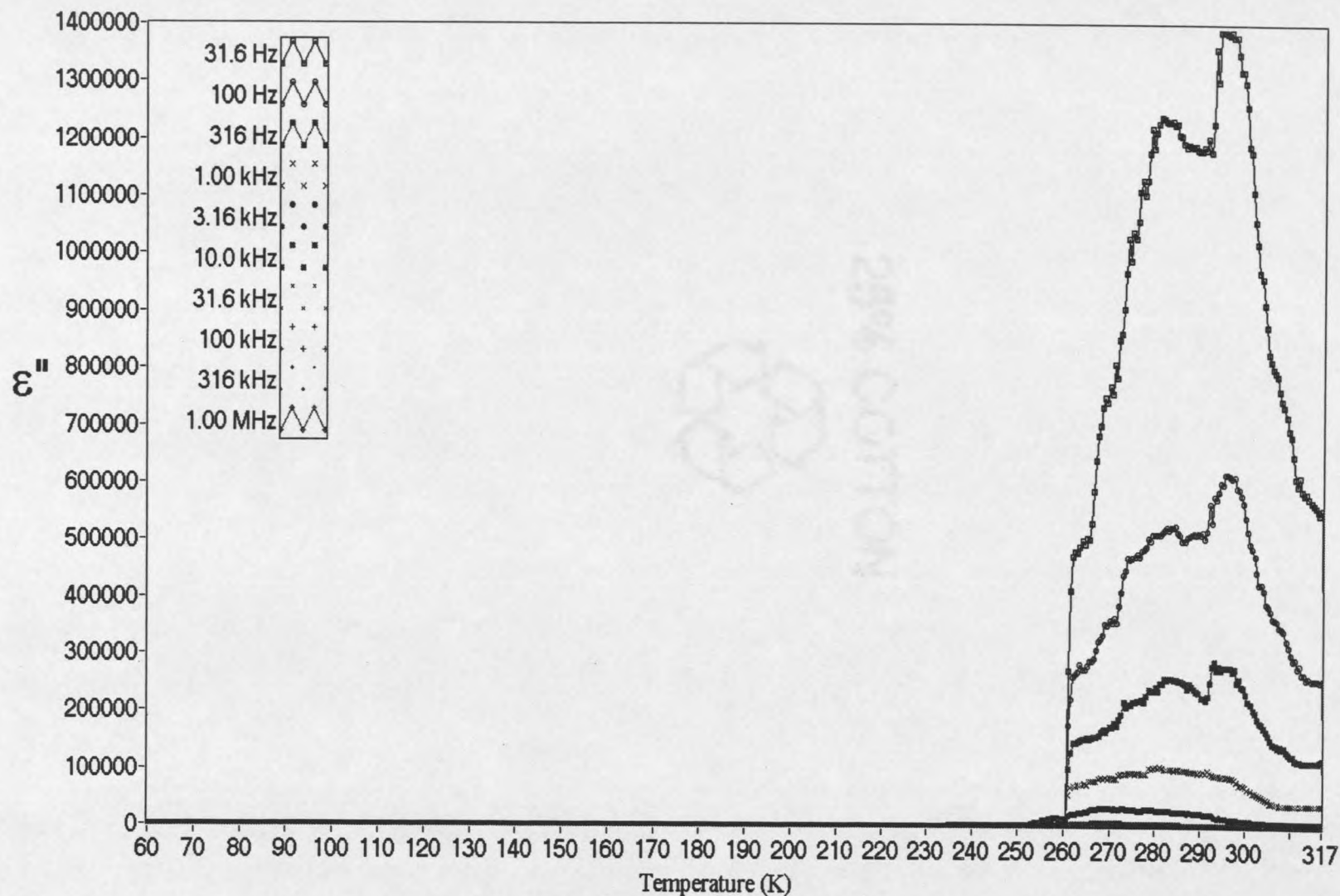


Figure 28. $\epsilon''_a(T)$ upon Heating of CADP.20.

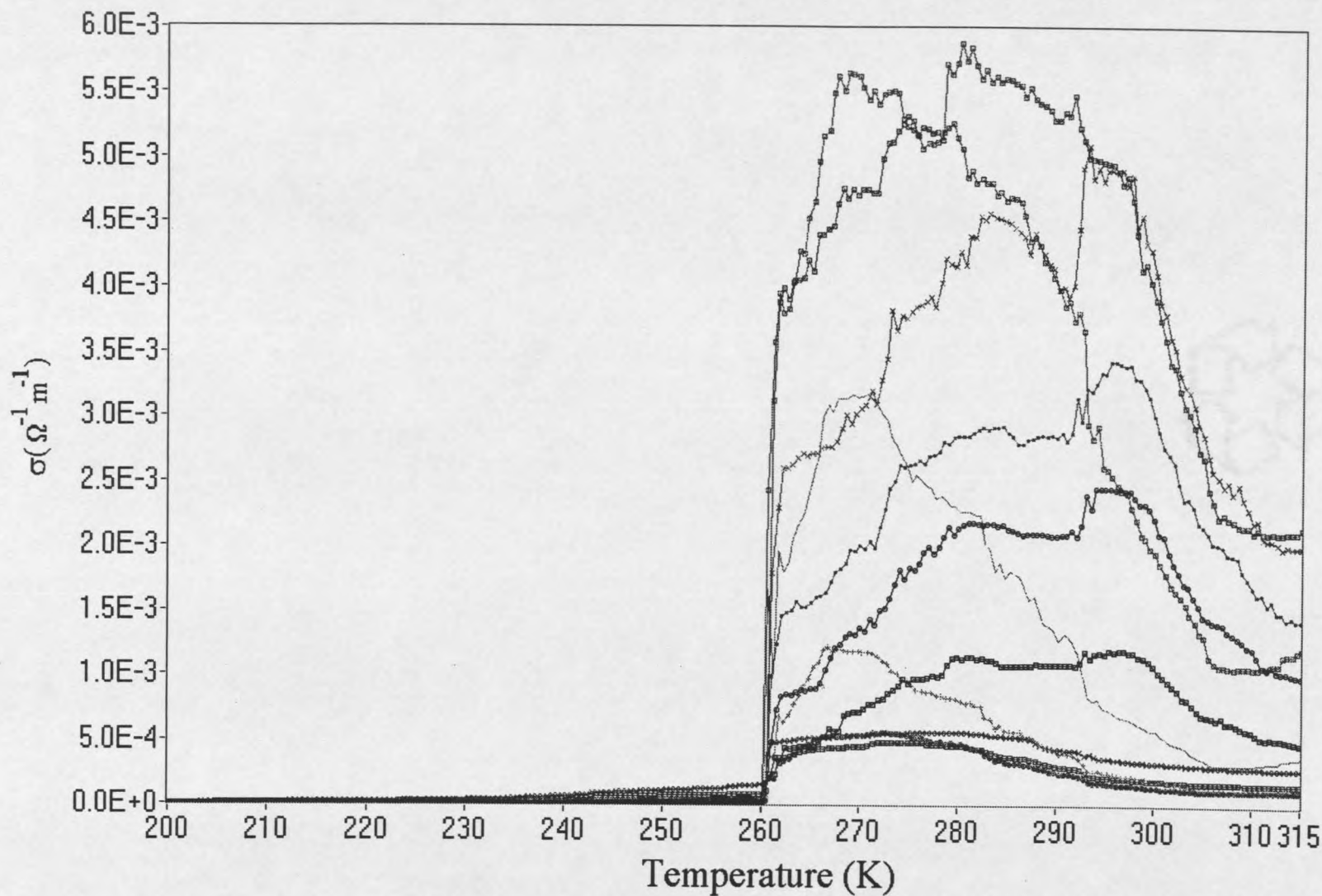


Figure 29. $\sigma'_a(T)$ upon Heating of CADP.20.

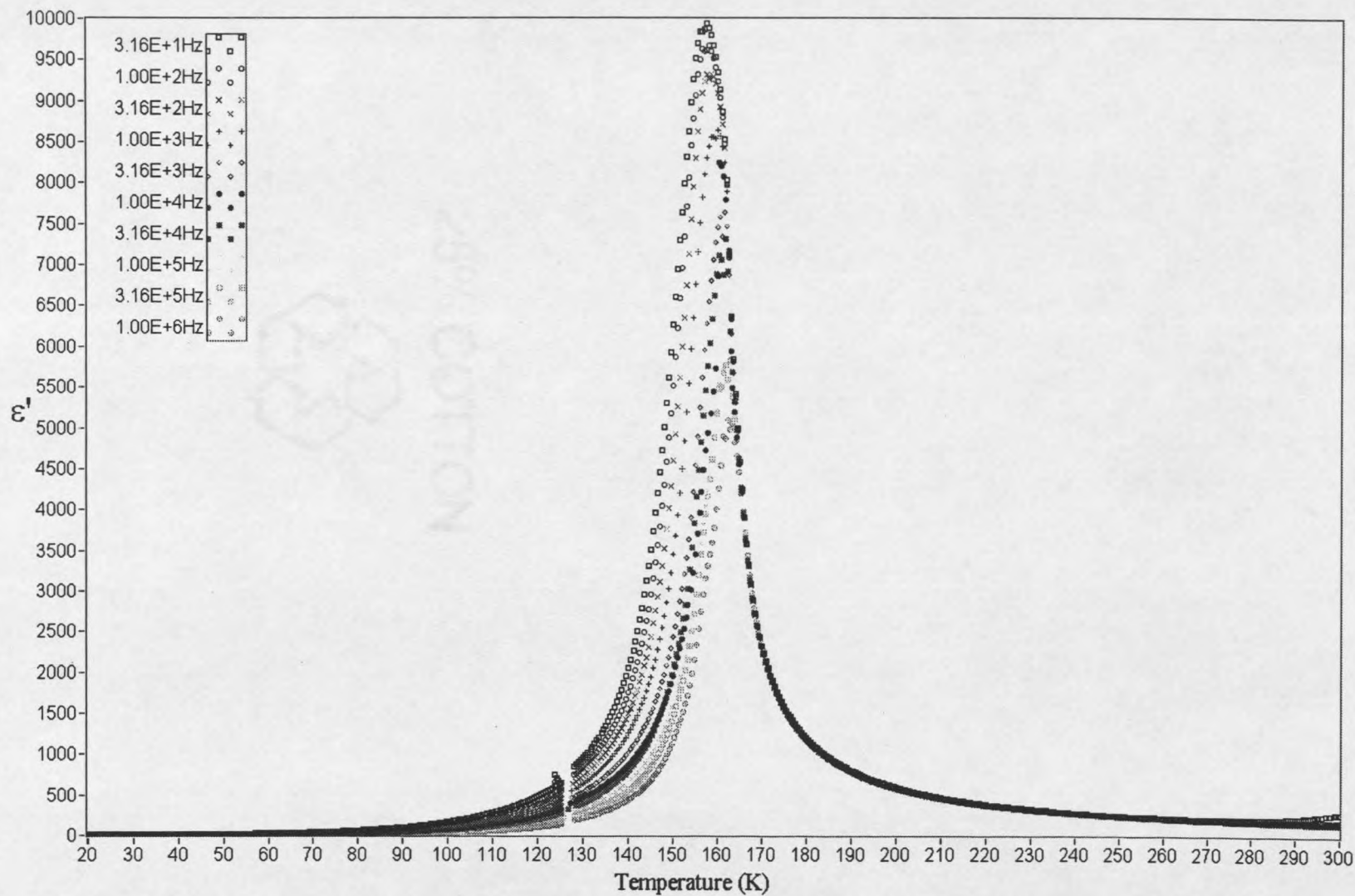


Figure 30. $\epsilon'_b(T)$ upon Cooling of CADP.20.

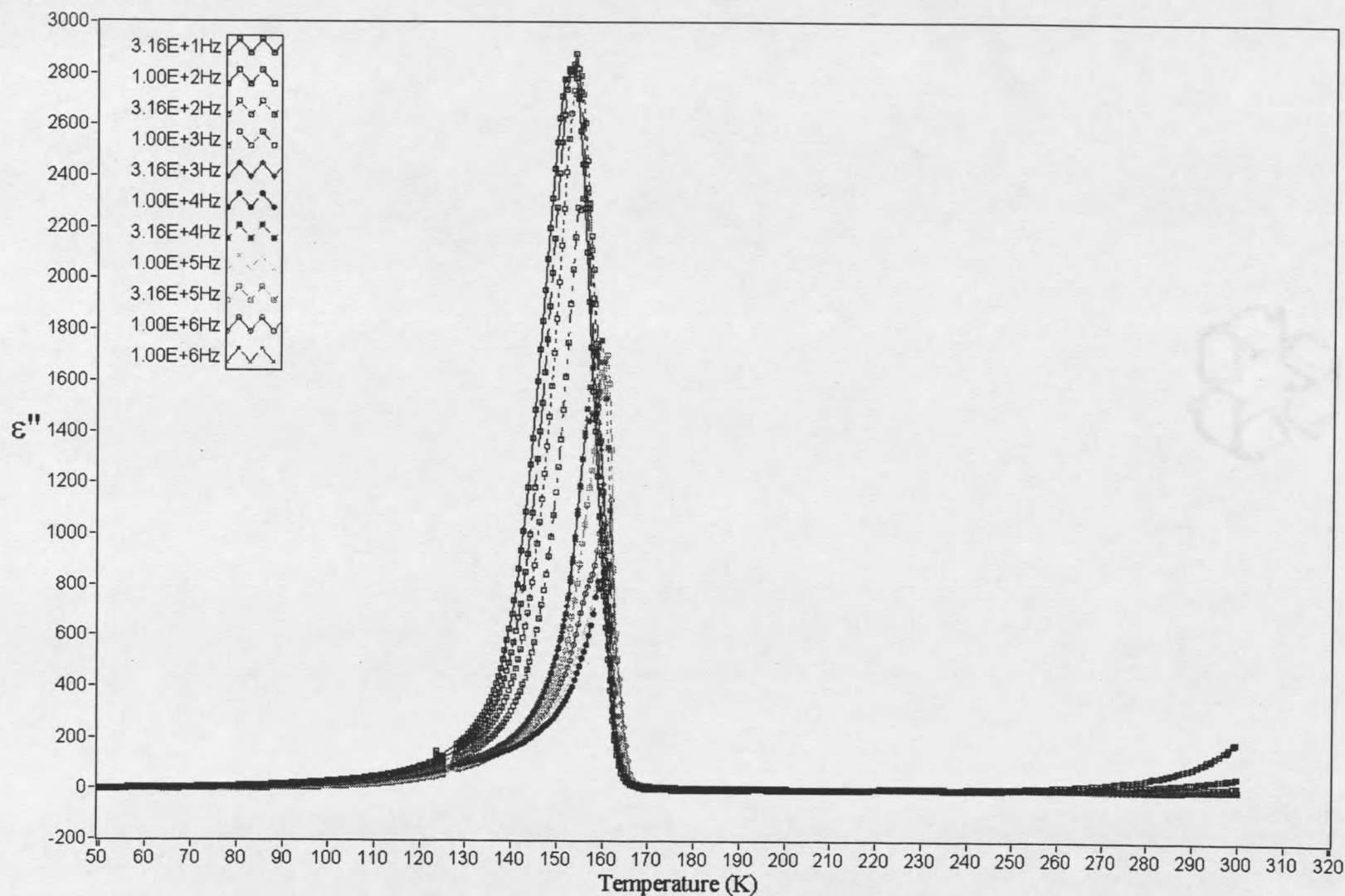


Figure 31. $\epsilon''_b(T)$ upon Cooling of CADP.20.

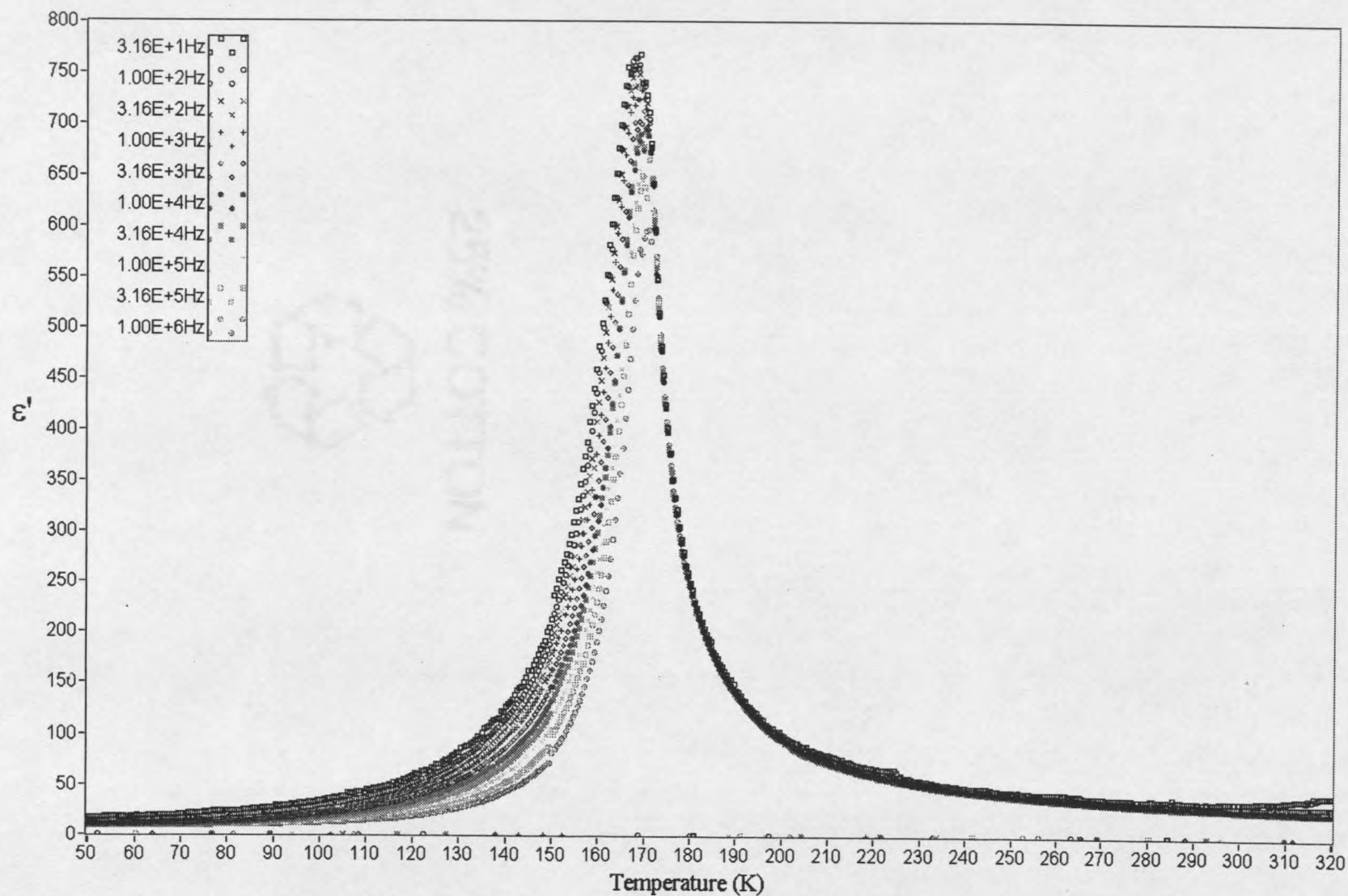


Figure 32. $\epsilon'_c(T)$ upon Cooling of CADP.20.

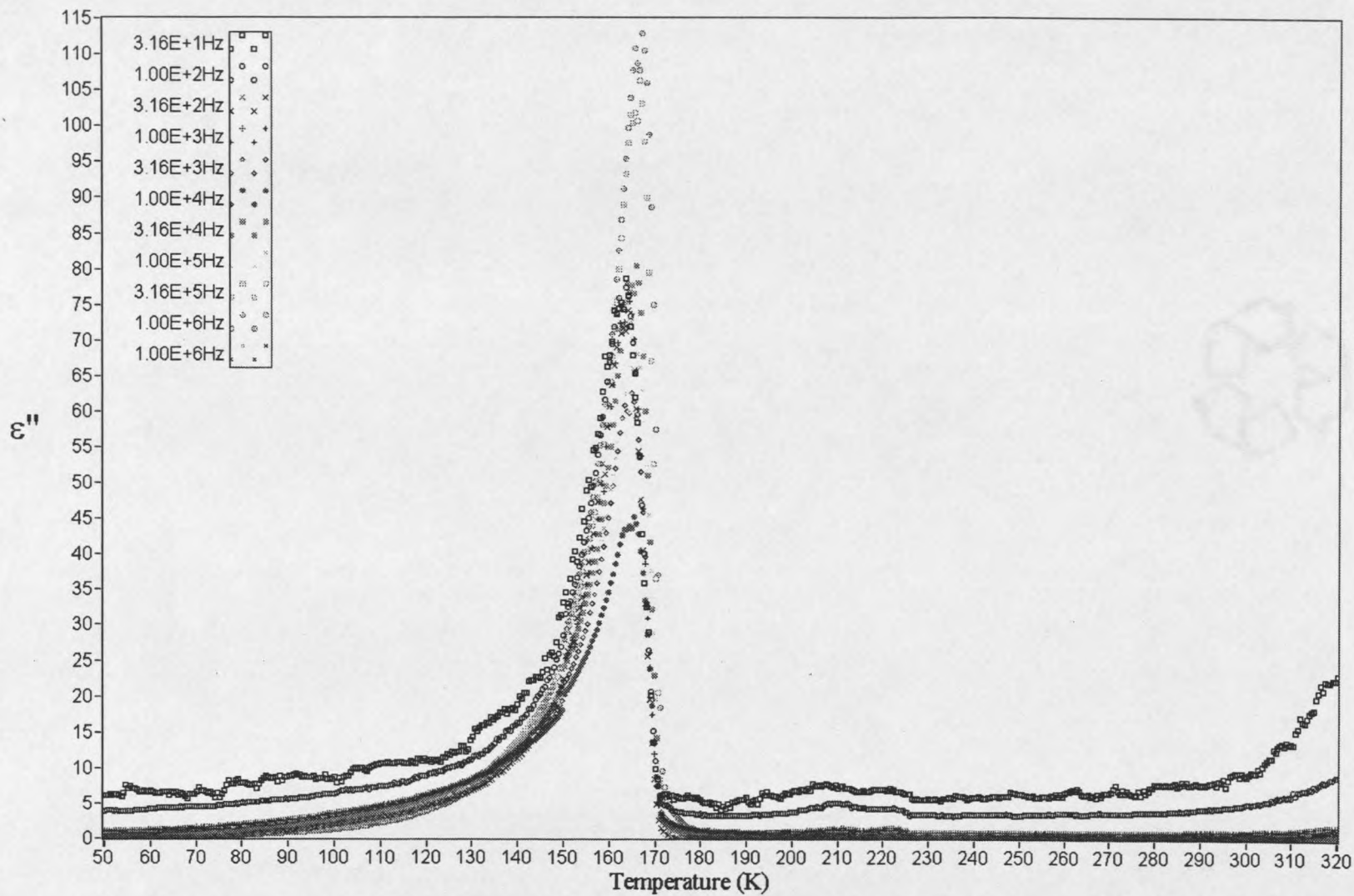


Figure 33. $\epsilon''_c(T)$ upon Cooling of CADP.20.

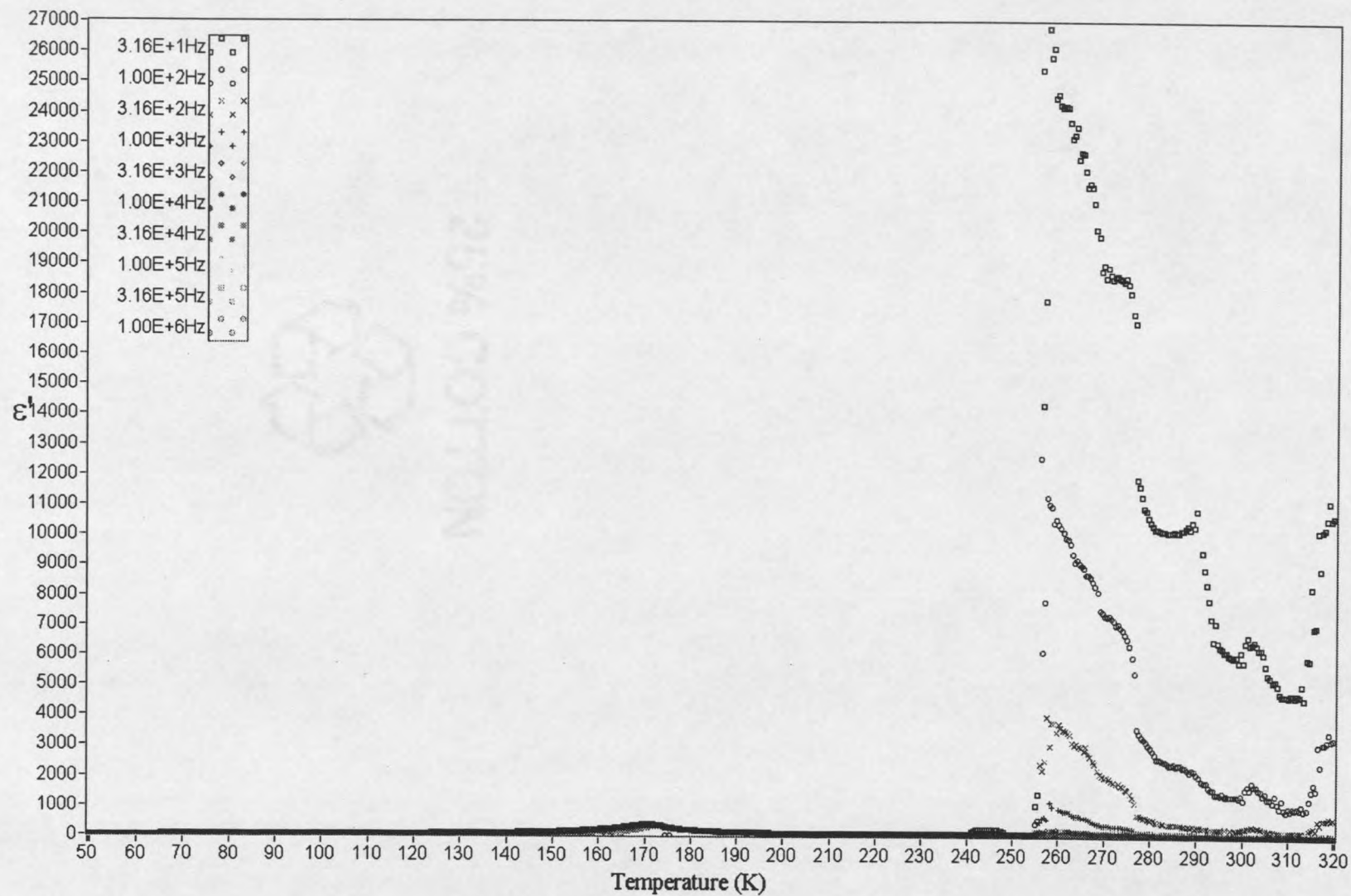


Figure 34. $\epsilon''(T)$ upon Heating of CADP.20.

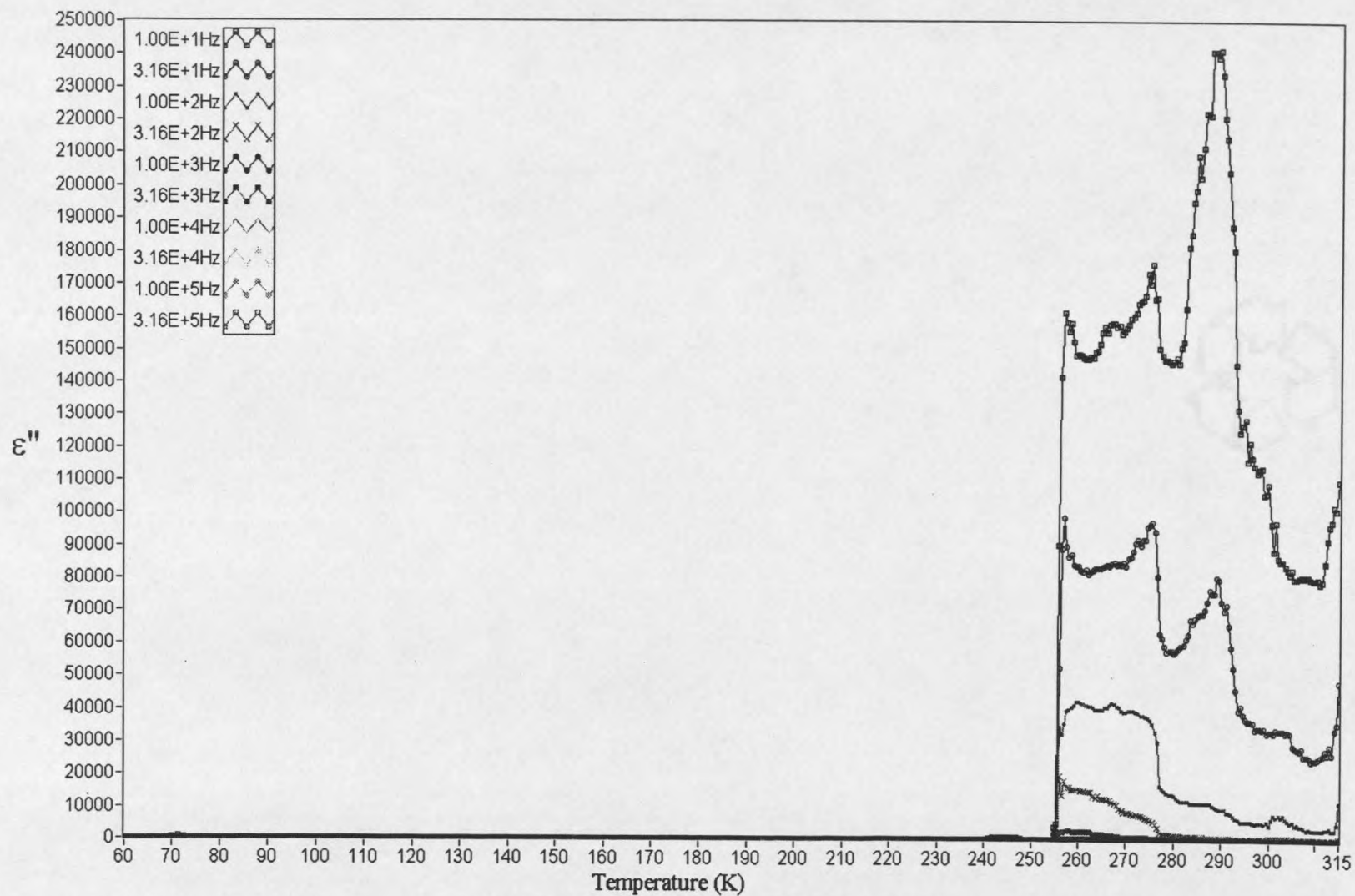


Figure 35. $\epsilon''_c(T)$ upon Heating of CADP.20.

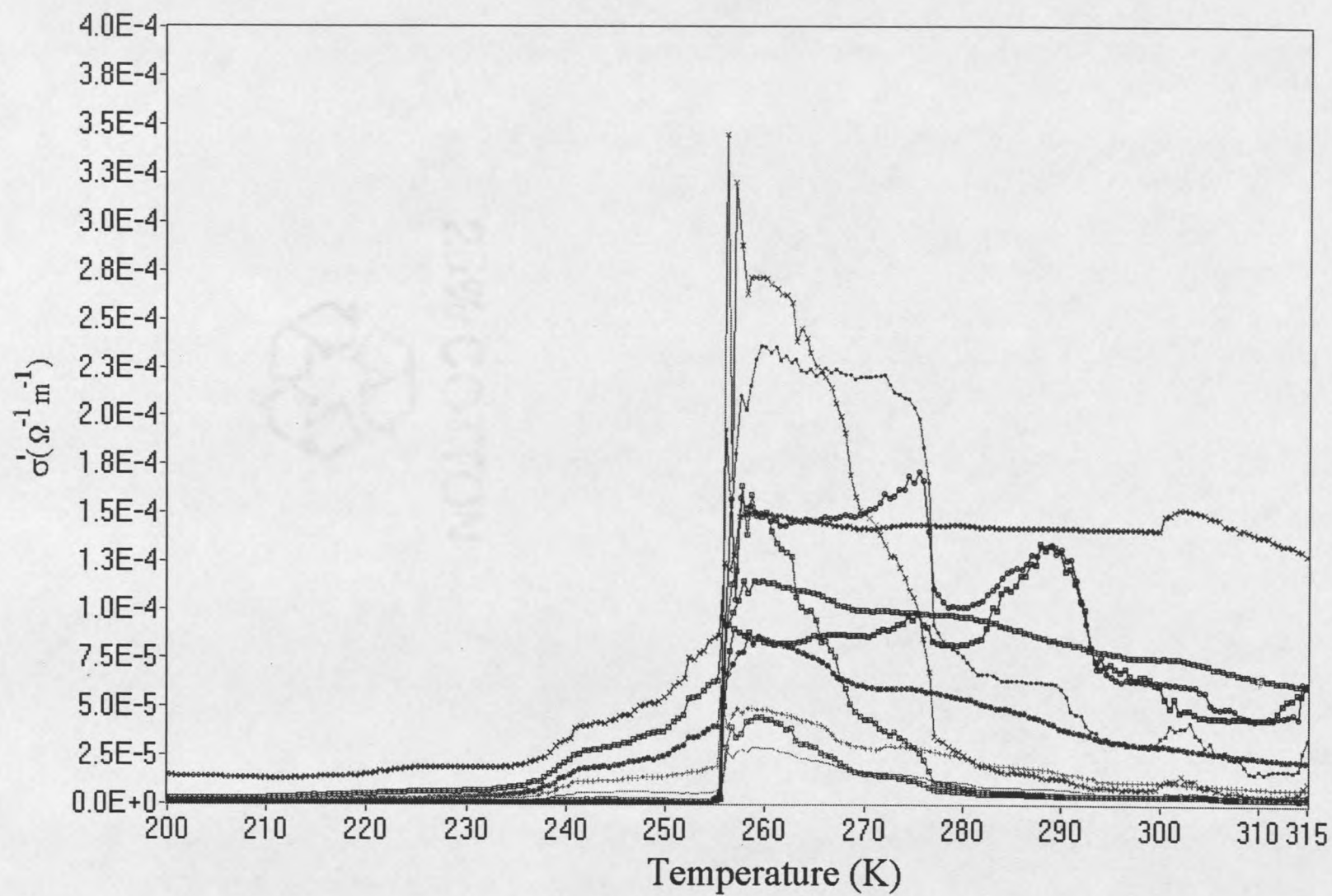


Figure 36. $\sigma'_c(T)$ upon Heating of CADP.20.

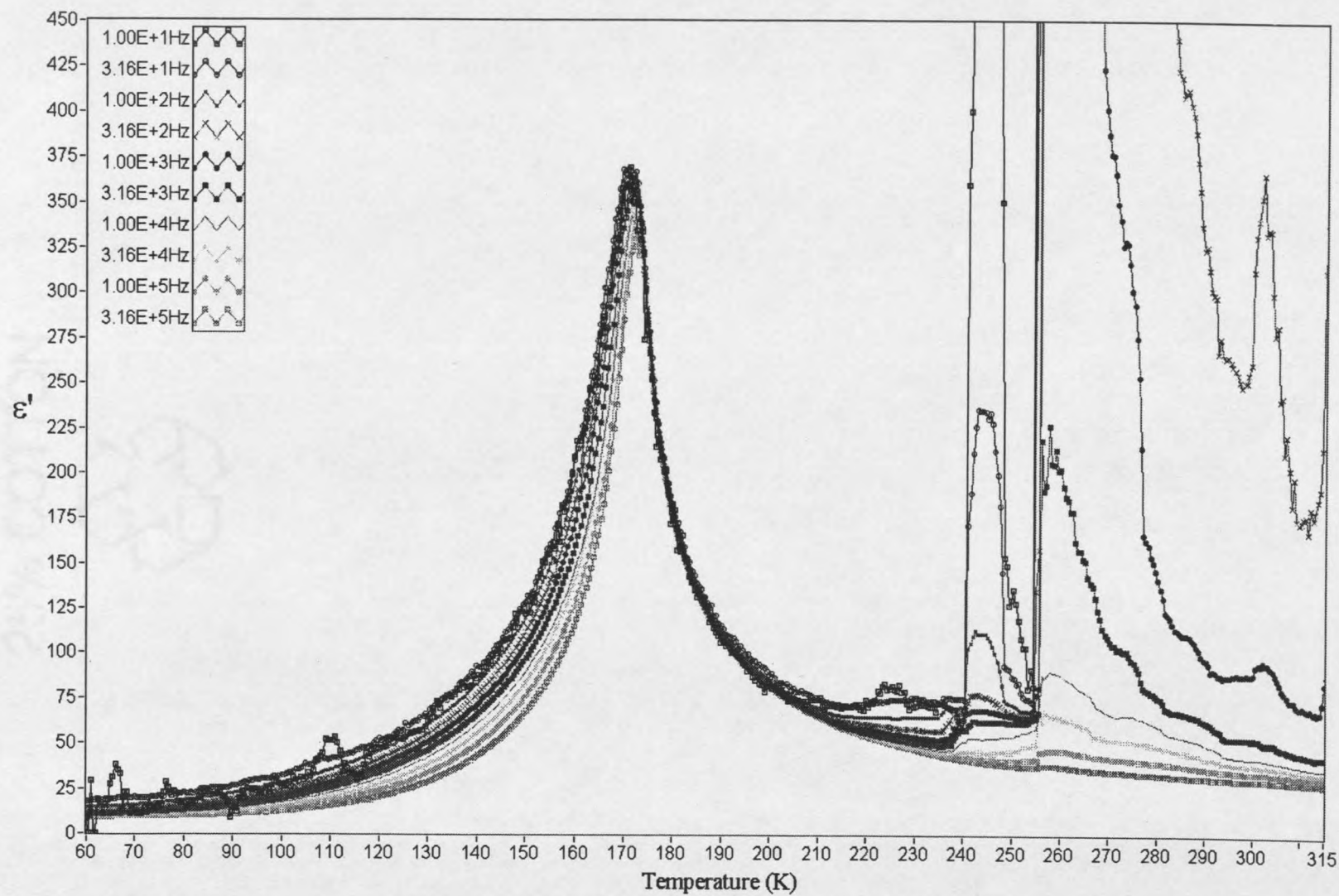


Figure 37. Magnified $\epsilon'_c(T)$ upon Heating of CADP.20

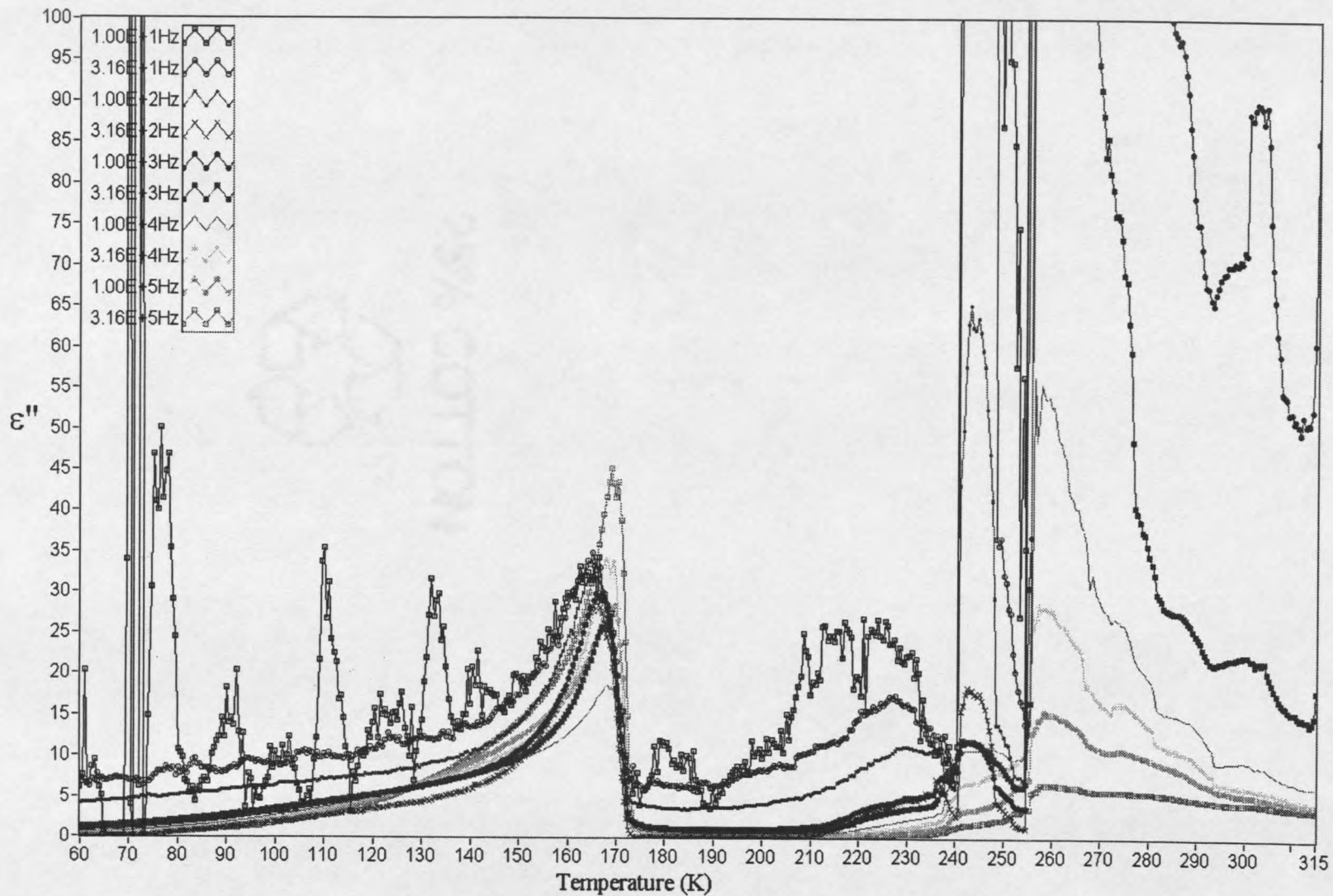


Figure 38. Magnified $\epsilon''_c(T)$ upon Heating of CADP.20.

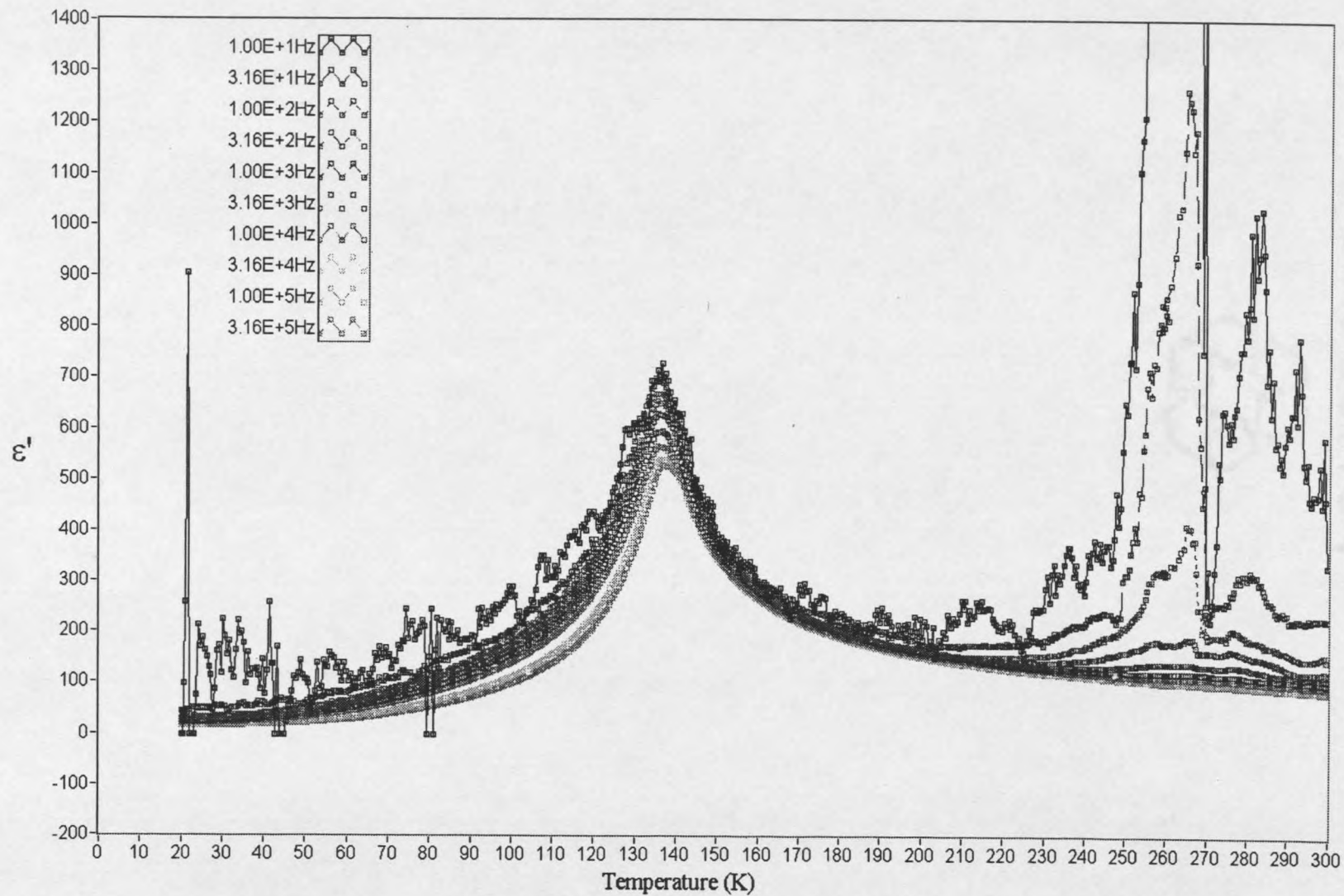
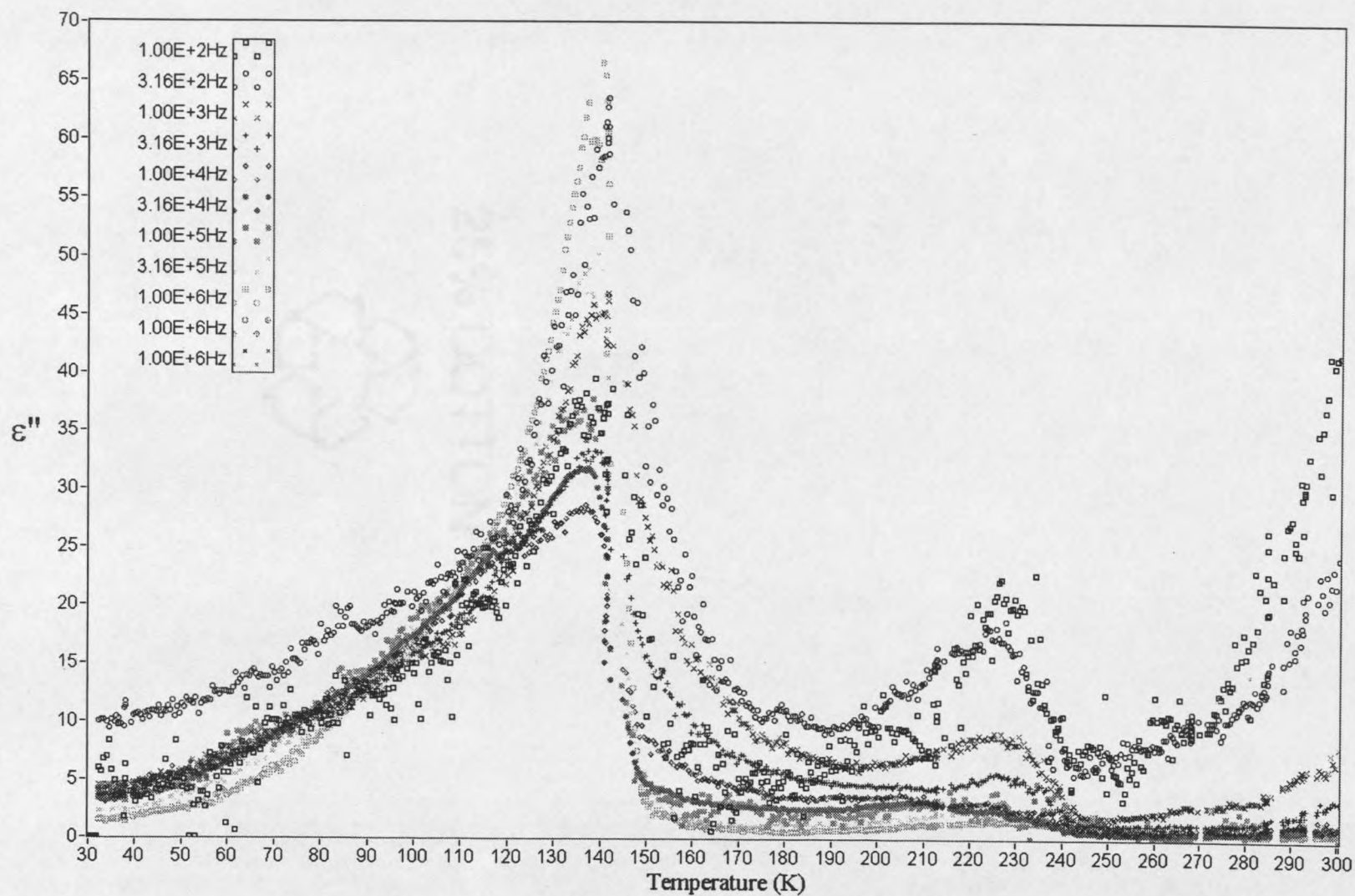


Figure 39. $\epsilon'_c(T)$ upon Cooling of CADP.40.



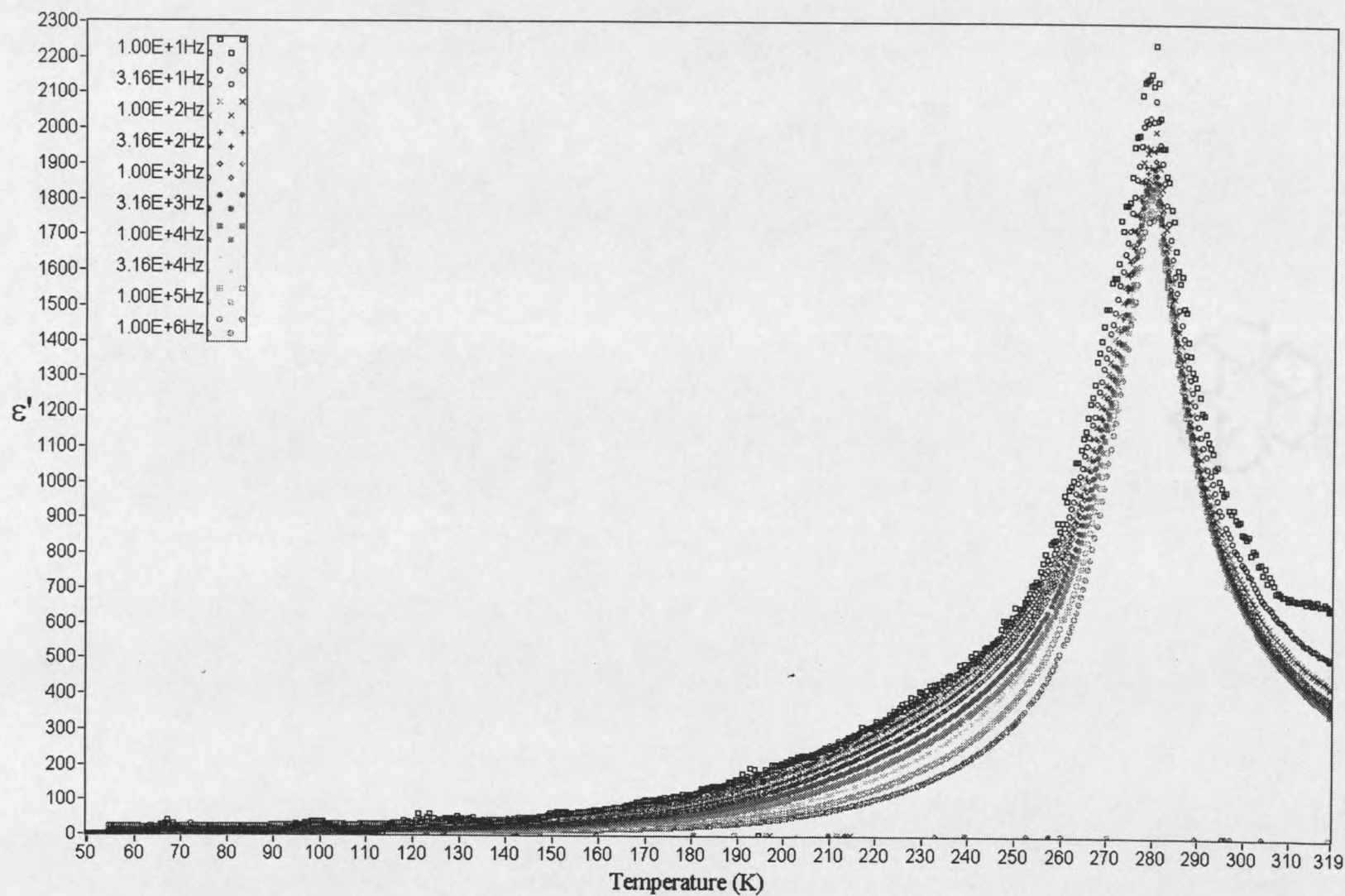


Figure 41. $\epsilon'_b(T)$ upon Cooling of DCADP.20.

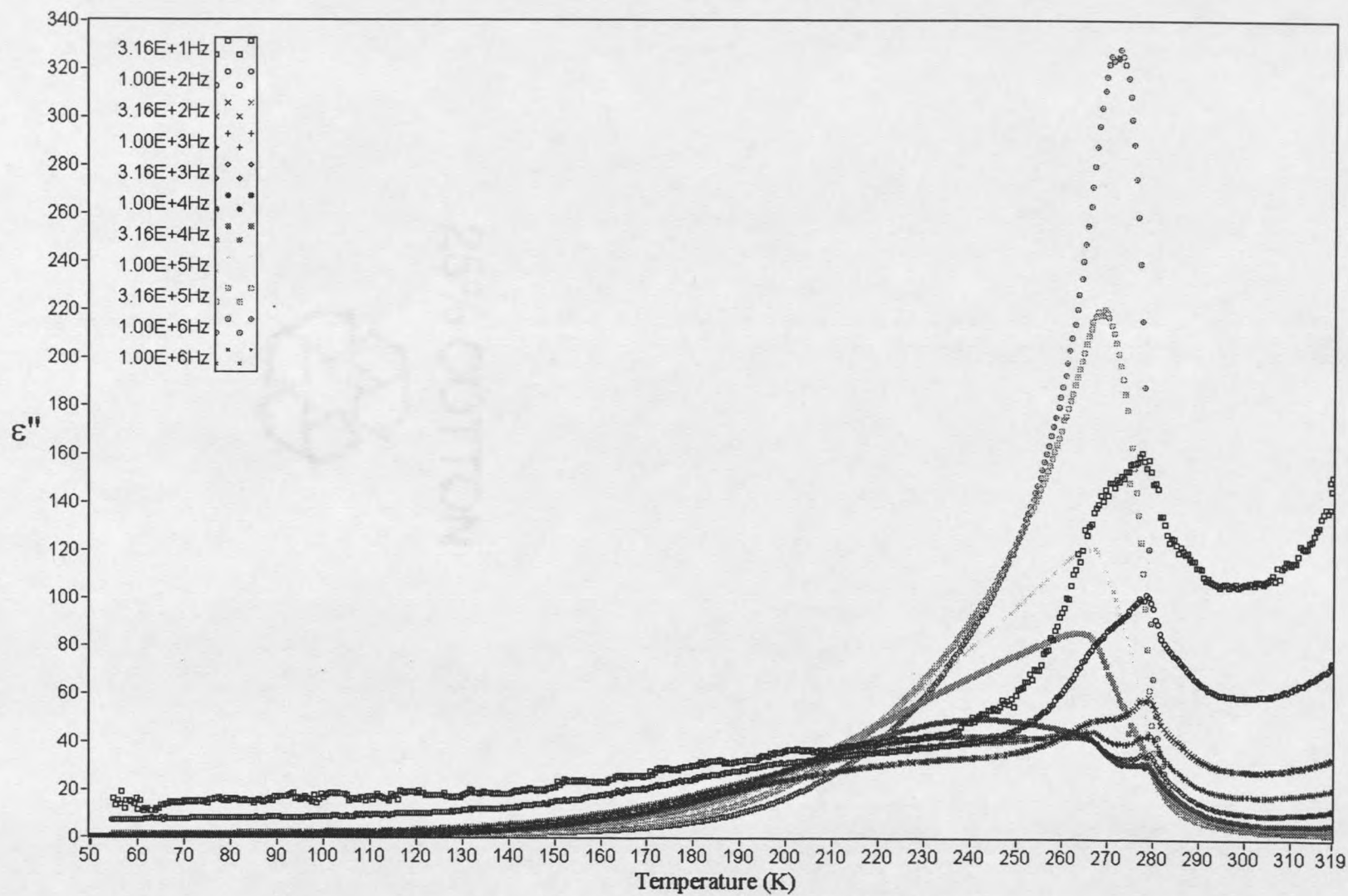


Figure 42. $\epsilon''_b(T)$ upon Cooling of DCADP.20.

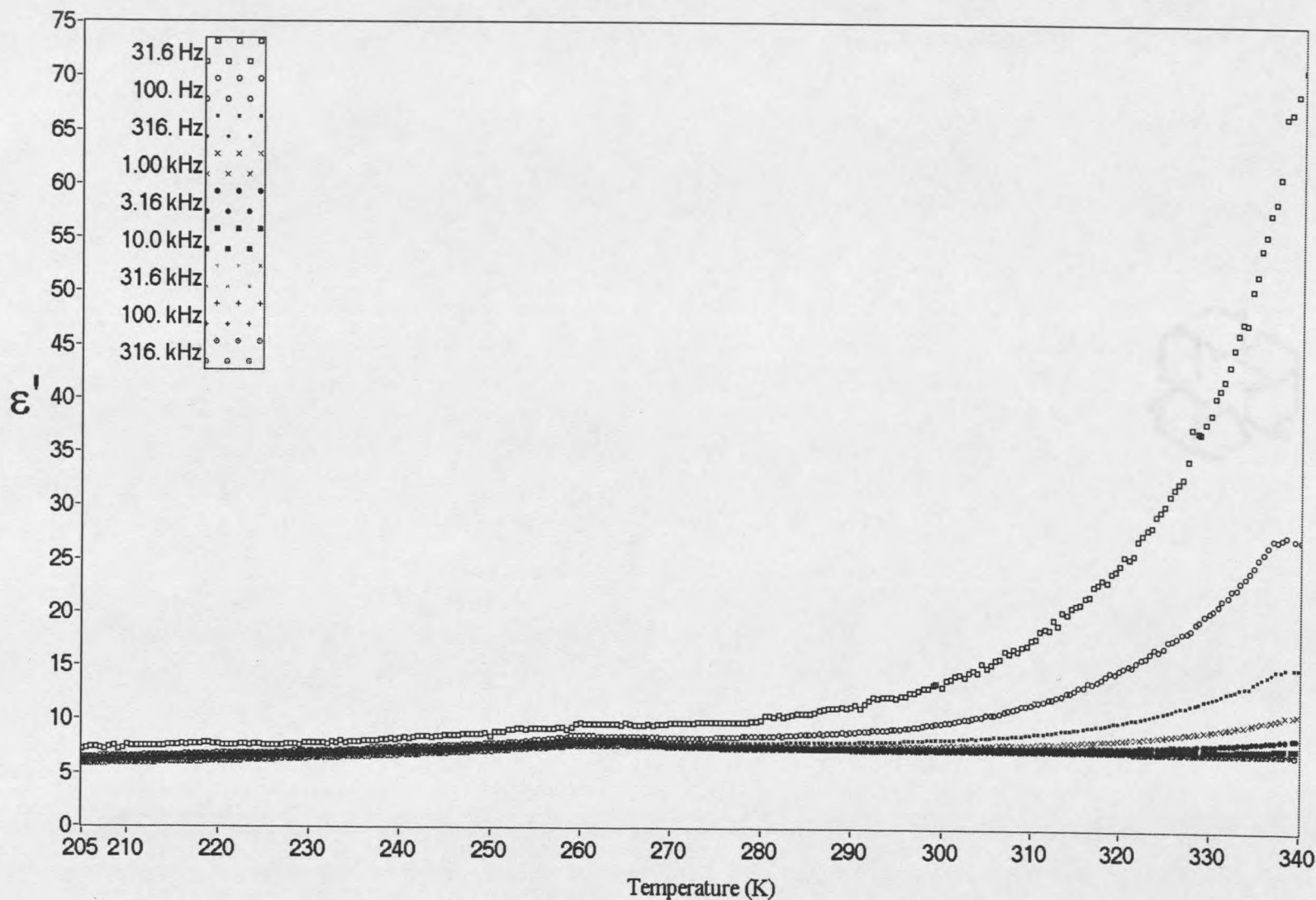


Figure 43. $\epsilon'_c(T)$ upon Cooling of DCADP.20.

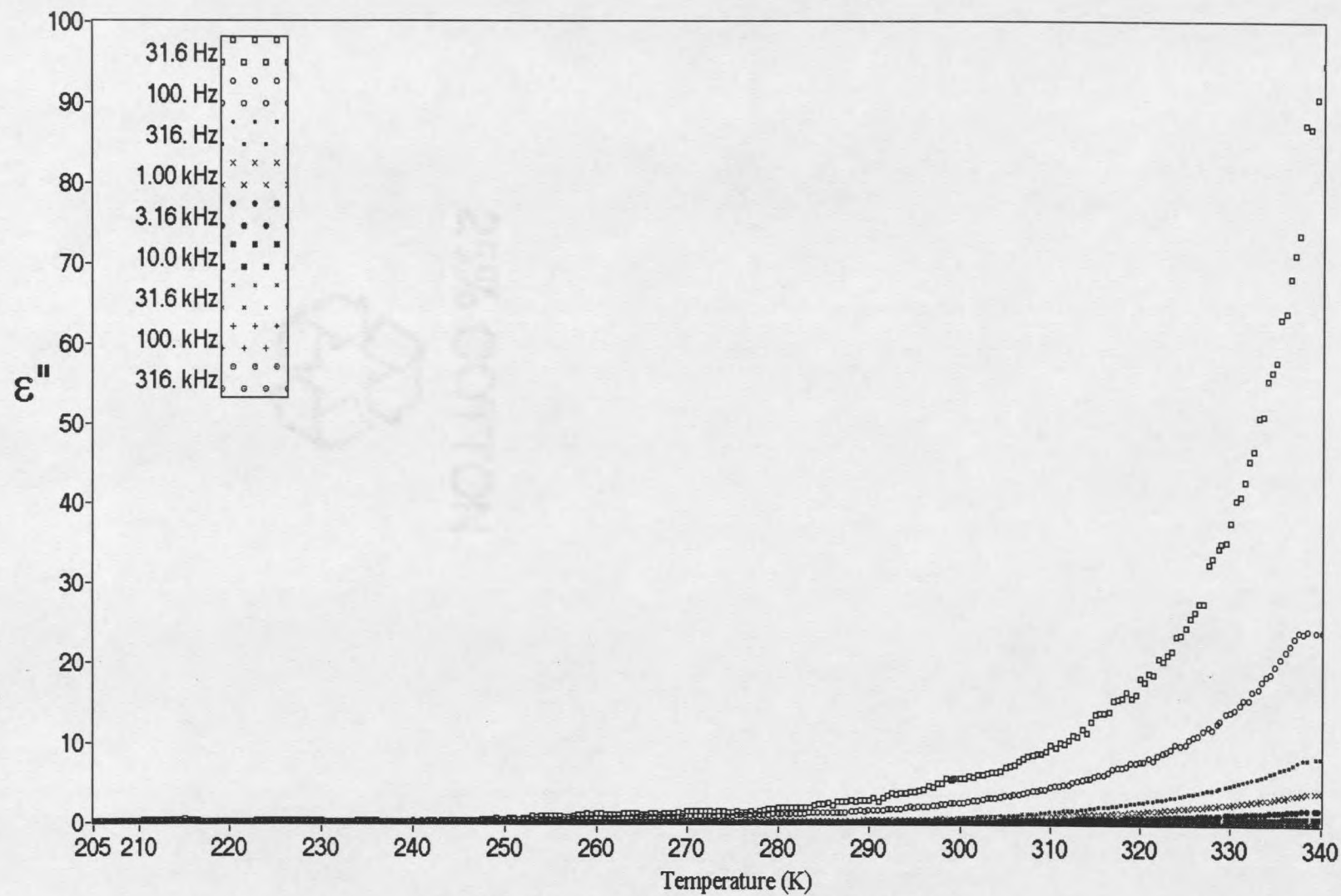


Figure 44. $\epsilon''_c(T)$ upon Cooling of DCADP.20.

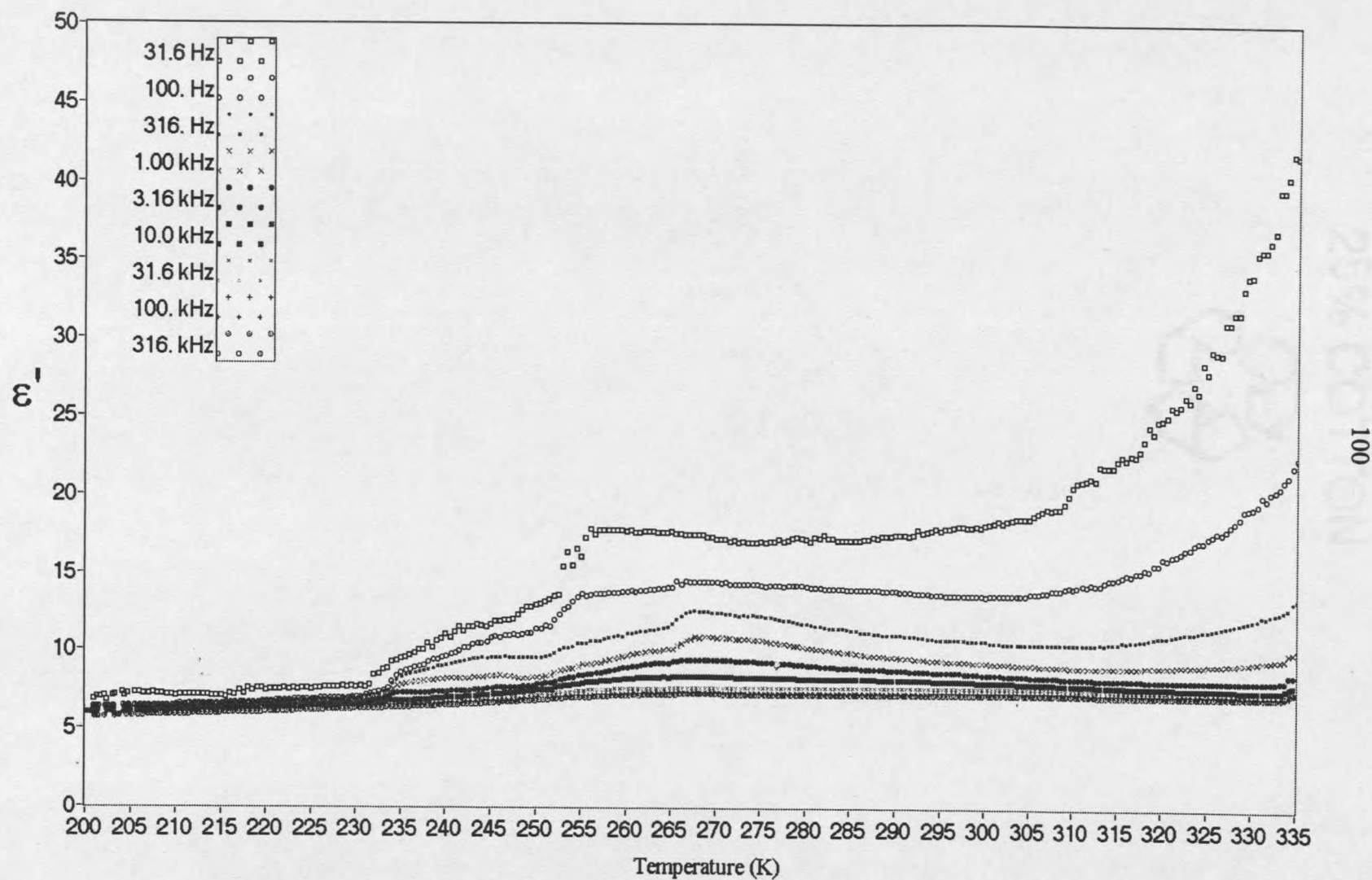


Figure 45. $\epsilon'_c(T)$ upon Heating of DCADP.20.

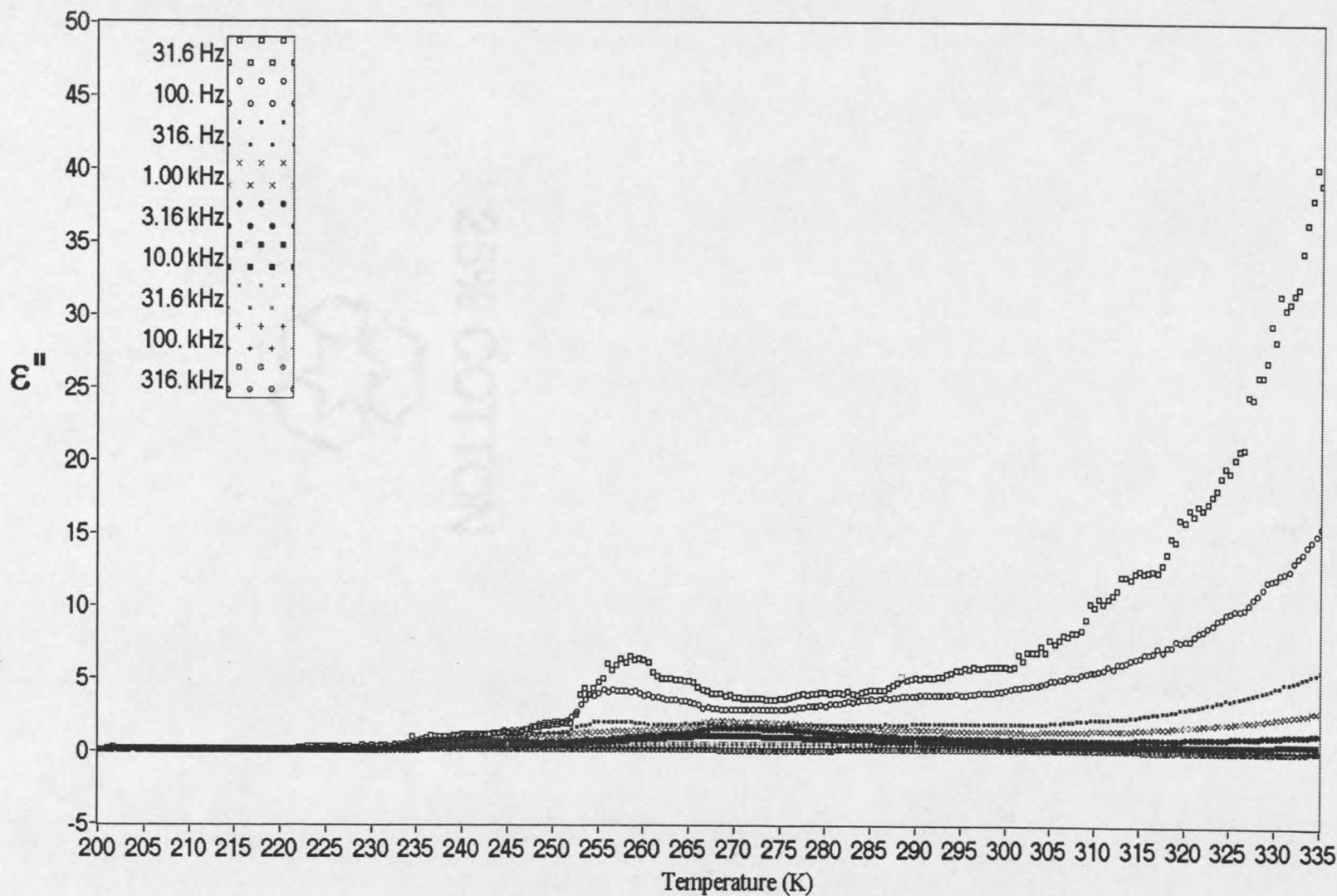


Figure 46. $\epsilon''_c(T)$ upon Heating of DCADP.20.

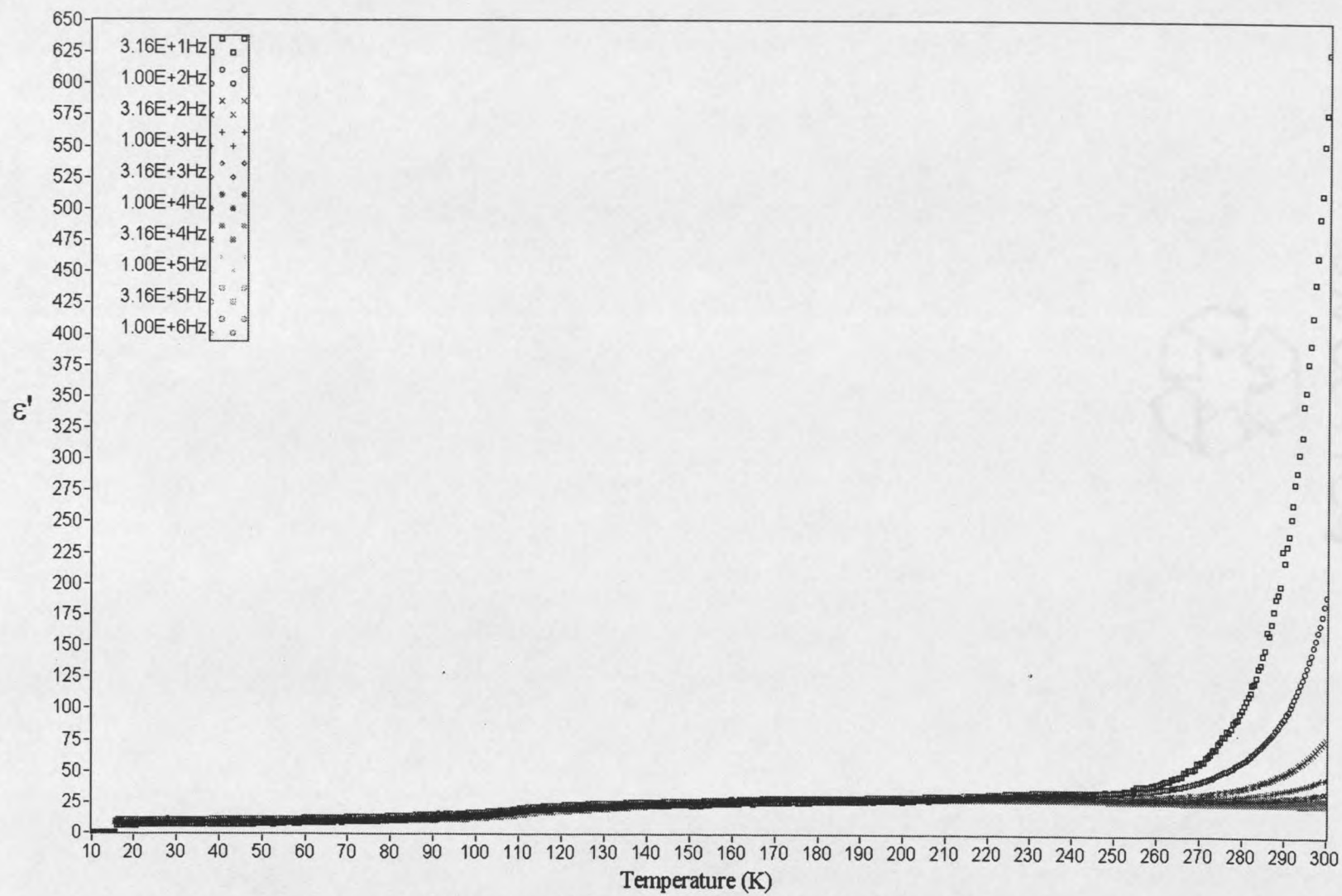


Figure 47. $\epsilon'(T)$ upon Cooling of CADP.20 Powder.

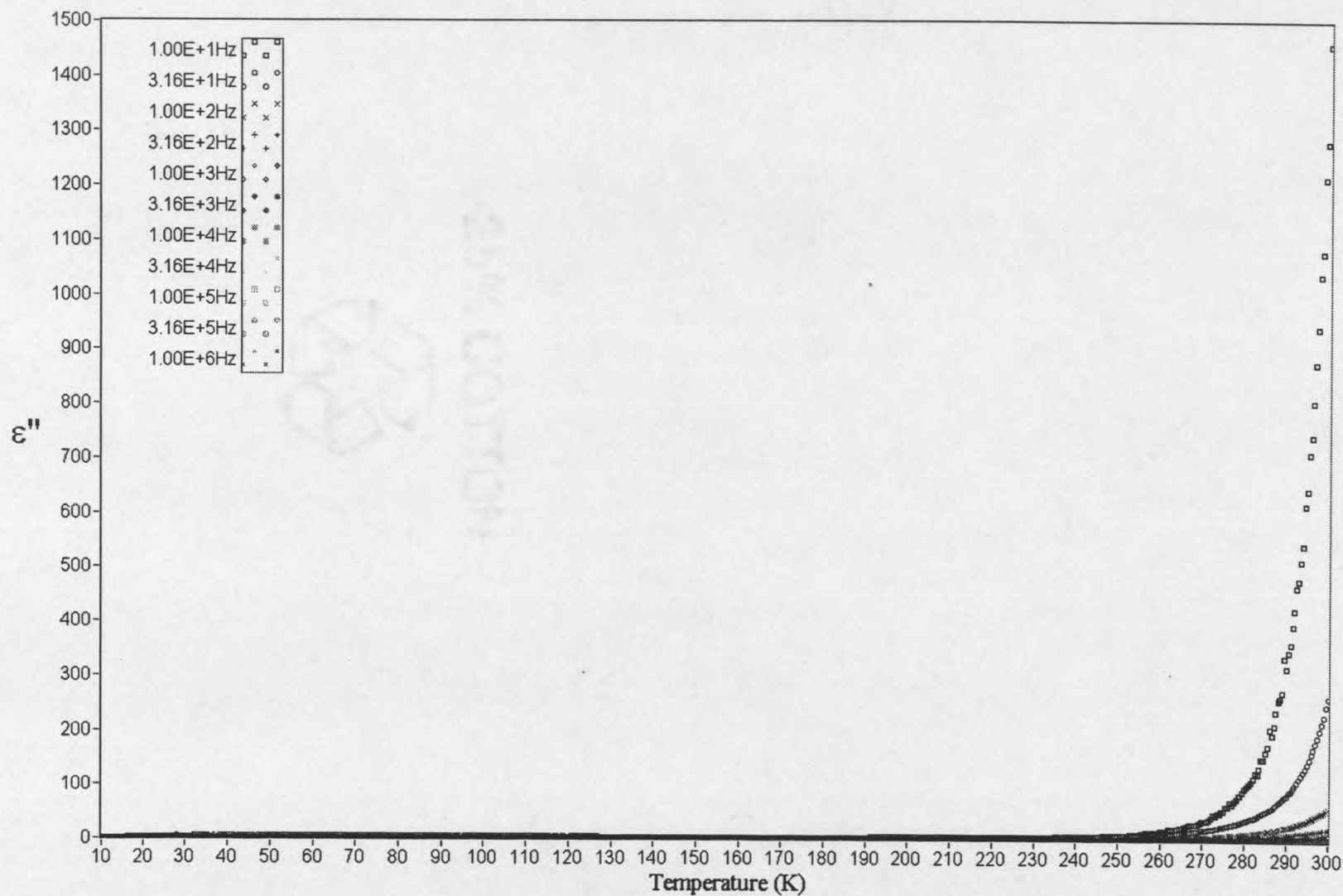


Figure 48. $\epsilon''(T)$ upon Cooling of CADP.20 Powder.

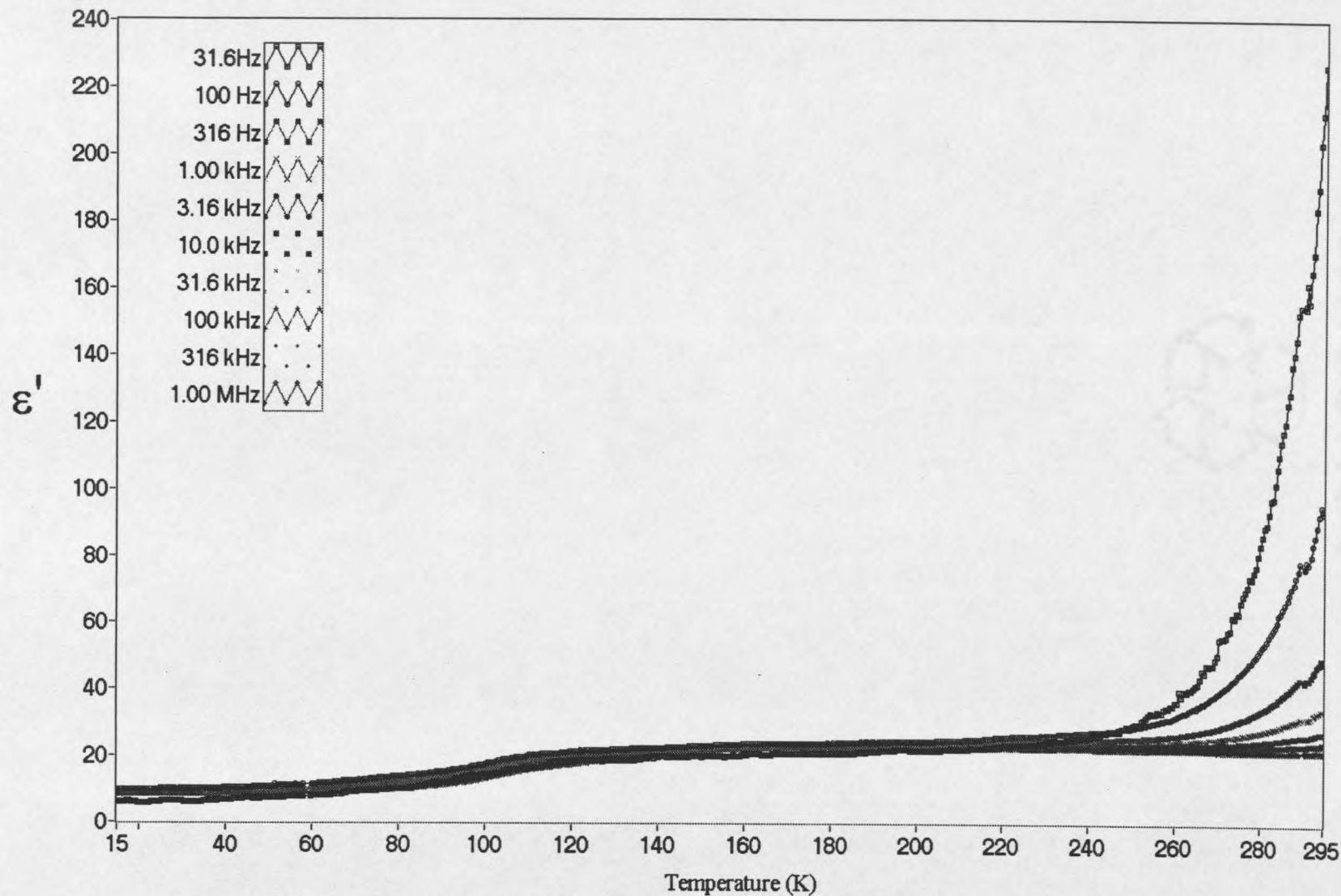


Figure 49. $\epsilon'(T)$ upon Heating of CADP.20 Powder.

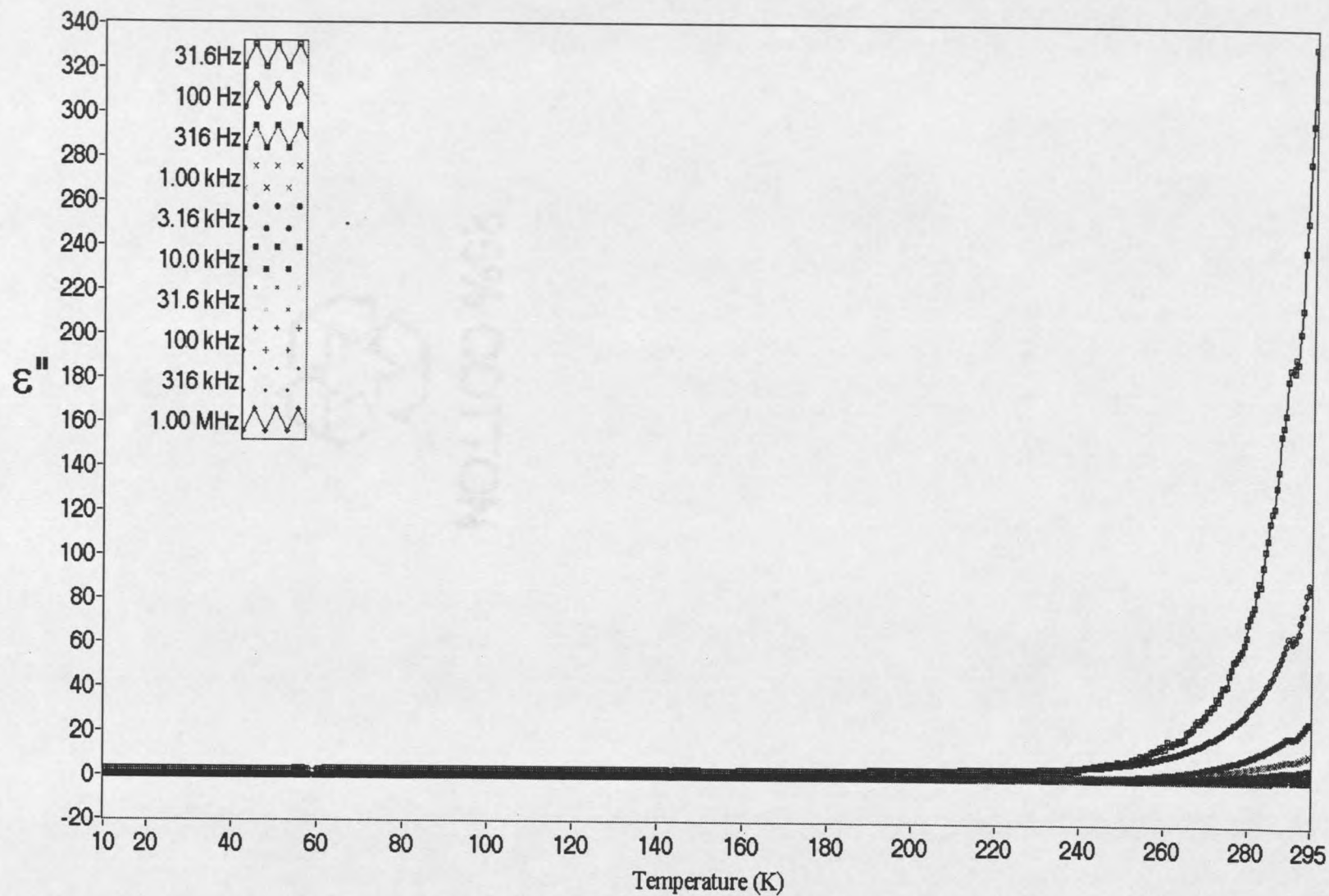


Figure 50. $\epsilon''(T)$ upon Heating of CADP.20 Powder.

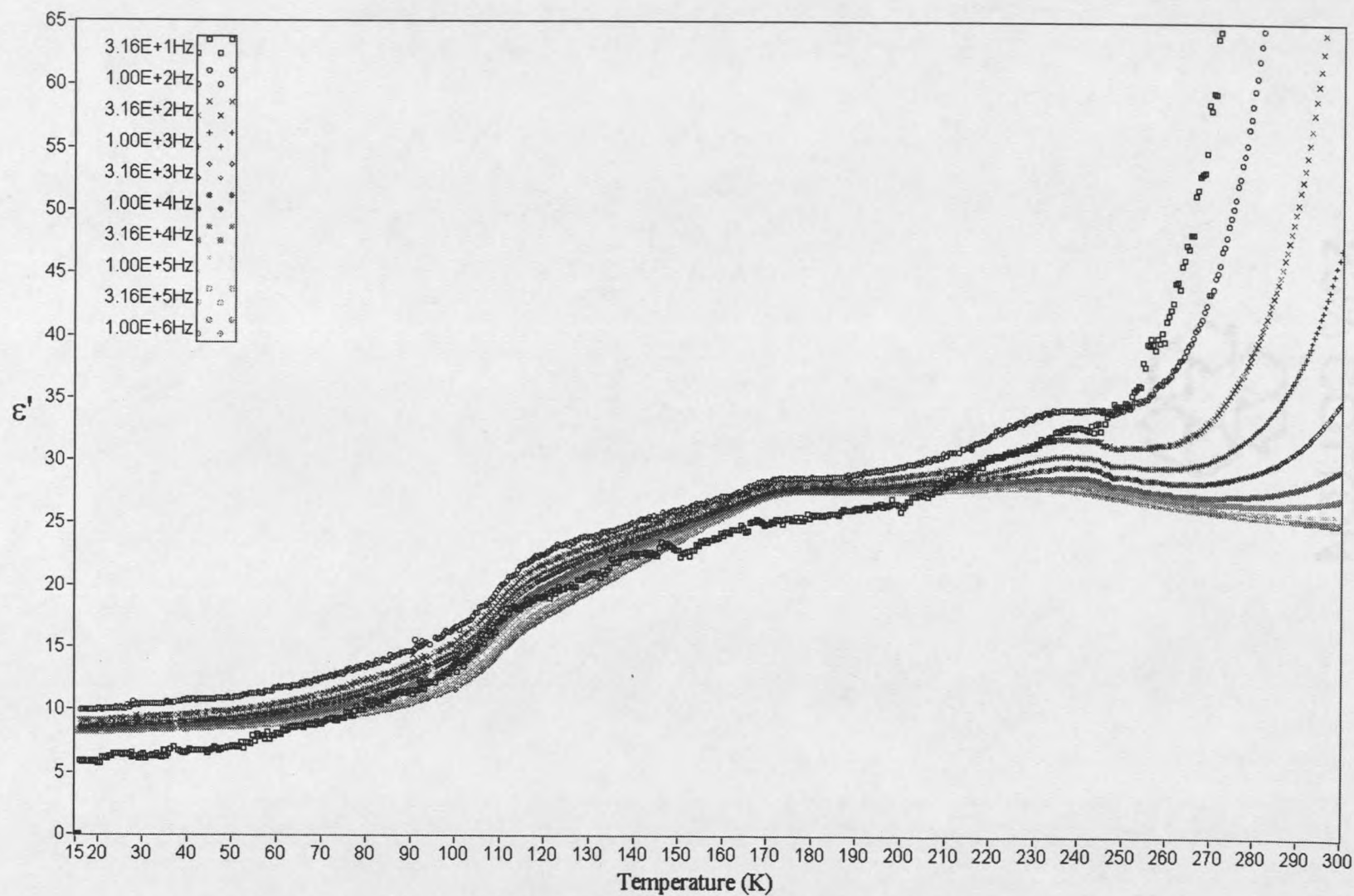


Figure 51. Magnified $\epsilon'(T)$ upon Cooling of CADP.20 Powder.

6.4. DISCUSSION

Because the concentrations of ammonium incorporated into the crystals of the three samples grown (CADP.10, CADP.20 and CADP.40) differed by less than 0.5%, this discussion will concentrate on the behavior of the sample with intermediate concentration, i.e., CADP.20.

There are three distinct anomalies in the dielectric response in CADP: a cusp in the permittivity near $T_m = 160$ K, associated with the ferroelectric phase transition, a highly-dispersive "conductive" anomaly at $T \cong 250$ K, associated with ammonium-assisted hydrolysis, and thermally activated protonic conductivity typical of hydrogen-bonded crystals, which is most evident above room temperature.

6.4.1. Ferroelectric Anomaly

Since the temperature at which the dielectric maximum occurs varies by as much as eight degrees over the measured frequency range of 10 Hz to 1 MHz, in the following discussion, T_m will refer to the maximum in the real part of the permittivity at 1 kHz.

Ammonium Concentration The effect of increasing ammonium concentration on decreasing the amplitude of the dielectric anomaly at T_m along the c axis is sufficiently dramatic that the error in the alignment of CADP.10 and CADP.40, which may be as much as five degrees, does not entirely account for the change in amplitude with increasing ammonium concentration. A misalignment of five degrees result in errors of $\cos^2(\theta)$ or about one percent, but the value of T_m along the c axis was ten percent of that along the b axis. Furthermore, misalignment should not affect the position of T_m , which

decreases with increasing ammonium concentration. Table 6 shows the shift in T_m along the a axis with increasing ammonium solution fraction x .

x	T_m (cooling)	T_m (heating)	T_m (average) [K]
0.00	(NA)	(NA)	(NA)
0.10	(NA)	(NA)	(NA)
0.20	169	171	170
0.40	132	136	134

Table 6. T_m Along the a Axis Versus Ammonium Solution Concentration, x .

Along the b axis, the $\epsilon_b(T_m)$ decreases from nearly 19,000 shown in Figure 2 to a value of 10,000 in CADP.20.

Unlike CDP, in which an anomaly in the dielectric response can only be found along the b axis,^{†††} ferroelectric anomalies in ϵ can be found along all three axes for CADP.20 and CADP.40. The b axis anomaly, $\epsilon''_b(T_m)$, is more than twenty times larger than that along the c axis, $\epsilon''_c(T_m)$, and more than one hundred times larger than the anomaly along the a axis. Table 7 shows how T_m depends on the crystallographic axis along which it is measured.^{‡‡‡} One might have suspected crystal misalignment as the cause of these non-zero amplitudes along the a and c axes, if it were not found that the dielectric responses along the three axes occurred at significantly different temperatures.

Axis	T_m (cooling)	T_m (heating)	T_m (average) [K]	$T_m(x=0.2) - T_m(x_s=0)$ [K]
c	169	171	170 ± 2	16
b	160	160	160 ± 1	6
a	158	153	(hysteretic)	(hysteretic)

Table 7. T_m Versus Axis for CADP.20.

^{†††} The small ferroelectric anomalies along the other axes in CDP may be accounted for by misalignment.

^{‡‡‡} T_m may differ from the transition temperature, T_c , which must be axis-independent.

We suggest that the ferroelectric responses along each of the three crystallographic axes come from hydrogens in O-H...O bonds along the respective axes. This proposal may seem problematic for the same reason that CDP cannot have any response along the c axis: Along the c axis most of the hydrogens must be in single, asymmetric potentials, since we know from x-ray analysis that the lattice structure of CADP x at all of the concentrations considered ($x = 0.1, 0.2$ and 0.4) is nearly identical to that of CDP. However, locally around an ammonium nucleus, the bonding should be similar to that in ADP, which may order three-dimensionally.

$\epsilon'_c(T_m)$ increases substantially with increasing ammonium concentration: $\epsilon'_c(T_m) = 8 \pm 1$ in CDP, as shown in Figure 17; $\epsilon'_a(T_m) = 7 \pm 1$ in CADP.10 as shown in Figure 21; $\epsilon'_c(T_m) = 360 \pm 45$ in CADP.20, as shown in Figure 37; and $\epsilon'_c(T_m) = 640 \pm 80$ in CADP.40, as shown in Figure 39.^{§§§} Because the error in $\epsilon'_c(T_m)$ between samples is so large, one cannot make precise conclusion on the basis of these values. However, it appears that $\epsilon'_c(T_m)$ depends strongly on the value x , suggesting that the effect is long-ranged, since an influence of a particular ammonium group only on nearest-neighboring hydrogens would have a linear dependence on concentration. Further support for such a long-ranged ammonium effect comes from noting that a concentration of ammonium in the crystal, x_A , of only six percent produces a dramatic effect along all three axes. An

^{§§§} Here, the errors represent standard deviation between experimental runs on different samples, which is about ten times larger than the error in a given run.

ammonium-induced lattice distortion of the otherwise symmetric O-H(2)...O bonds would be consistent with these results.

In this scenario, the P-O-H lattice in CDP cannot accommodate the large cesium atoms within the KDP-type three-dimensional lattice of P-O-H bonds. It therefore minimizes the strain by breaking the bonds along the a axis and compressing the bonds along the c axis, in order to fully accommodate the cesium atoms along the a axis. Conversely, in the vicinity of ammonium groups, the lattice achieves a lower energy state by forming more hydrogen bonds.

The value of T_m along the c axis could not be compared with the pure system because no dielectric anomaly was found in pure CDP along this direction.^{15****} This is a surprising fact, considering that anomalies in the sound velocity V were discovered along all three axes.³⁵

Comparison with Quasi-One Dimensional Ising Model The dielectric permittivity, ϵ , in the one-dimensional Ising model is given by Equation 13. The experimental and theoretical properties of DCDP have been discussed elsewhere on the basis of this model.^{76,22}

It is interesting to compare the free parameters of this theory $J_{\perp}$, $J_{\parallel}$ and A with those obtained for pure CDP and DCDP. From Table 8 one sees that A for CADP.20 near the transition is considerably larger than for CDP and that the ratio of $J_{\parallel}$ to $J_{\perp}$ is

**** Note that T_m in mixed systems may bare any relation to the T_m of the pure systems. For example, the melting point in metal alloys may be either higher or lower than that of both of the pure metals or anywhere in between.

significantly smaller. These facts, together with the fact that the anomalies along the a and c axes are nonzero in the mixed system, strongly suggest that the addition of ammonium decreases the one-dimensional character of the ferroelectric ordering.

Material	A	$J_{\perp}/k_B$	$J_{\parallel}/k_B$	ϵ_{∞}	Reference
CDP	6780	6.0	266	15	77
	4650	3.6	305	0	23
	7600	2.1	278	0	78
	6500	1.9	287	0	26
	6383 ± 140	3.4 ± 2.1	284 ± 11	4 ± 4	77
DCDP	2980	2.1	611	15	33
	2361	0.8	342	0	78
	4700	2.5	535	0	26
	8100	3.8	467	0	-
	4535 ± 2560	2.3 ± 0.9	413 ± 81	6 ± 6	-
CADP.20	23340	40.4	85	0	
	12860	14	156	48	-
DCADP.20	5766	17	365	-34	-
	2958	7.1	480	0	-

Table 8. $J_{\parallel}$ and $J_{\perp}$ for CADP.20 and CDP.

The quasi-one-dimensional Ising model fits the dielectric permittivity in both CADP and DCADP very well. The fit of this model to $\epsilon'_b(T)$ for CADP.20 is shown in Figure 52.

The quasi-one-dimensional Ising correlation length parallel to the ferroelectric axis, $\xi_l(T)$, is given by⁷⁹

$$\xi_l(T) = \left(\frac{kT_c}{2J_{\parallel}} \right)^{1/2} \left(\frac{1}{2} d_{\parallel} e^{2\beta J_{\parallel}} \right) \left| \frac{T_c}{T - T_c} \right|^{1/2}, \quad \text{Equation 26}$$

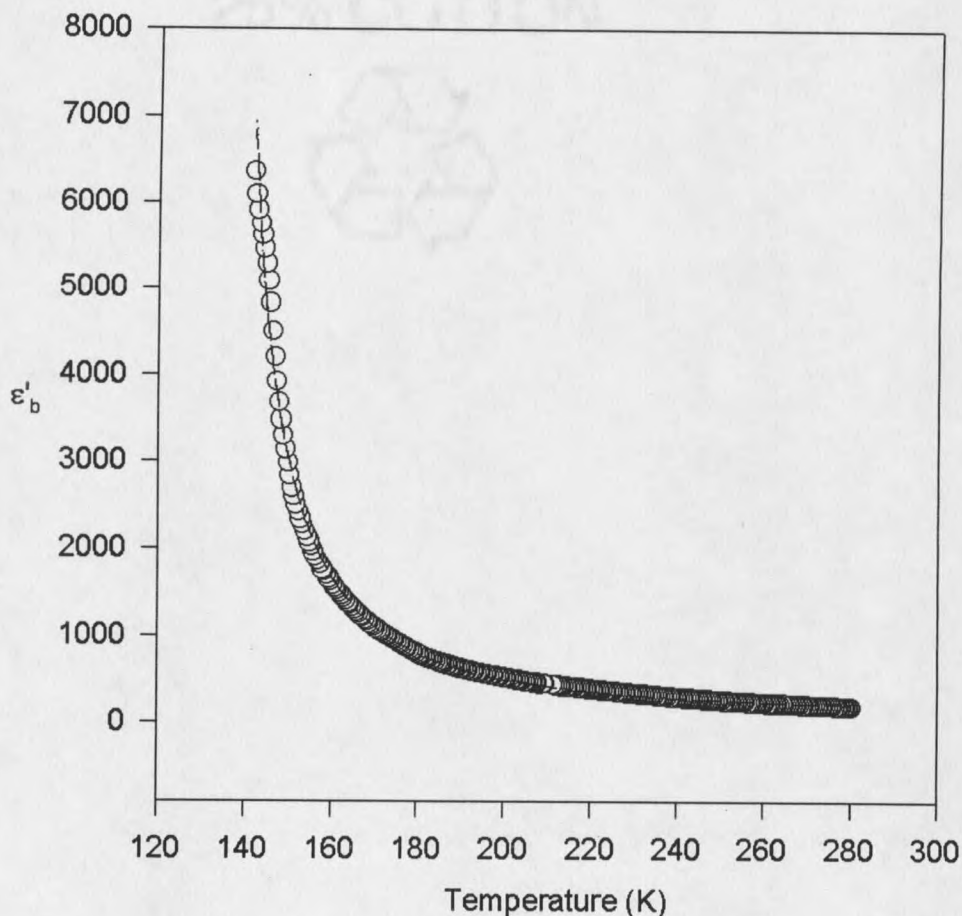


Figure 52. Quasi-One-Dimensional Ising Fit to $\epsilon'_b(T)$ for CADP.20.

where $d_{||}$ is the distance between spins parallel to the chains, $\beta = 1/k_B T$ and $J_{||}$ is the exchange coupling along the chain. Assuming CDP bond lengths and employing Equation 27,

$$d_{||} = (d_{O(2)-H(3)}^2 + d_{O(2)-H(3)'}^2 - 2 d_{O(2)-H(3)} d_{O(2)-H(3)'} \cos(\phi))^{1/2}, \quad \text{Equation 27}$$

with $d_{O(2)-H(3)} = 0.100$ nm, $d_{O(2)-H(3)'} = 0.146$ nm and $\phi = 174.4^\circ$, we obtain $d_{||} = 0.246$ nm.

For CDP, with $T_m = 154$ K and $J_{||}/k_B = 284$ K, we obtain $\xi_l(T = T_m + 1) = 31$ nm and $\xi_l(T = T_m + 10) = 8.0$ nm. For CADP.20 with $T_m = 160$ K and $J_{||}/k_B = 156$ K, we obtain

considerably smaller correlation lengths: $\xi_I(T = T_m + 1) = 7.7$ nm and $\xi_I(T = T_m + 10) = 2.2$ nm.

The prediction of this model concerning the behavior of the transition temperature as a function of $J_{\parallel}$ and $J_{\perp}$ is given by⁷⁹

$$T_m \cong 2 J_{\parallel} / \ln(J_{\parallel}/J_{\perp}). \quad \text{Equation 28}$$

Although this equation gives $T_m = 188$ K, which is considerably higher than the actual value of T_m , 170 K, it accurately predicts the direction of the temperature shift by the addition of ammonium since $T_m(\text{CDP}) = 128$ K according to this model. The model predicts that $T_m = 227$ K for DCADP.20, instead of the actual value of $T_m = 276$ K.

Bias Field The variation in $\epsilon'_b(T_m)$ with bias field of CADP.20 is shown in Figure 55. Figure 53 and Figure 54 shows the shift of T_m to higher temperatures with increasing applied field for CADP.20 and DCADP.20, respectively. These behaviors support the assertion that the anomaly at T_m is associated with a ferroelectric phase transition.

Effect of Deuteration As in CDP, deuteration dramatically increases T_m in CADP.20 for the b axis permittivity. This is shown in Table 9. This dramatic effect that

Sample	T_m (K) cooling	T_m (K) heating	T_m (K) average	Reference
CDP	-	-	154 ± 2	82
DCDP	-	-	263 ± 2	82
CADP.20	160	160	160 ± 1	-
DCADP.20	275	277	276 ± 2	-

Table 9. $T_m(b)$ for CADP.20 and DCADP.20.

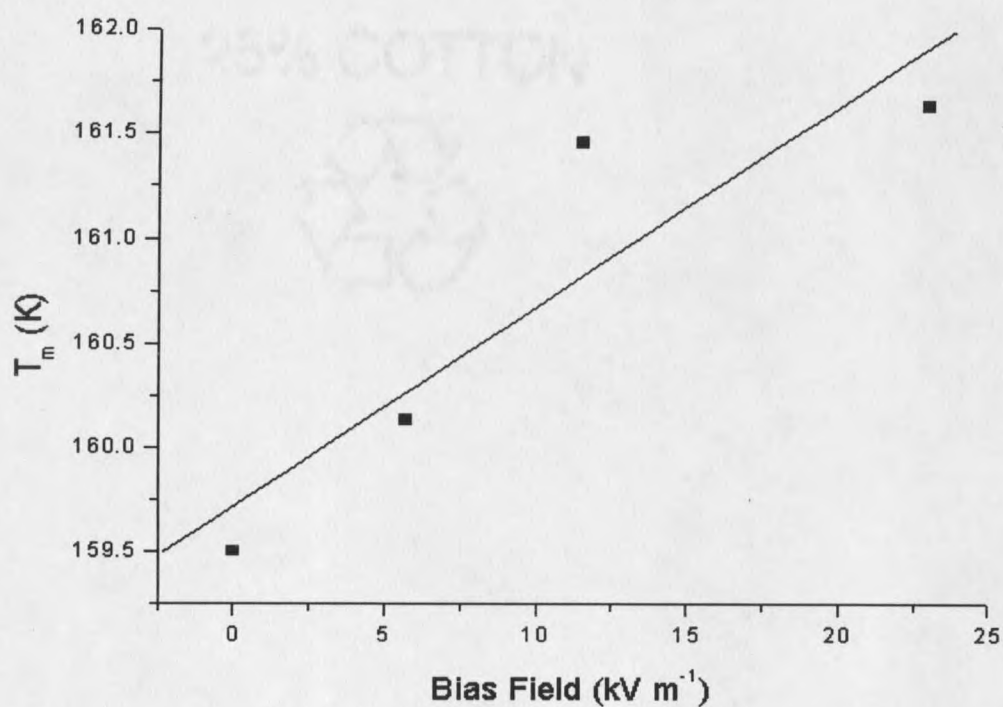


Figure 53. T_m Versus Bias Field for CADP.20.

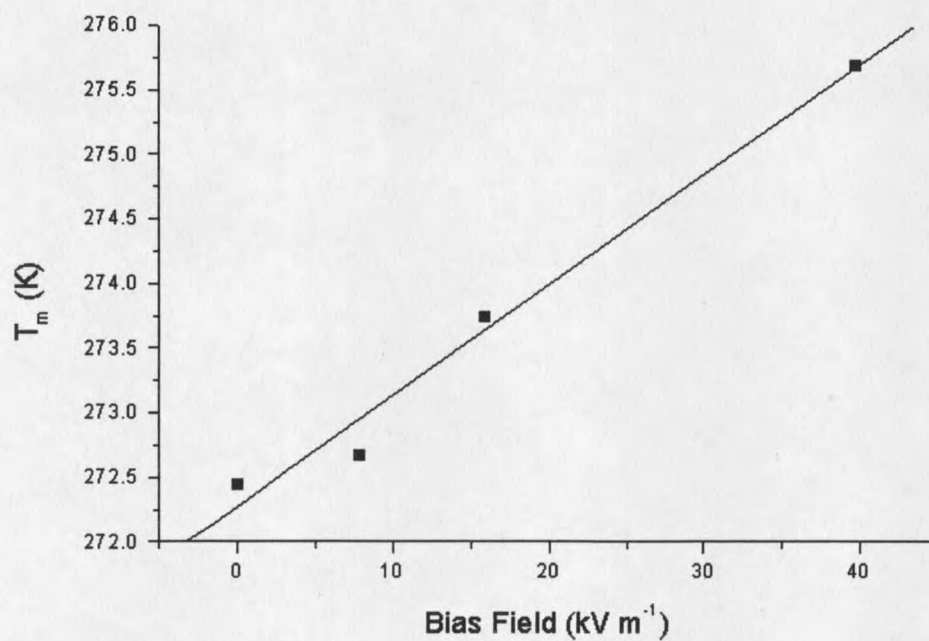


Figure 54. T_m Versus Bias Field for ϵ'_b in DCADP.20.

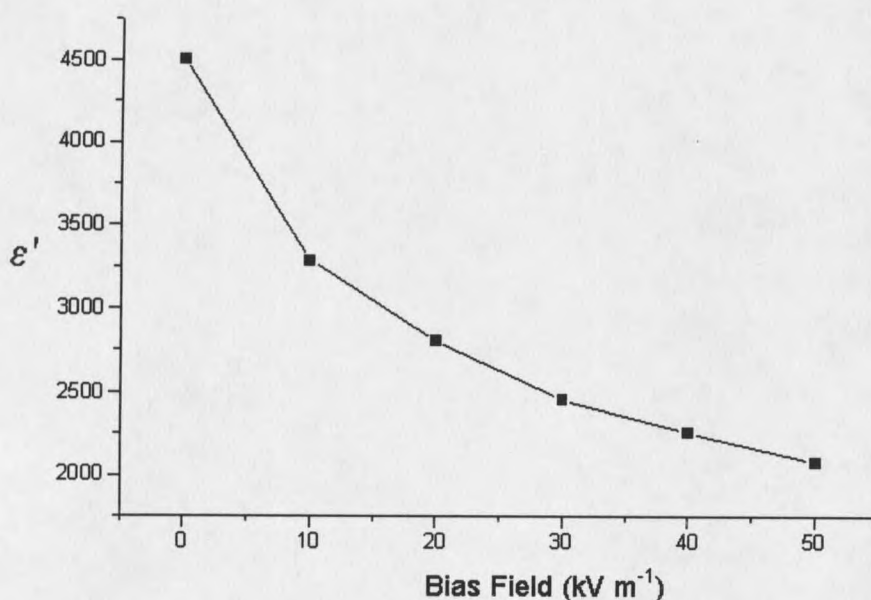


Figure 55. $\epsilon'_b(T)$ Peak Height Versus Electric Bias Field for CADP.20.

deuteration has on T_m indicates that hydrogen is involved in the ferroelectric phase transition. This does not necessarily mean, however, that the displacement of the H(2) hydrogen atoms within the O(3)-H(2)...O(3) bonds is the primary source of the spontaneous polarization, since the ordering of the hydrogens induces the polar phosphate groups to rotate.

The fact that T_m is raised by the addition of ammonium is not seen in any of the other ammonium-containing KDP isomorphs, which actually show a marked decrease in T_m . It is encouraging that this increase in T_m is seen consistently in both CDP and DCDP.

$\epsilon'(T)$ and $\epsilon''(T)$ along the c axis of DCADP.20 upon cooling are shown in Figure 43 and Figure 44, respectively. Ordinary protonic conductivity is the only feature that is clearly evident from these measurements. $\epsilon'(T)$ and $\epsilon''(T)$ along the c axis of DCADP.20 upon heating are shown in Figure 45 and Figure 46, respectively. Upon heating the

conductive anomaly, although considerably smaller, occurs at about the same temperature as in CADP.20 upon heating along the same axis.

The Quasi-One-Dimensional Fit for DCADP is shown in Figure 56. The fit parameters are given in Table 8. Like CDP, DCADP has considerably more three-dimensional character than its pure parent crystal, as evidenced by the larger ratio of $J_{\parallel}$ to $J_{\perp}$.

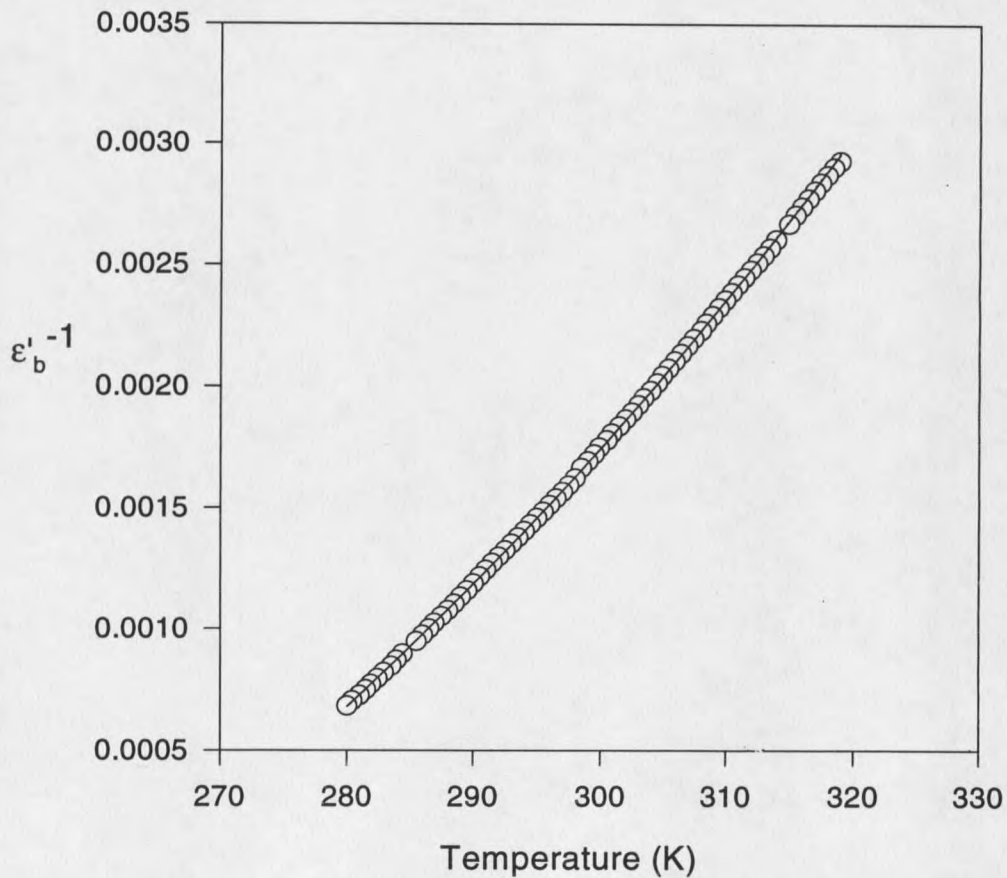


Figure 56. Quasi-One-Dimensional Ising Fit to $1/\epsilon'_b(T)$ for DCADP.20.

Dispersion Analysis One can obtain information about the rates of the dielectric responses from the frequency dependence of the dielectric permittivity. At audio frequencies in ferroelectrics, the response along the ferroelectric axis is usually associated

with domain wall motion below T_c and polarization reorientation, rather than with individual local ion motion, since ion motion is generally more rapid.⁶² The frequencies associated with the maxima of the arcs in a Cole-Cole plot correspond to the dielectric relaxational frequencies of the material. Figure 57 shows such a plot for CADP.20 taken upon heating along the a axis at the temperature of the onset of the conductive anomaly, $T = 250$ K. At this temperature, there are two distinct relaxation mechanisms with frequencies of 30 kHz and 5 Hz. Both of these frequencies are well below those usually associated with individual ionic relaxation rates. The association of these relaxation rates with two distinct polarization relaxation mechanisms is more reasonable. However, we believe that the longer relaxation process is instead connected with ammonium-phosphate-assisted hydrolysis. This will be discussed in more detail in the next section.

Frequently the current resulting from an applied field, $i(\tau)$, is considered as the sum of the contributions from independent, parallel relaxation mechanisms, each with its own relaxation time, τ . If we define a distribution of relaxation times $g(\tau)$, then the current density is given by the integral over these individual exponential relaxations:

$$i(t) = \int e^{-t/\tau} g(\tau) d\tau. \quad \text{Equation 29}$$

Inversion yields

$$g(\tau) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} i(t) e^{\gamma t} dt \quad \text{Equation 30}$$

But permittivity and current are related by the Fourier transform

$$\epsilon^* - \epsilon_\infty = \epsilon_0 E^{-1} (2\pi)^{-1} \int e^{i\omega t} i(t) dt, \quad \text{Equation 31}$$

where ϵ^* is the complex conjugate of the complex permittivity and ϵ_∞ is the value of ϵ at frequencies above the dispersive regime.

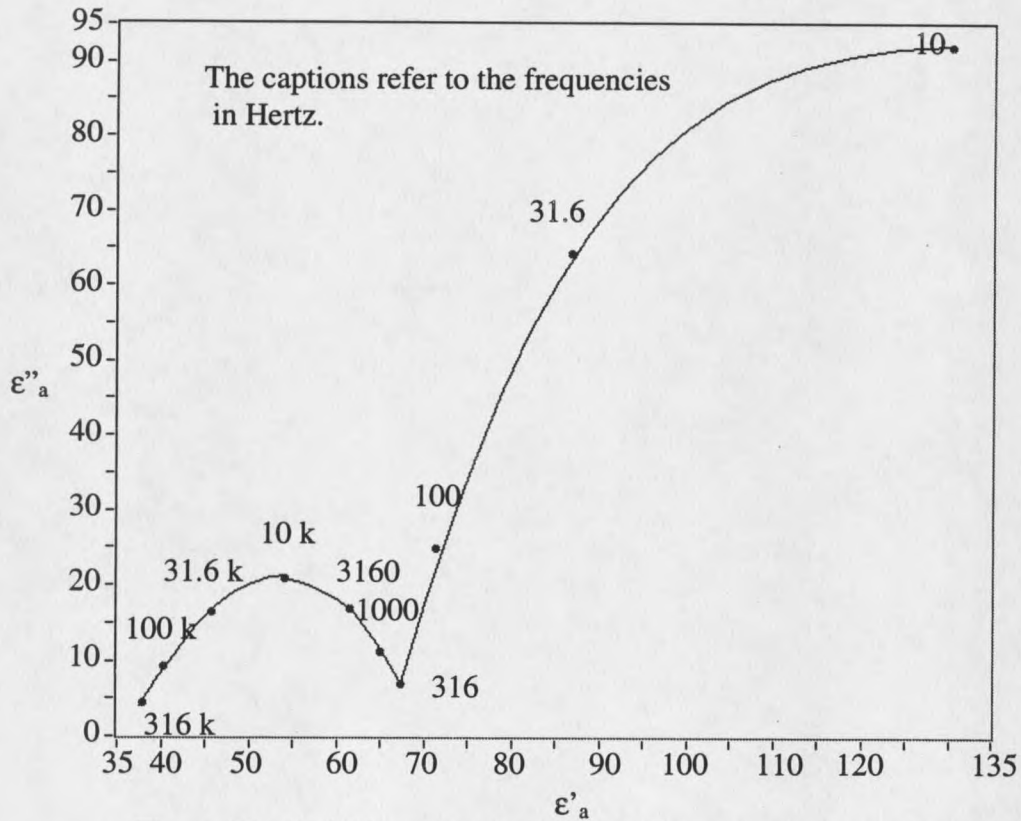


Figure 57. $\epsilon''_c(f)$ Versus $\epsilon'_c(f)$ for CADP.20 upon Heating at $T = 250$ K.

Together these equations yield the Debye relation between the distribution, $g(\tau)$, and the permittivity, $\epsilon(\omega)$:

$$\epsilon^*(\omega) - \epsilon_\infty = \int \frac{g(\tau) d\tau}{1 + i\omega\tau} \quad \text{Equation 32}$$

If $g(\tau) \equiv \tau$ and ϵ'' is well separated from other relaxation mechanisms, then the plot of $\epsilon''(f)$ versus $\epsilon'(f)$, known as the Cole-Cole plot, should be a semicircle which is centered

on the ε' axis.⁵ That this is frequently not the case, however, has led to a variety of other proposed $g(\tau)$. One of these distribution of relaxation times that has had considerable success is the Vogel-Fulcher form: $\ln(\tau/\tau_0) = E_b/(T - T_{VF})$, where T_{VF} is the Vogel-Fulcher temperature.⁶²

Figure 57 is a Cole-Cole plot of CADP.20 at the beginning of the conductive anomaly upon heating along the c axis. These arcs correspond to two distinct relaxation times of $1 \cdot 10^{-4}$ s and $3 \cdot 10^{-1}$ s. Just as in CADP.20, a second, longer relaxation time is also found at audio frequencies in KADP above $T = 250$ K.⁸⁰ These second relaxation times are not seen, however, in the parent crystals which do not contain ammonium.

Figure 57 shows sets of frequency-dependent thermal isomorphs of $((\varepsilon''(f, T)), (\varepsilon'(f, T)))$ points connected by lines, which are evenly-spaced by $\Delta T = 4$ K between $T = 4$ K and $T = 320$ K, as measured along the b axis of CADP.20. In the figure, the frequencies decrease from left to right for each of the thermal isomorphs.

In order to obtain information from this map, we can think of each curve as being the result of a superposition of semicircles, corresponding to simple, well-defined Debye relaxation frequencies. From this consideration, a stretched arc corresponds to a broad set of relaxation times, where the inverse of the frequency at the maximum corresponds to the most probable relaxation time, and multiple arcs correspond to several well-separated relaxation times.

As in NMR, the data clearly exhibit at least two distinct relaxation times far below T_m and more complicated relaxational behavior at higher temperatures. In addition,

Figure 57 indicates that the relaxation time of one of the processes decreases as T_m is approached from below.

The fact that the low-frequency data in CDP reveal only one relaxation time, together with the fact that the second relaxation mechanism appears precisely at the start of the anomaly in the conductivity at $T = 250$ K, strongly suggest that the lower-frequency relaxation is associated with the substitution of cesium with ammonium.

6.4.2. Anomalous Conduction

Along all three axes there are "conductive" anomalies in the dielectric response, which share several characteristics:

- a jagged dielectric permittivity ($d\epsilon(T)/dT > 0$) in a finite temperature region,
- large dispersion at audio frequencies,
- a response that grows upon thermally cycling below T_m ,
- an $\epsilon''(T)$ that is much larger than $\epsilon'(T)$,
- a response which is orders of magnitude larger upon heating than upon cooling,
- and almost total destruction by external bias fields as small as 200 V m^{-1} .

Interestingly, the larger the conductive anomaly is along an axis, the smaller the ferroelectric anomaly: The conductive anomaly is largest along the c axis and smallest along the b axis.

The fact that the measurement of $\epsilon'_c(T)$ produced similar results with painted electrodes and with vacuum-deposited gold electrodes indicates that the conductive anomaly did not arise from surface conduction resulting from the solvation of any

extrinsic liquids having a significant vapor pressure at ambient temperatures and vacuum conditions, such as water or paint solvent.

The results that the conductive anomaly is more than a thousand times smaller after cooling to and heating from $T = 200$ K at a rate of 100 s /K than after cooling to and heating from $T = 50$ K at the same rate, suggest that the sample undergoes a fundamental change in the ferroelectric phase, which is not completely reversed when the crystal becomes paraelectric again. Since we know from x-ray diffraction that the crystal point group does not change, then the change may be in a reorganization of the basis. This reorganization may involve reorientation of the phosphate ions. The sublattice structure lies in the orientation of the phosphate ions. A reorientation of these ions that brings the ammonium hydrogens closer to the phosphate ions might induce *auto-hydrolysis*, an internally-induced dissociation of the hydrogen and oxygen atoms due to the proximity of the ammonium hydrogens to the phosphate groups.

The fact that similar conductive anomalies occur in other mixed, ammonium-containing KDP isomorphs further suggests that the carriers involved in the conductive anomaly involve ammonium ions.

The conductive anomaly seemed unusual at first, since CDP did not exhibit any such behavior. Two suggestions regarding this anomaly were somewhat discounted: The first suggestion was that the conductivity resulted from significant occlusions of water. Such solvated ions might explain such a large response to an applied electric field. However, such occlusions were not visible even with 10X magnification and it seemed implausible that a significant density of minute occlusions might exist, given the fact

from x-ray analysis that the samples were truly single crystals. Such occlusions would probably disrupt the growth front of the crystal, resulting in misaligned crystal segments. However, the crystals were indeed shown to be single crystals of good quality by the sharpness of the reflection peaks seen in x-ray scattering.

A second suggestion was that the anomalies resulted from surface effects. Such surface effects would have to result from conductivities thousands of times larger than the measured values, because of the small area/thickness ratios of any film which was not thick enough to be clearly visible. Such high conductivities might be possible, if CADP was solvated on the surfaces. In this case, the ions near the surface would be free to move in the solution. The only two liquids that came into contact with the crystal were (deuterated) water and the solvent from the silver-loaded paints used to electrode the samples. The latter option was eliminated after measuring one of the samples with evaporated gold electrodes gave similar behavior. The fact that the samples were at 300 K in a vacuum of 1×10^{-5} mm of Hg for several hours also made it implausible that any other solvent remained on the surface. The strong anisotropy in the anomaly between the different axes, despite the sample dimensions being nearly equal for measurements along all three axes, further suggested that the anomalies were intrinsic in character.

Furthermore, if the conductive anomaly results from surface effects then it seems that the powder samples should show a very large conductive anomaly, rather than no measurable anomaly.

The conductive anomaly was also observed in other KDP isomorphs containing ammonium. In the mixed KDP isomorph, potassium ammonium dihydrogen phosphate

(KADP), in addition to the dielectric anomaly associated with the glass transition, which occurs at 23 K, others found pronounced anomalies in the temperature dependence of ϵ' near $T = 240$ K for ammonium concentrations $x = 0.5$ and $x = 0.6$ and near $T = 250$ K for $x = 0.3$.⁸⁰ As in CADP, the anomaly in KADP is much larger upon heating than cooling.⁸⁰ While double cation salts, viz. $M\text{HAO}_4$, $M\text{H}_3(\text{AO}_4)_2$ and $M\text{H}_2\text{BO}_4$, with $M = \text{K, Rb, NH}_4$ and Cs , $A = \text{S and Se}$, and $B = \text{P and As}$, have higher thermally-activated conductivities than their pure parent compounds^{80,81,82,83}, the very large anomaly occurring at $T \cong 250$ K seems to be characteristic of mixed KDP isomorphs containing ammonium ions. Interestingly, KADP and CADP have different crystal structures and exhibit the same anomaly at nearly the same temperature, suggesting that the anomaly is connected with an intrinsic property of the ammonium ion itself.

Knowing that NH_3 gas evolves from ADP above 313 K, it is reasonable to infer that proton vacancies are generated in the lattice by the incipient decomposition associated with the formation of NH_3 and H_3PO_4 .⁶² Such vacancies would improve proton conductivity by providing sites to which other protons could hop.

The conductive anomaly in CADP may clarify the conductivity mechanism in ADP, presented in the introduction. Although part of the discrepancy within the literature may be attributed to an oversimplification of the plots of the natural logarithm of the conductivity versus inverse temperature as simply two linear regions, the rest may result from an unappreciated sensitivity of ADP to the particular thermal and/or electric field histories to which it was exposed; our results in CADP suggest that these histories are crucial to the conductive response: In CADP.20, the temperature at which the conductive

anomaly occurred ranged from 218 K to 268 K. In CADP.10, the conductive anomaly ranged from $T = 285$ K to $T = 315$ K.

Explanations of the anomalously large conductivity in KADP based solely on disorder⁸⁰ appear to be erroneous in light of the results obtained in CADP. CADP incorporates a smaller fraction of ammonium than other mixed KDP isomorphs, for example, KADP,⁸⁰ but it exhibits an anomaly at least one hundred times larger. If substitutional disorder alone accounted for the increased conductivity in ammonium-containing KDP isomorphs, then an increased conductivity should also be observed in mixed systems that do not contain ammonium. However, this is not seen in, for example, $\text{Rb}_{1-x}\text{Cs}_x\text{D}_2\text{PO}_4$.⁸⁴

6.4.3. Ordinary Protonic Conductivity

Along all of the axes in CADP and in pure CDP, a slowly-varying, increase in the conductivity is evident at temperature above ~ 290 K, and in some cases as low as 250 K. This conductivity appears to be the ordinary protonic conductivity seen in other hydrogen-bonded systems such as, cesium dihydrogen arsenate (CDA), KDP, Rubidium Dihydrogen Phosphate (RDP) and rubidium dihydrogen arsenate (RDA).⁴² Assuming a thermally activated conductivity such that $\sigma = \sigma_0 \exp(-E_A / k_B T)$, where σ_0 is the intrinsic conductivity, ^{††††} E_A is the activation energy, k_B is Boltzmann's constant and T is

^{††††} $\sigma = \epsilon_0 \epsilon'' \omega$, where ϵ_0 is the permittivity of the vacuum and ω is the 2π times the frequency of the measurement.

temperature, the activation energies can be calculated and the number of charge carriers estimated.

E_A was obtained from a least squares fit of each of the straight linear segments of the graphs of $\ln(\sigma)$ versus $1/(k_B T)$ after subtracting the baseline value of σ . Figure 58 shows the negative of the least squares fits of overlapping sets of seven values of $\sigma(T)$ points after a baseline value of $\sigma = 1 \cdot 10^{-7} \Omega \text{ m}^{-1}$ has been subtracted.

One can see from this plot that there is a large constant region in which the conductivity is well described by an activated process. One can also obtain an estimate of the accuracy σ_0 from the fluctuation in its value as the set of points used to determine its value in the constant region of σ_0 is systematically varied: σ_0 , as determined by least square fits to sets of seven points in the temperature range in which σ is thermally activated, varies by about two orders of magnitude in the region. Given this large error in the evaluation of σ_0 , σ_0 is within the narrow range expected for protonic conductivity, i.e., $\sigma_0 = 10^{5 \pm 1} \Omega \text{ m}^{-1}$. The value of E_A for the powder, as determined from this method for a frequency of 100 kHz and a baseline of $\sigma = 1.9 \cdot 10^{-7} \Omega^{-1} \text{ m}^{-1}$, ($E_A = 0.50 \pm 0.05 \text{ eV}$) agrees well with that obtained from NMR for the relaxation of the acid protons ($E_A = 0.46 \pm 0.05 \text{ eV}$), but neither result agrees very well with the liquid-like, theoretical value that we calculated in the NMR section ($E_A = 0.35 \text{ eV}$). Reliable results for E_A and σ_0 along the three axes of CADP.20 could not be obtained because of the small values of ϵ'' in the thermal region of interest.

In Table 10, the most significant features of the dielectric behavior of all of the measured crystals is summarized. In the chart, "CA" denotes that the results for E_A and σ_0 were obtained by fitting the logarithm of conductivity versus inverse temperature in the temperature region of 220 K to 260 K, after subtracting off a baseline value. "NPC" denotes normal protonic conductivity, meaning that the results were obtained from the temperature region above 260 K.

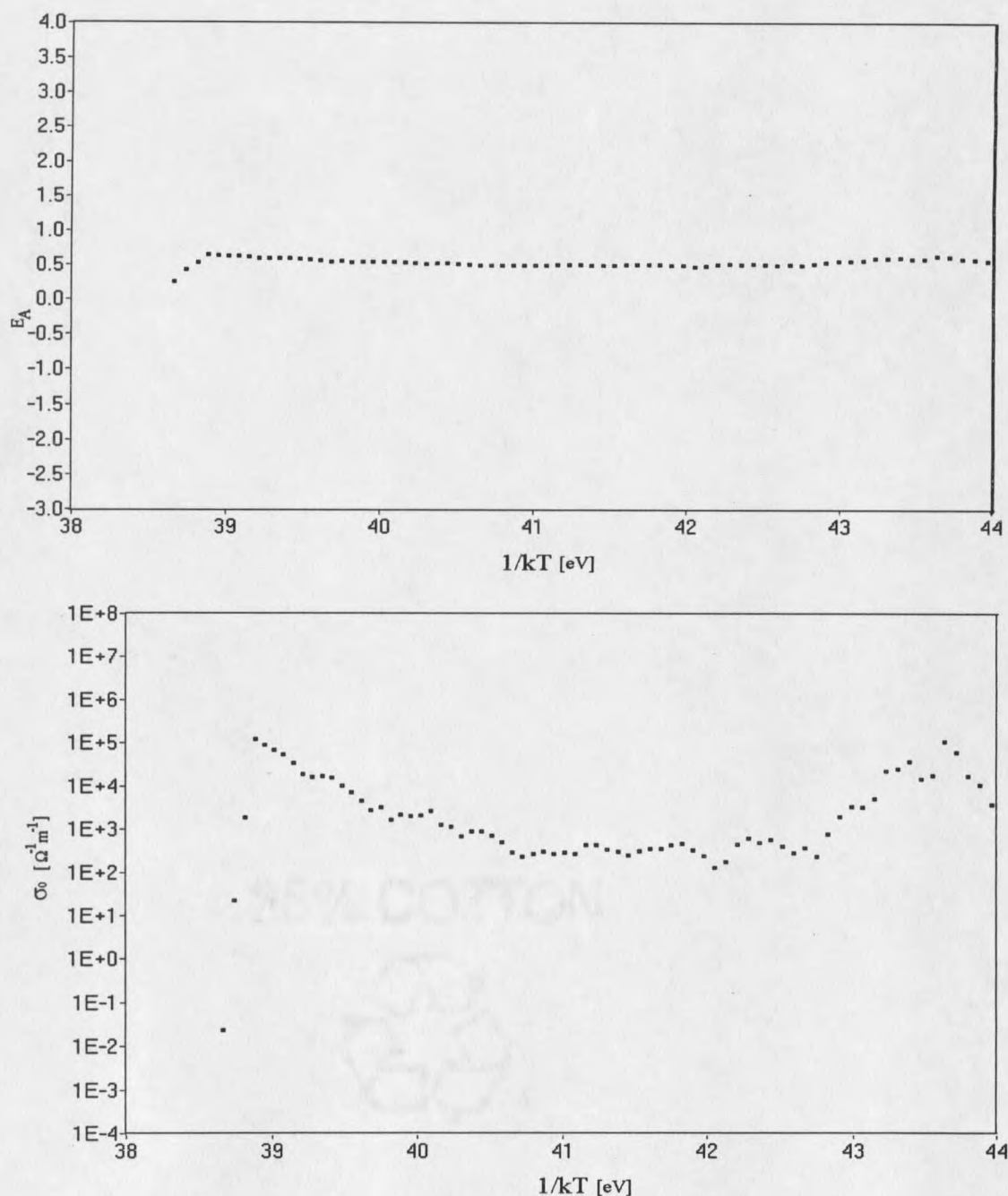


Figure 58. E_A and σ_0 Versus $1/kT$

E_A and σ_0 could not be obtained in some cases because either the ferroelectric response or anomalous conductivity overlapped the temperature region in which normal protonic conductivity would otherwise have been evident.

The values of E_A for the normal protonic conduction processes differ slightly along each of the three axes and for differing concentrations. The effect of deuteration on ordinary protonic conductivity appears to be negligible.

Material	Axis	T_m	$\epsilon'(T=T_m)$	T_n	$\epsilon''(T=T_n, f = 31.6 \text{ Hz})$ heating	E_A [eV] ± 0.05	$\log_{10}(\sigma_0)$ [$\Omega^{-1}\text{m}^{-1}$] ± 1	Notes
CDP	<i>b</i>	154	15000	-	-	-	-	-
	<i>c</i>	-	-	-	-	-	-	-
DCDP	<i>b</i>	263	-	-	-	-	-	-
CADP.10	<i>c</i>	-	-	266	4	-	-	CA
	<i>c</i>	"	"	"	"	-	-	NPC
CADP.20	<i>a</i>	155	250	205	$2.6 \cdot 10^4$	-	-	-
	<i>b</i>	160	10000	-	< 4	-	-	-
	<i>c</i>	170	363	290	$1.0 \cdot 10^5$	-	-	-
CADP.40	<i>c</i>	134	700			-	-	-
CADP.20 (powder)	-	-	-	-	-	0.50	4	-
DCADP. 20	<i>b</i>	276	2300	-	-	-	-	-
	<i>c</i>	262	31	255	3	-	-	cooling
	<i>c</i>	"	"	"	"	-	-	heating

Table 10. Summary of Dielectric Responses.

6.4.4. Effect of Pulverization

Some groups have assumed that the nature of the phase transition would not be altered by the use of microcrystalline powder instead of crystalline samples.⁸⁵ Others have purported to show that the glassy behavior of powder samples is very similar to that of pure crystals.^{86,87} However, our dielectric measurements of powdered CADP.20 were entirely different from the angularly-averaged dielectric behavior of the three axes of the single crystal. Interestingly, our NMR measurements on powdered CDP seemed to be sensitive to both the FE transition and the conductive anomaly seen in the powder. This

may be because NMR is sensitive to the microscopic environment of the crystalline powder, whereas dielectric measurements measure macroscopic behavior.

Although the dielectric behavior of CADP has many similarities with other mixed KDP isomorphs, it also has and many striking differences.

- The addition of ammonium to CADP increases T_m , whereas in KADP⁸⁸ and RADP,^{89,90} the addition of ammonium decreases T_m .
- KADP and RADP have smeared dielectric responses relative to their pure parent crystals, whereas the ferroelectric anomaly in CADP along the b axis is qualitatively identical to that in pure CDP, differing only in that it occurs several degrees higher in temperature. ⁺⁺⁺
- The conductive anomaly has not been reported in the literature for KADP,⁸⁸ KADA⁹¹, RADP^{89,90} or RADA⁹². However, we have also observed it in deuterated rubidium ammonium dihydrogen phosphate, DRADP.20 and DRADP.25, but not in DRADP.19. $\epsilon'_a(T)$ for heating DRADP.20 is shown in Figure 59.

In order to explain why the conductive anomaly is orders of magnitude larger along the a and c axes than along the b axis, we suggest that there must be either linear structures along the b axis that either modulate the conductivity or are constrained to drift perpendicular to their length or highly conductive planar structures normal to the b axis.

⁺⁺⁺ It seems that our results cannot be reconciled with the random-field smearing models, in which random fields are supposedly induced by the random tilting of the protonic double-well potential by the ammonium groups. Such a proposal suggests that all ammonium-containing KDP isomorphs should exhibit smearing of the dielectric response.

One possibility for the planar scenario would be that the ammonium is concentrated in a - c planes. The ammonium may provide large numbers of carriers within these planes by an auto-hydrolysis mechanism. Such a planar arrangement of ammonium could account for the fact that the anomalous conductivity is orders of magnitude larger along the a and c axes than along the b axis.

Furthermore this theory could explain why there is no smearing of the dielectric responses in CADP as a result of substitution with ammonium. The correlation length in CDP along the b axis is 60 nm near T_c , and about 3 nm perpendicular to the b axis.¹⁶ This considerable correlation length gives a high probability of intersection of a correlated region with an ammonium plane. Because of the long extension of the correlated regions it is probable that all correlated regions are in similar environments. Therefore, the transition temperature for all regions is shifted by the same amount.

T_c increases by this model because of the increasing isotropic character of the correlations caused by redirection of the CDP chains. Since purely one-dimensional Ising system cannot undergo phase transitions, while higher dimensional systems can, increasing the dimensionality lowers the energy required for the formation of the ordered phase, and, therefore, increases the transition temperature. Similarly, since the other KDP isomorphs are already three-dimensionally correlated, the addition of impurities lowers T_c in these systems, by disrupting the correlated region.

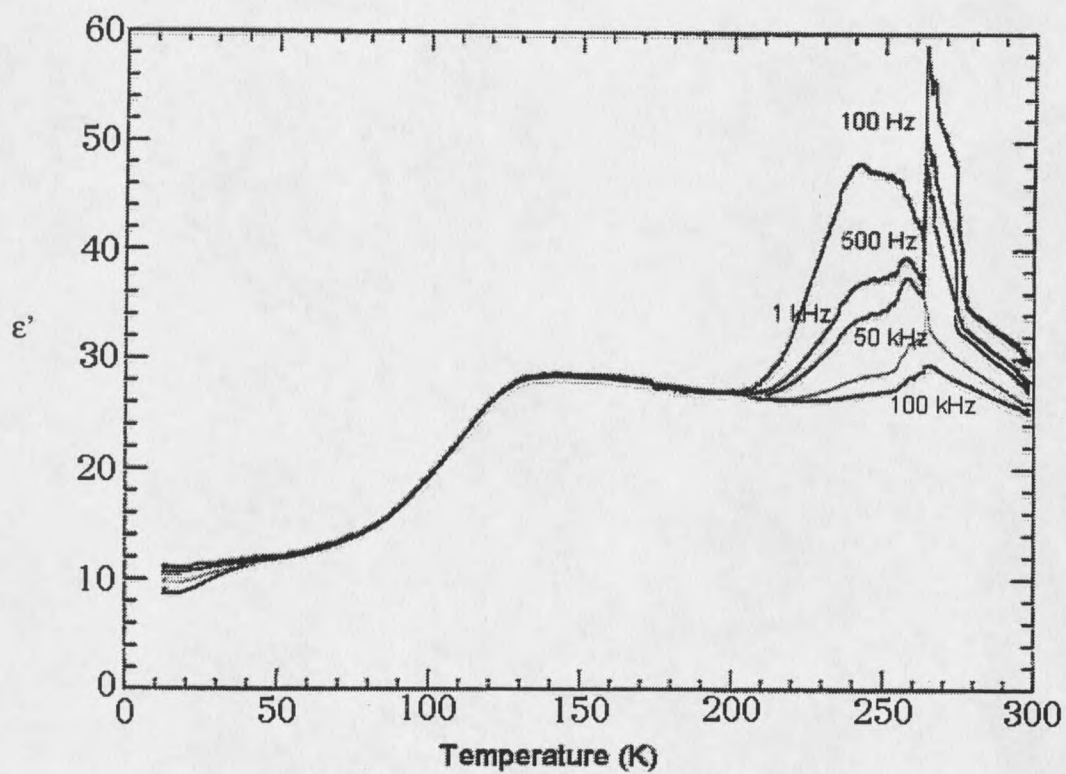


Figure 59. $\epsilon'_a(T)$ Upon Heating of DRADP.20.

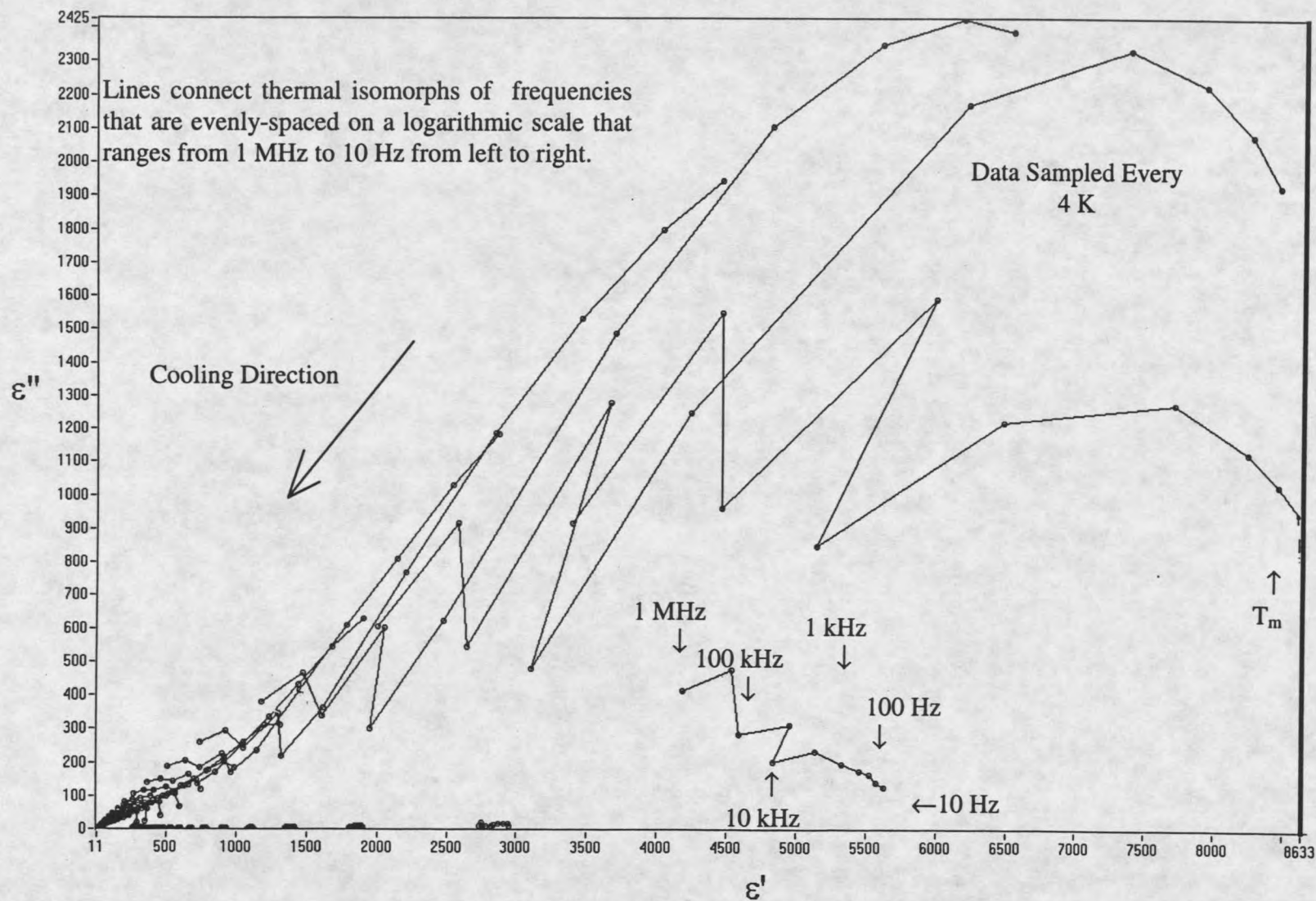


Figure 60. $\epsilon''_b(f; T)$ Versus $\epsilon'_b(f; T)$ upon Cooling of CADP.20.

7. CONCLUSION

7.1. CONTRIBUTIONS

$\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (CADP $_x$) crystals of good quality with $x > 0$ can be grown. For solutions with molar concentrations of ammonium as high as forty percent the crystals have room-temperature lattice structures and space groups that are identical to that of CsH_2PO_4 (CDP). Unlike CDP, which exhibited dielectric responses associated with the ferroelectric phase transition only along the b axis, CADP $_x$ with $x > 0$ exhibited such responses along all three axes. The greater isotropy of the ferroelectric transition was supported by a smaller ratio of the quasi-one-dimensional Ising model parameters $J_{||}$ and $J_{\perp}$, which were obtained by fitting the divergence of the dielectric permittivity as the ferroelectric transition temperature was approached from above. The effect of deuteration in CADP, as in CDP, is to greatly increase the value of T_m . Pulverizing the sample completely eliminated the ferroelectric response. In addition, pulverization increased the relaxational (broad, small and dispersive) dielectric character of CADP far beyond what might be expected solely on the basis of random orientation of the axes.

Dielectric measurements indicated and nuclear magnetic resonance confirmed the idea that there were mobile hydrogens in at least two distinct environments, which contributed to the ferroelectric and conductivity anomalies to different extents. Both measurements obtained similar results for the activation energy of ordinary protonic conductivity, i.e., 0.50 eV and 0.46 eV.

CADP crystals have many interesting properties that are unique among mixed ammonium-containing KDP isomorphs:

- The value of T_m is higher in the mixed system than the transition temperatures to the ordered phases of either of the parent crystals: $T_m(\text{CADP.20}) = 160 \text{ K}$, whereas $T_m(\text{CDP}) = 154 \text{ K}$ and $T_m(\text{ADP}) \cong 148 \text{ K}$.
- The molar fraction of ammonium incorporated into the crystals was determined to be less than 10 % for all of the crystals, which, in the cases of CADP.40 and CADP.20, was substantially less than the concentrations of the solutions from which the crystals were grown.
- The addition of ammonium does not significantly alter the character (i.e., sharpness, amplitude) of the response of the dielectric permittivity to the ferroelectric phase transition; only the temperature at which the dielectric response occurs.

In the high-temperature phase the ordinary thermally-activated protonic conductivity of hydrogen bonded crystals was observed.

In addition, all of the crystals of CADP_x with $x > 0$ that were studied exhibited an anomaly in their dielectric responses between $T = 200 \text{ K}$ and $T = 300 \text{ K}$ which, except for certain crystals of DRADP_x with certain values of x , has not been observed in any other ammonium-containing mixed KDP isomorphs. This anomaly has many distinguishing characteristics:

- A jagged dielectric permittivity ($d\epsilon(T)/dT \gg 0$).
- A strong dependence on thermal history: The dielectric permittivity is orders of magnitude larger upon heating than upon cooling. In addition, thermal cycling below

the ferroelectric phase transition increased the magnitude of the anomaly, but thermal cycling much above T_c destroyed the anomaly.

- Complete suppression by applying electric bias fields as low as 0.2 kV m^{-1} or by pulverizing or deuterating the crystals.

The normal protonic conductivity associated with all hydrogen-bonded systems was observed in CADP. As in CDP below $T = 380 \text{ K}$, the normal protonic conductivity in CADP is axis dependent. Interestingly, at $T = 300 \text{ K}$ the ordinary protonic conductivity in the powdered sample is larger than that along any of the three axes of the unpulverized crystal.

7.2. FUTURE WORK

This work was only concerned with the nature of CADP $_x$ for small values of solution concentration, x . A logical continuation of this work would thus be to extend the study to over the whole range of x . It would be interesting also to compare the relative amplitude of the reflection peaks of x-rays scattered from CADP $_x$ in the temperature region of the conductive anomaly following heating from the ferroelectric phase, with the corresponding peaks following cooling from elevated temperatures ($\sim 320 \text{ K}$). We predict that the relative reflection intensities of a given CADP $_x$ crystal subjected to these thermal histories will significantly differ because such relative intensities are dependent on the orientation of the sublattice.

Several questions remain unanswered concerning the microscopic distribution of ammonium in the crystal: Does the ammonium exist in microscopic voids or does it

substitute into the lattice? Is the ammonium distributed truly randomly or does it concentrate along lines, planes or some fractal dimensional structure? How does the concentration distribution depend on the temperature and acidity of the solution from which the crystals are grown? How would these parameters effect the physical properties of the crystals, such as dielectric permittivity, heat capacity, sound velocity, etc.

Perhaps answers to these questions could be obtained by dividing the sample into a matrix and analyzing the pieces by molecular beam epitaxy or by cleaving small layers at low temperatures and examining the cross sections by scanning nuclear magnetic resonance spectroscopy.

In addition, Raman, infrared and/or Brillouin scattering studies should be performed in order to examine the mode structure and dynamics of the phase transition.

BIBLIOGRAPHY

- ¹ F. Jona and G. Shirane, *Ferroelectric Crystals*, Dover Publications, Inc., New York (1983), p. 104.
- ² J. D. Axe and M. E. Lines, *Encyclopedia of Physics*, 2nd ed., VCH Publishers, Inc., New York (1990).
- ³ J. D. Jackson, *Classical Electrodynamics*, 2nd ed., John Wiley & Sons, New York (1962).
- ⁴ A. I. Baranov, V. P. Khiznichenko and L. A. Shuvalov, *Ferroelectrics* **47**, 25, 1983.
- ⁵ U. T. Höchli, K. Knorr and A. Loidl, *Adv. Phys.* **39**, 5, 405, 1990.
- ⁶ A. Loidl and R. Böhmer, *Disorder Effects on Relaxational Processes*, R. Richert and A. Blumen, eds., Springer-Verlag, Berlin (1994), p. 659.
- ⁷ S. Lanceros-Méndez, Ph. D. thesis, Universität Würzburg, Ed. Wissenschaft, Reihe Physics, Bd. 29, Tectum Verlag, Marburg (1996).
- ⁸ R. K. Pathria, *Statistical Mechanics*, Pergamon Press, Oxford (1972), p. 374.
- ⁹ P. Ehrenfest, *Proc. Kon. Amsterdam Acad.*, **33**, 153, 1933.
- ¹⁰ F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw Hill Book Co., New York (1965), p. 305.
- ¹¹ H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford (1971).
- ¹² D. ter Harr, ed., *Collected Papers of L. D. Landau*, Gordon and Breach, New York (1965).
- ¹³ A. I. Kitaigorodsky, *Mixed Crystals*, Springer-Verlag, Berlin (1984).
- ¹⁴ F. Seidl, *Tschermaks Mineral Petrogr. Mitt.* **1**, 432, 1950.
- ¹⁵ A. Levstik, R. Blinc, P. Kadaba, S. Cizikov, I. Levstik and C. Filipic, *Solid State Comm.* **16**, 1339, 1975.
- ¹⁶ B. C. Frazer, D. Semmingsen, W. D. Ellensen and G. Shirane, *Phys. Rev.* **B20**, 2745, 1979.
- ¹⁷ R. N. P. Choudhary and R. J. Nelmes, *Ferroelectrics* **21**, 443, 1978.
- ¹⁸ H. Matsunaga, K. Itoh and E. Nakamura, *Jour. of the Physical Society of Japan* **48**, 6, (1980).
- ¹⁹ C. Lagier, A. Olivieri, D. Apperley and R. Harris, *Sol. State Nucl. Mag. Res.* **1**, 205, 1992.
- ²⁰ D. Semmingsen, W. D. Ellenson, B. C. Frazer and G. Shirane, *Phys. Rev. Lett.* **38**, 7, 1299, 1977.
- ²¹ J. Selinger, V. Žagar and R. Blinc, *J. Chem. Phys.* **81**, 7, 3247, 1984.
- ²² S. Žumer, *Phys. Rev.* **B21**, 1298, 1980.
- ²³ R. Blinc, B. Žekš, A. Levstik, C. Filipič, J. Slak, M. Burgar, I. Zupančič, L. Shuvalov and A. Baranov, *Phys. Rev. Letters* **43**, 231, 1979.
- ²⁴ R. J. Nelmes and R. N. P. Choudhary, *Solid State Comm.* **26**, 823, 1978.
- ²⁵ Y. Uesu and J. Kobayashi, *Phys. Status Solidi* **A34**, 475, 1976.
- ²⁶ K. Imai, *J. Phys. Soc. Jpn.* **52**, 11, 3690, 1983.
- ²⁷ E. Kanda, A. Tamaki and T. Fujimura, *J. Phys.* **C15**, 3401, 1982.
- ²⁸ N. Yasuda, M. Okamoto, H. Shimizu, S. Fujimoto, K. Yoshino and Y. Inuishi, *Phys. Rev. Lett.* **41**, 1311, 1978.
- ²⁹ K. Gesi and K. Ozawa, *Jpn. J. Appl. Phys.* **17**, 435, 1978.
- ³⁰ P. J. Schuele and R. Thomas, *Jpn. J. Appl. Phys.* **24**, Suppl. 24-2, 935, 1985.
- ³¹ R. Youngblood, B. C. Frazer, J. Eckert and G. Shirane, *Phys. Rev.* **B22**, 228, 1980.
- ³² A. V. De Carvalho and S. R. Salinas, *J. Phys. Soc. Jpn.* **44**, 238, 1978.
- ³³ K. Deguchi, E. Okaue and E. Nakamura, *J. Phys. Soc. Jpn.* **50**, 2783, 1981.
- ³⁴ K. Deguchi, E. Nakamura, E. Okane and N. Aramaki, *J. Phys. Soc. Jpn.* **51**, 3575, 1982a.
- ³⁵ E. D. Yakushkin, A. I. Baranov and L. A. Shuvalov, *JETP Lett.* **33**, 24, 1981.
- ³⁶ G. Spörl, D. D. Chat and E. Hegenbarth, *Phys. Stat. Sol.* **A82**, K27 1984.
- ³⁷ E. Kanda, M. Yoshizawa and T. Fujimura, *J. Phys.* **C15**, 2401, 1982.
- ³⁸ T. Nattermann, *Phys. Stat. Sol.* **B85**, 291, 1978.
- ³⁹ M. A. Krivoglaz, *Sov. Phys.: Solid State* **5**, 2526, 1964.
- ⁴⁰ M. Kasahara and I. Tatsuzaki, *Ferroelectrics Lett.* **44**, 21, 1982.

-
- ⁴¹ Y. Ishibashi, M. Wada and A. Sawada, J. Phys. Soc. Jpn. **45**, 2045, 1978.
- ⁴² A. I. Baranov, V. P. Khiznichenko and L. A. Shuvalov, *Ferroelectrics* **100**, 136, 1989.
- ⁴³ M. Wada, A. Sawada and Y. Ishibashi, J. Phys. Soc. Jpn. **47**, 429, 1982.
- ⁴⁴ A. Aijaz, A. Jahn and W. Baur, *Acta Cryst.* **B29**, 2721, 1973.
- ⁴⁵ C. C. Stephenson and A. C. Zettlemoyer, J. Am. Chem. Soc. **66**, 1405, 1944.
- ⁴⁶ J. J. O'Dwyer, *Dielectric Breakdown of Solids*, Oxford University Press, London (1964), p. 3.
- ⁴⁷ F. Seitz and D. Turnbull, *Solid State Physics - Advances in Research and Applications*, Academic Press, Inc., New York (1957), p. 155.
- ⁴⁸ T. Chiba, J. Chem. Phys. **41**, 1352, 1964; *Bull. Chem. Soc. Jpn.* **38**, 490, 1965.
- ⁴⁹ R. O. Keeling, Jr. and R. Pepinsky, *Z. Krist.* **106**, 236, 1955.
- ⁵⁰ L. Tenzer, B. C. Frazer and R. Pepinsky, *Acta Cryst.* **11**, 505, 1958.
- ⁵¹ E. A. Wood, W. J. Merz and B. T. Matthias, *Phys. Rev.* **87**, 544, 1954; W. P. Mason and B. T. Matthias, *Phys. Rev.* **88**, 477, 1952.
- ⁵² G. A. Samara and B. Morosin, *Phys. Rev.* **B8**, 1256, 1973.
- ⁵³ J. F. Ryan, R. S. Katiyar and W. Taylor, *J. Phys. Paris* **33**, C2-49, 1972.
- ⁵⁴ H. Meister, J. Skalyo, B. C. Frazer and G. Shirane, *Phys. Rev.* **184**, 550, 1969.
- ⁵⁵ R. S. Viswanath and P. J. Miller, *Solid State Comm.* **32**, 703, 1979.
- ⁵⁶ V. K. Subhadra, U. Syamaprasad and C. P. G. Vallabhan, *J. Appl. Phys.* **54**, 2593, 1983.
- ⁵⁷ L. P. Pereverzeva, N. Z. Pogosskaya, Y. M. Poplavko, V. I. Pakhomov, I. S. Rez, G. B. Sil'nitskaya, *Fiz. Tver. Tela* **13**, 3199, 1971.
- ⁵⁸ A. Abdel-Kader, *J. Mat. Sci.: Mat. Electr.* **2**, 7, 1991.
- ⁵⁹ E. J. Murphy, *J. Appl. Phys.* **32**, 2609, 1964.
- ⁶⁰ C. T. Perrino and P. Wentreck, *J. Solid State Chem.* **10**, 36, 1974.
- ⁶¹ M. Sharon and A. K. Kalia, *J. Solid State Chem.* **21**, 171, 1977.
- ⁶² L. B. Harris and G. J. Vella, *J. Chem. Phys.* **58**, 10, 4452, 1973.
- ⁶³ S. Chandra and S. A. Hashmi, *J. Mat. Sci.* **25**, 2460, 1990.
- ⁶⁴ A. I. Kitaigorodsky, *Mixed Crystals*, Springer-Verlag, Berlin (1984).
- ⁶⁵ G. H. Stout and L. H. Jensen, *X-Ray Structure Determination - A Practical Guide*, 2nd ed., Wiley Interscience, New York.
- ⁶⁶ L. Arnberg, S. Hovmoller, and S. Westman, *Acta Cryst.* **A35**, 497, 1979.
- ⁶⁷ A. H. Simone, E. H. Simone and C. P. Cresman III, *J. Sci. Food Ag.* **V73**, 39, 1997.
- ⁶⁸ R. C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Inc., Boca Raton (1987), p. F160.
- ⁶⁹ L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, 1960.
- ⁷⁰ N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.* **73**, 679, 1948.
- ⁷¹ R. Blinc, I. Zupancic, G. Lahajnar, J. Slak, V. Rutar, M. Verbec and S. Zumer, *J. Chem. Phys.* **72**, 6, 1980.
- ⁷² J. W. Hennel and J. Klinowski, *Fundamentals of Nuclear Magnetic Resonance*, Longman Scientific and Technical, Essex, 1993, p. 65.
- ⁷³ E. Fukushima and S.B. Roeder, *Experimental Pulse NMR - A Nuts and Bolts Approach*, Addison-Wesley Publishing Co., Inc., London (1981), p. 29.
- ⁷⁴ P. J. Schuele, Ph. D. thesis, Montana State University, University Microfilms Intl., Ann Arbor (1988).
- ⁷⁵ J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.
- ⁷⁶ B. Topič, V. Rutar, J. Slak, M. I. Burgar, S. Žumer and R. Blinc, *Phys. Rev.* **B21**, 2695, 1980.
- ⁷⁷ K. Deguchi, E. Okaue and E. Nakamura, *J. Phys. Soc. Jpn.* **51**, 11, 3569, 1982.
- ⁷⁸ E. Kanda, M. Yoshizawa, T. Yamakani and T. Fujimura, *J. Phys.* **C15**, 6823, 1982.
- ⁷⁹ D. J. Scalapino and Y. Imry, *Phys. Rev.* **B11**, 5, 1975.
- ⁸⁰ A. I. Baranov, L. A. Shuvalov and V. H. Schmidt, *Ferroelectrics* **127**, 245, 1992.

-
- ⁸¹ R. Blinc, I. Dolinšek, G. Lahinar, I. Zupancic, L. A. Shuvalov and A. I. Baranov, *Phys. Status Solidi B123*, K 83, 1984.
- ⁸² M. Pham Thi, P. H. Colomban, A. Novak and R. Blinc, *Solid State Comm.* **55**, 1985.
- ⁸³ A. I. Baranov, V. P. Khiznichenko, V. A. Sandler, L. A. Shuvalov, *Ferroelectrics* **81**, 183, 1988.
- ⁸⁴ M. Sumita, T. Osaka and Y. Makita, *J. Phys. Soc. Jpn.* **53**, 8, 2784, 1984.
- ⁸⁵ T. K. Song, S. E. Moon, K. H. Noh and S. I. Kwun, *Phys. Rev. B* **50**, 10, 6637, 1994.
- ⁸⁶ O. J. Kwon and J. J. Kim, *Phys. Rev. B* **48**, 6639, 1993.
- ⁸⁷ J. J. Kim and W. F. Sherman, *Phys. Rev. B* **36**, 5651, 1987.
- ⁸⁸ C. S. Tu, V. H. Schmidt and A. A. Saleh, *Phys. Rev. B* **48**, 0, 4567, 1993.
- ⁸⁹ E. Courtens, *J. Physique Lett.* **43**, L199, 1982.
- ⁹⁰ T. Masaaki, H. Terauchi, Y. Miura and S. Hoshino, *J. Phys. Soc. Jpn.* **54**, 9, 3250, 1985.
- ⁹¹ Z. Trybula, S. Loś, C. S. Tu and V. H. Schmidt, *J. Phys.: Condens. Matter* **7**, 947, 1994.
- ⁹² N. J. Pinto, K. Ravindran and V. H. Schmidt, *Phys. Rev. B* **48**, 5, 3090, 1993.

APPENDIX

The user interface for the program that was created for the measurement of the dielectric permittivity is shown in Figure 61.

In the programming language, LabView from National Instruments, coding consists of defining constants and variables (controls) and connecting them via "wires". The object-oriented programming methodology that LabView employs is somewhat inefficient in terms of code optimization, but highly efficient in terms of code reuse and portability: The same code was run on an Apple Macintosh II si, an Apple Quadra and a Cyrix 686 with little modification. Furthermore, by simply swapping the icons corresponding to the two devices, the code for a Wayne-Kerr 6245 impedance analyzer was exchanged for that of a QuadTech 7600A, nearly as easily as the physical instruments were exchanged.

Each frame in the sequence of the program is represented by a border containing small squares on the top and bottom. The execution order of the other program objects is partially determined by whether they have data at all of their input terminals.

Figure 62, labeled "Preparation", calculates the completion time of the experiment, disables the controls that should not be varied during the experiment, sets the scale of the temperature axis and initializes both the temperature controller and impedance analyzer via the IEEE-488.2 interface.

Because rapid thermal changes may damage the samples, the frame in Figure 63 controls the rate at which the starting temperature of the experiment is approached.

The subframes in Figure 64 through Figure 66 collect permittivity data for either a single heating or cooling run or for both. The subframe in Figure 64 automatically creates file names. Such automated file name creation requires a way of handling duplicates. The "Rename If Duplicate" subprogram, whose diagram is shown in Figure 72, prevents files larger than 2 Kbytes from being overwritten by appending a number to a file name until it is no longer degenerate. This subframe also creates an additional file with an .inf extension, which contains the relevant parameters used in the front panel.

The subframe in Figure 65 generates spreadsheet headings and a legend for the frequencies displayed on the front panel of the program.

The subframe in Figure 66 contains the actual data collection loops. Both the outer and inner loops cooperate in order to vary the temperature as smoothly as possible, while maintaining synchronous timing. The inner loop increments the frequencies through eleven values that are equally spaced on a logarithmic scale within the range of the impedance analyzer. The data from a set of frequencies is stored on disk during execution, in order to minimize data loss in the case that the experiment terminates prematurely.

The icon labeled " ϵ ", whose diagram is shown in Figure 71, calculates the real and imaginary parts of the dielectric permittivity, ϵ' and ϵ'' respectively, based on the relations $\epsilon' = C d / \epsilon_0 A$ and $\epsilon'' = \epsilon' D$, where C is the capacitance, d is the sample thickness, A the cross-sectional area of the sample, ϵ_0 the permittivity of the vacuum and D , the dissipation factor, is the tangent of the phase angle between the real and imaginary parts of ϵ .

The subframe in Figure 66 also contains code that compensates for instability in the Lake Shore 330 control algorithm of the temperature. Although the Lake Shore 330 has an optional proprietary algorithm for the selection of the proportional, P , integral, I , and derivative, D , control parameters, this algorithm resulted in the sample temperature either oscillating or lagging considerably behind the temperature setpoint. After considerable experimentation, it was found to be preferable to vary P as the approximate inverse of the sensitivity of the silicon diode temperature sensor: P decreases linearly with temperature up to $T = 25$ K, at which point P decreases with a much steeper slope. The I and D parameters were less crucial to the performance of the temperature controller and, after some experimentation, were set as fixed ratios of P at the beginning of the experiment, 20 and 100, respectively.

The frames in Figure 67 through Figure 70 automatically produce a backup copy of the acquired data on a networked computer and prepare the QuadTech 7600A for local operation.

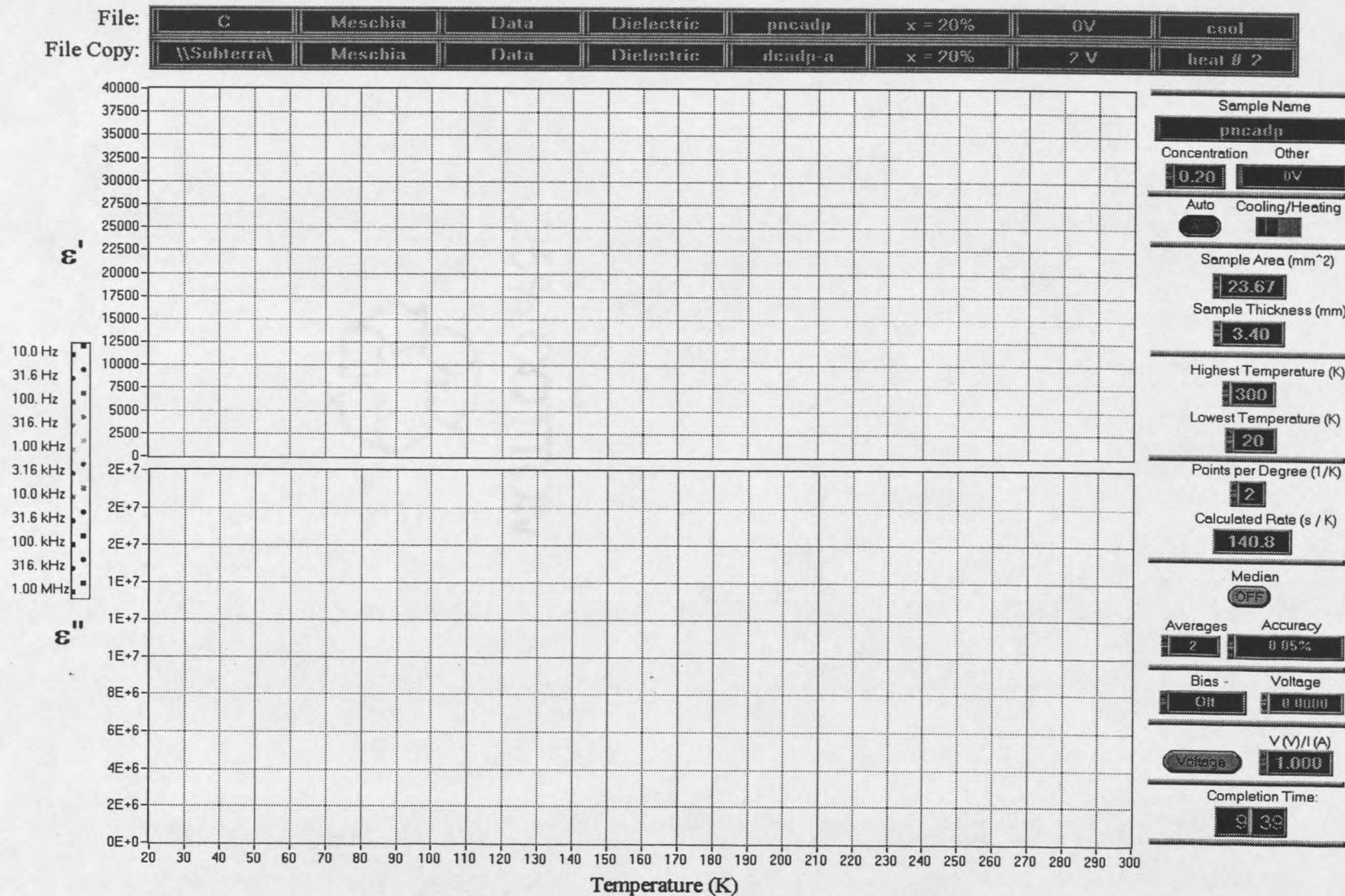


Figure 61. Front Panel of Dielectric Measurement Program.

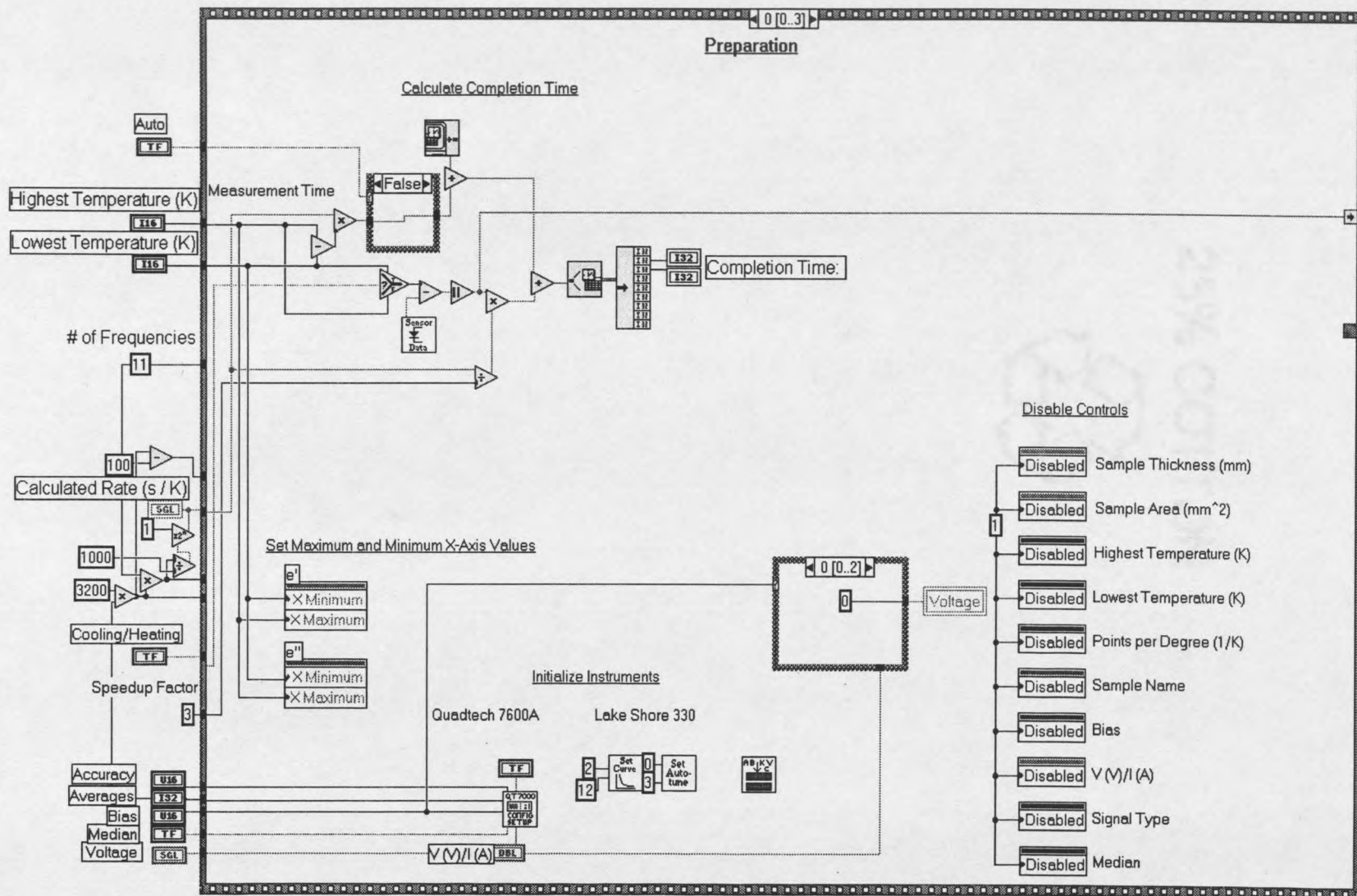


Figure 62. Frame 0 of Dielectric Measurement Program.

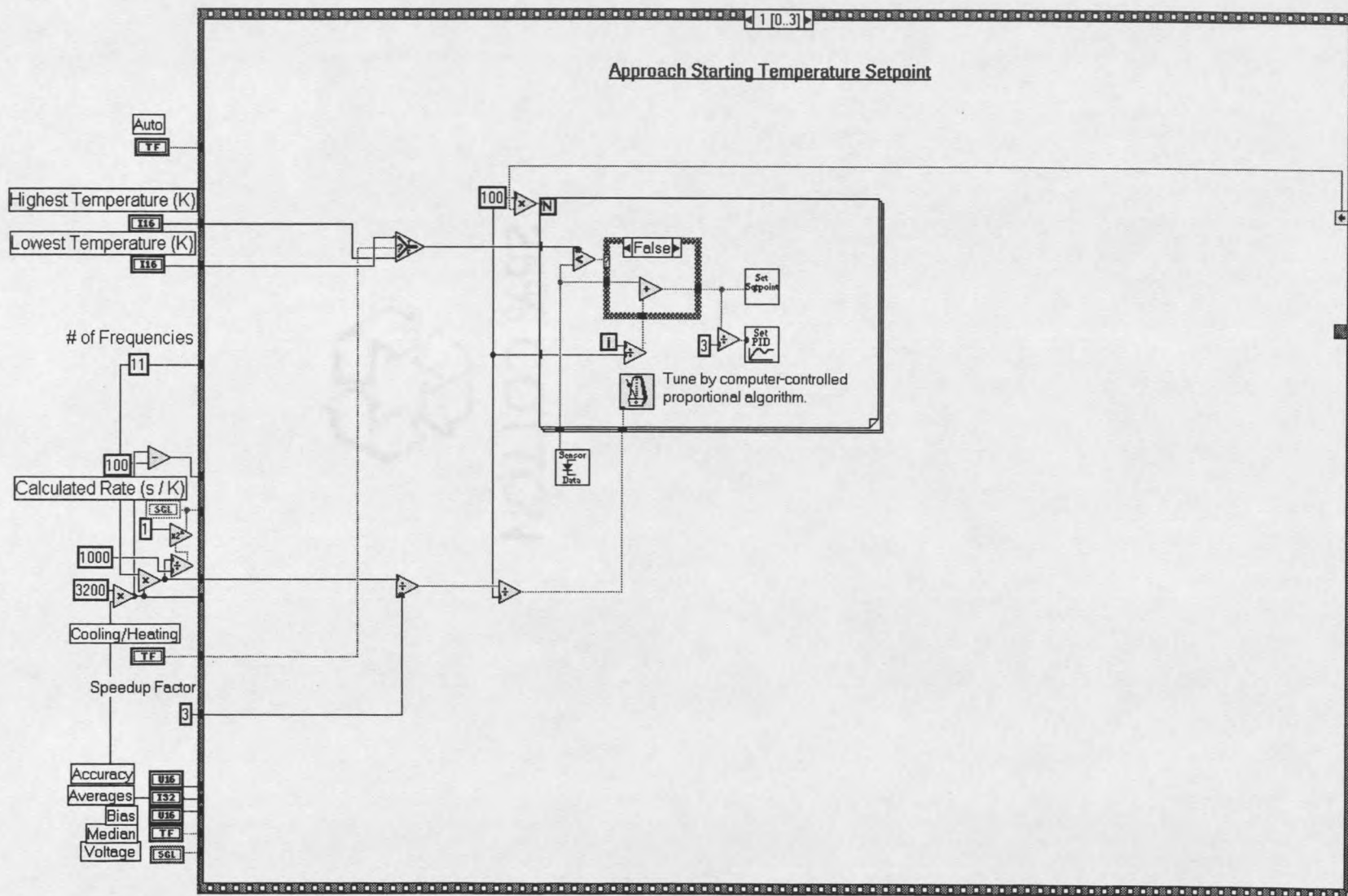


Figure 63. Frame 1 of Dielectric Measurement Program.

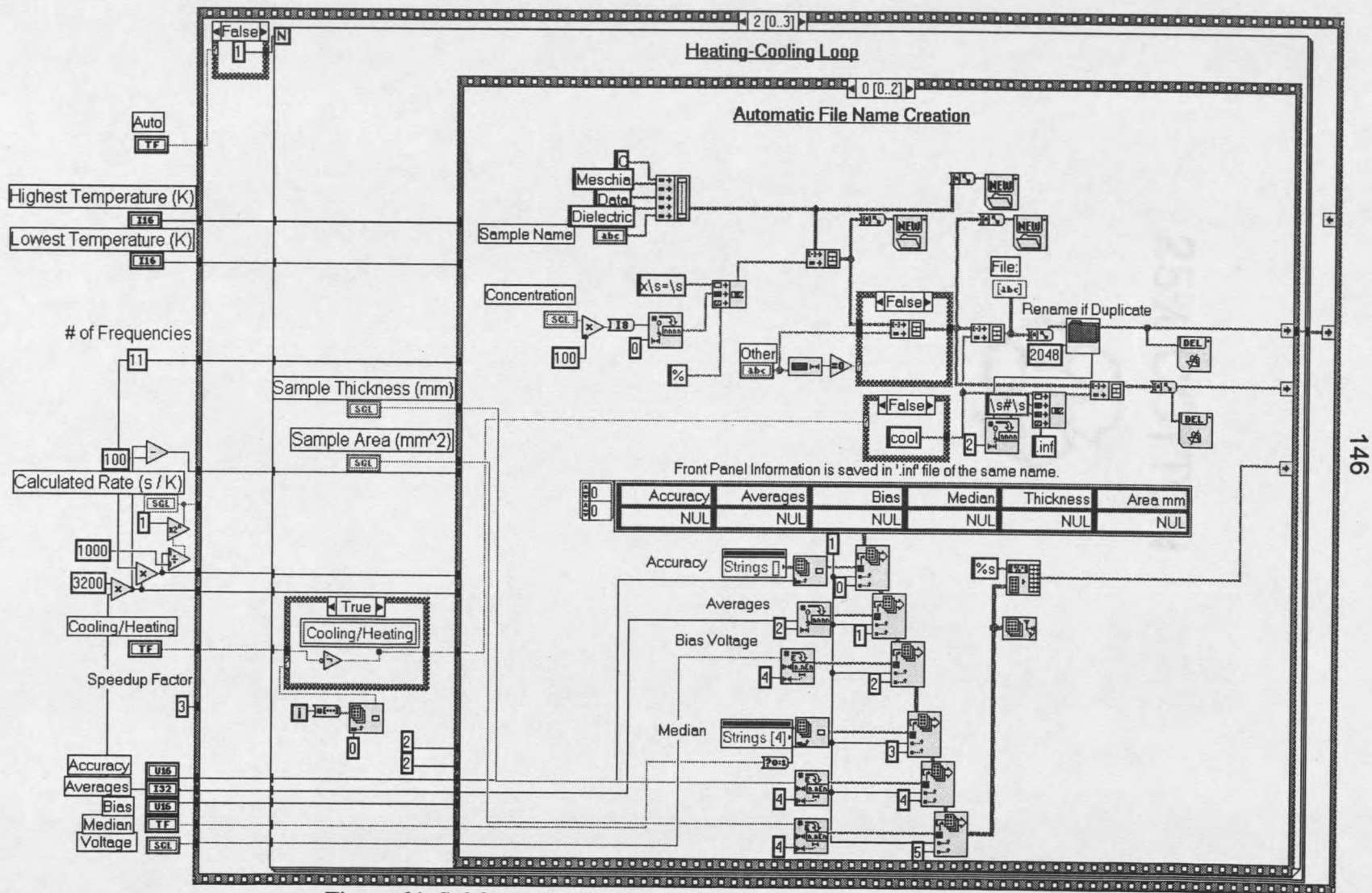


Figure 64. Subframe 0 of Frame 2 of Dielectric Measurement Program.

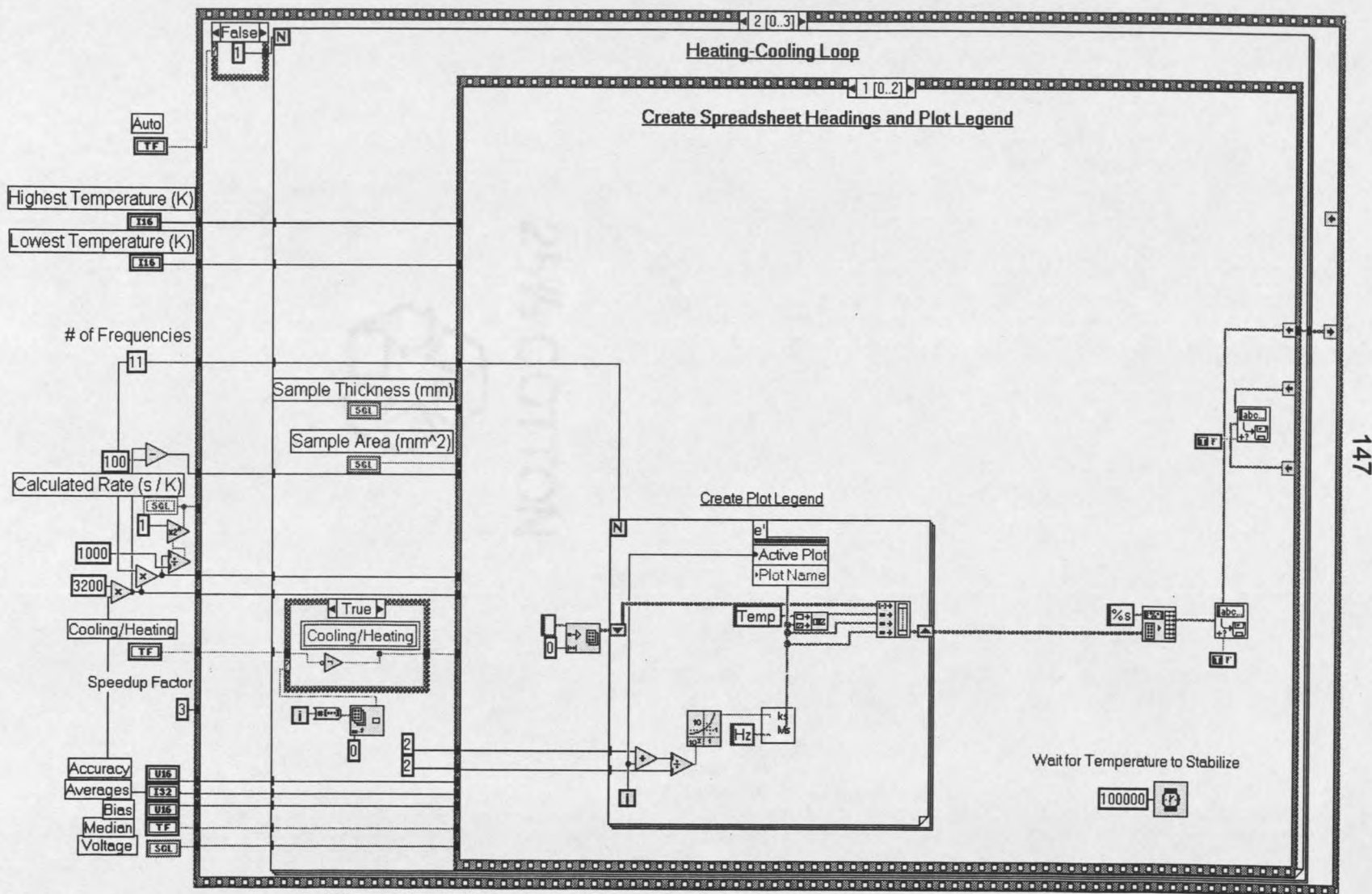


Figure 65. Subframe 1 of Frame 2 of Dielectric Measurement Program.

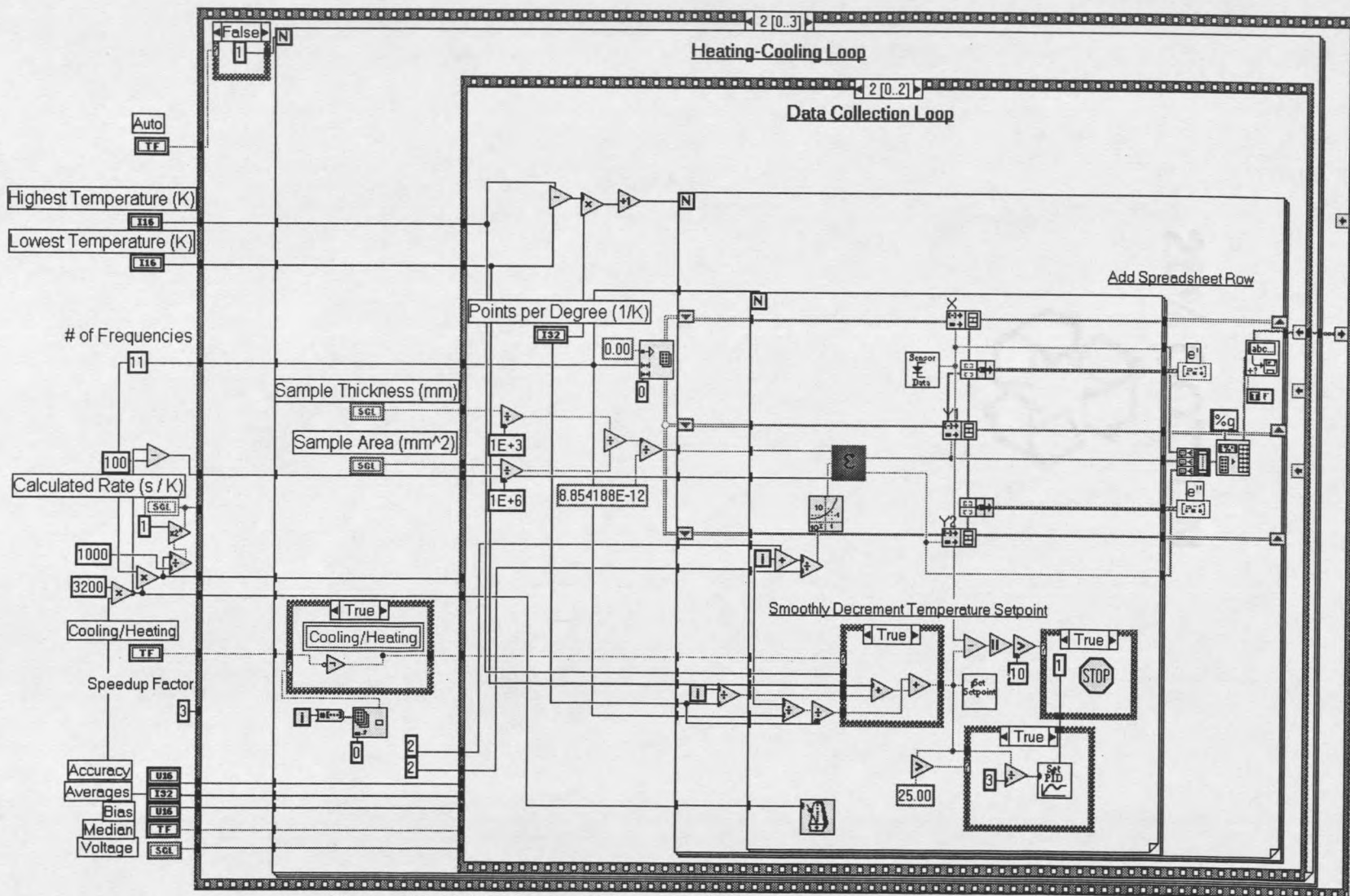


Figure 66. Subframe 2 of Frame 2 of Dielectric Measurement Program.

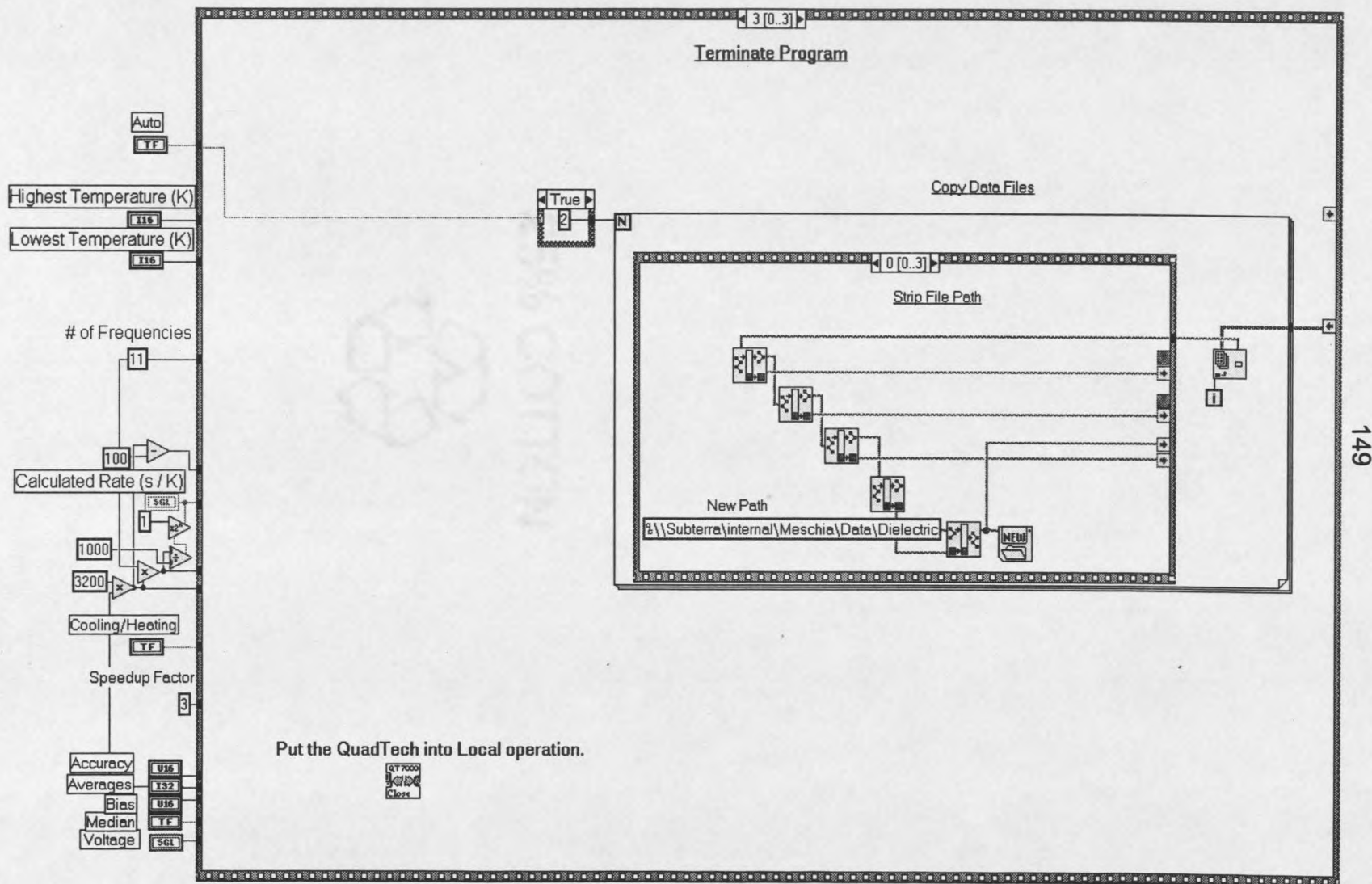


Figure 67. Subframe 0 of Frame 3 of Dielectric Measurement Program.

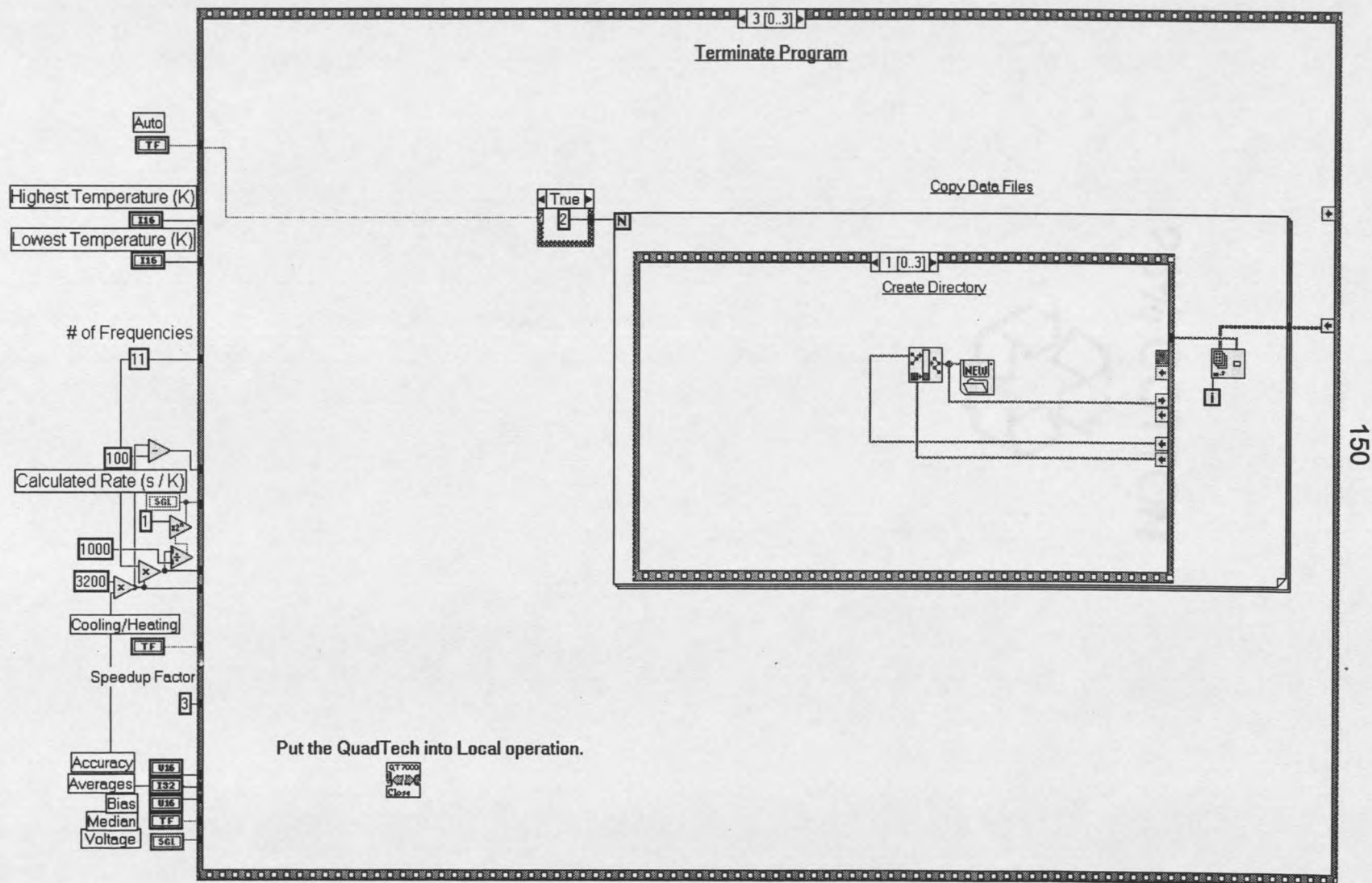


Figure 68. Subframe 1 of Frame 3 of Dielectric Measurement Program.

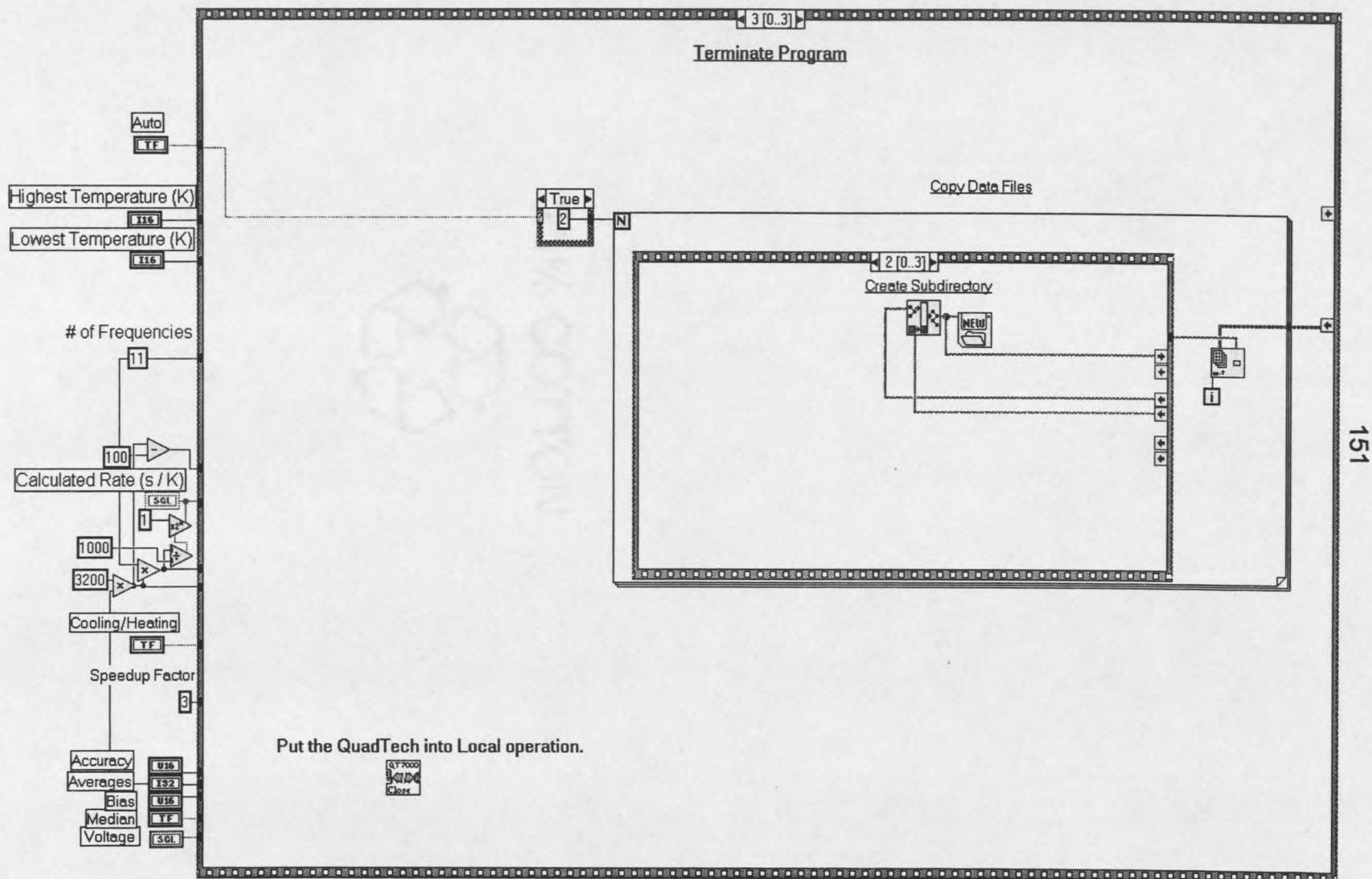


Figure 69. Subframe 2 of Frame 3 of Dielectric Measurement Program.

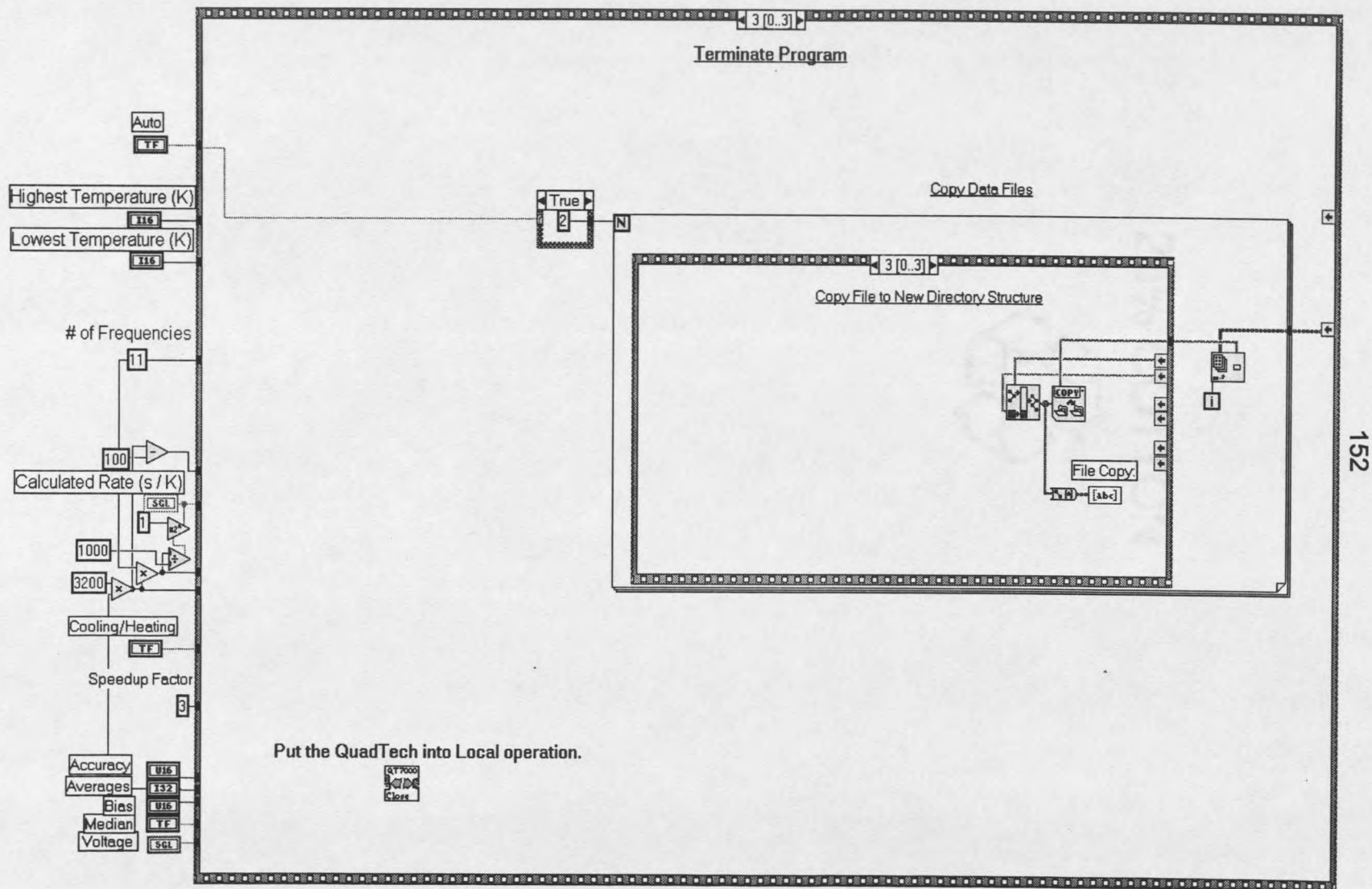


Figure 70. Subframe 3 of Frame 3 of Dielectric Measurement Program.



Figure 72. “Rename If Duplicate” Diagram

