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^{133}Cs NMR STUDY OF THE FERROELECTRIC AND ANTIFERROELECTRIC TRANSITIONS IN CsH_2PO_4

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Abstract Pressure and temperature effects on the one dimensional (1D) and higher-dimensionality correlations associated with the ferroelectric (FE) and antiferroelectric (AFE) phase transitions in cesium dihydrogen phosphate were studied using ^{133}Cs nuclear magnetic resonance at 6.5 MHz. The spin-lattice-relaxation time T_1 was measured at temperatures down to the FE Curie point T_c at pressures of 1 bar and at 1.5 and 3.0 kbar, down to the triple point T_t=124.6 K at 3.3 kbar, and down to the AFE Neel point T_N at 3.6 kbar. Far from the transition T_1 decreases exponentially with decreasing temperature due to 1D fluctuations associated with the J_b interactions in disordered hydrogen-bonded chains running along the b axis. As temperature is decreased further, T_1 decreases linearly as the J_c interaction between hydrogen-bonded chains in b-c planes becomes important. From these results the pressure dependences of J_b, J_c and the interplanar interaction J_a were calculated. At 3.3 kbar J_a changes sign, so the stacking of ordered planes becomes AFE rather than FE. At pressures above about 9 kbar, where the interaction J_c extrapolates to zero, a new AFE phase is predicted in which each b-axis chain is oriented AFE with respect to nearest neighbors in both the a and c directions.

INTRODUCTION

Cesium dihydrogen phosphate (CDP) is a hydrogen bonded system which is paraelectric (PE) at room temperature and undergoes a ferroelectric (FE) phase transition at 153 K.[1] In addition dielectric[2] and neutron diffraction measurements[3] at high pressure have revealed a third antiferroelectric (AFE) phase at pressures above 3.3 kbar and temperatures less than 125 K.

In the paraelectric phase CDP is monoclinic ($P2_1/m$) with two formula units per unit cell. Cesium atoms and PO_4 groups are centered on mirror planes perpendicular to the b axis at the fractional coordinates y = 1/4 and 3/4. Phosphate groups are linked together by hydrogen bonds of two inequivalent types; hydrogens in bonds approximately parallel to the c axis are ordered at off center sites in the hydrogen bond, while hydrogens linking phosphate groups in zig-zag chains along the b axis are positionally disordered in double minimum potential wells. Thus PO_4 groups are linked by a square network of hydrogen bonds producing a series of b-c planes separated by cesium atoms. In the ferroelectric phase b-chain hydrogens[4] order in one of the two off center sites in the O-H...O while the positions of hydrogens in c-axis H-bonds are unaffected. This hydrogen ordering is accompanied by a shift of Cs^+ and PO_4^{3-} groups along the b axis which yields a spontaneous polarization along b. In the pressure induced AFE phase the structure doubles along the a axis due to antiferroelectric stacking of FE ordered b-c planes.[3]

Neutron diffraction experiments[5,6] have shown strong quasielastic scattering in narrow reciprocal space planes perpendicular to the ferroelectric b axis on approaching T_c. This indicates that the correlations associated with ferroelectric ordering are strongly one dimensional along the b-axis hydrogen bonds. The interactions between adjacent b-axis chains linked by c-axis hydrogen bonds are weaker by about a factor of 100 and correlations in the a direction are weaker still. In addition correlations along a and c decrease rapidly with increasing temperature above T_c while the b-axis correlations are apparent as much as 50 K above T_c.

In addition to the neutron scattering experiments,[5,6] evidence for long range correlations has been observed in dielectric susceptibility,[7,8] electron paramagnetic resonance (EPR),[9] and nuclear magnetic resonance (NMR)[10-15] experiments. The NMR work includes ^{31}P, ^{17}O, deuteron, and ^{133}Cs resonance studies.

EXPERIMENTAL PROCEEDURE

The experimental arrangement consists of a conventional electromagnet which accommodates a high-pressure, low-temperature apparatus described elsewhere.[16,17] The apparatus provided long-term thermal stability of ±2 mK with helium gas pressure medium which was pressurized as high as 3.6 kbar. Long-term pressure stability was limited by a helium leak causing a pressure loss rate of 2 bar/hr at 3.6 kbar.

The sample was cut from an optically clear single crystal grown by slow evaporation from an aqueous solution of Cs_2CO_3 and P_2O_5. It was mounted with the b axis parallel to the applied static magnetic field H_0 and the c axis parallel to the NMR field H_1. At this orientation the quadrupolar splitting collapses,[14] so the NMR response consistes of a single Zeeman line with a well defined spin lattice relaxation time (T_1).

The NMR spectrometer was operated at a fixed frequency of 6.5 MHz which corresponds to a field of 1.1639 T for ^{133}Cs nuclei. To measure the spin-lattice relaxation time T_1, the spin system was first saturated by a comb of 90^o pulses, and then after a waiting time τ the response to a 90^o pulse was observed. The free induction decay after the pulse was digitized and the response amplitude I was noted, and compared to the amplitude I_0 for long τ. Semilogarithmic plots of I_0-I against τ yielded straight lines, indicating a single relaxation time T_1.

Most of our T_1 measurements were made from about 220 K down to 2 or 3 degrees above the ferroelectric or antiferroelectric transition temperature, which ranged from 153 K at 1 bar to 123 K at 3.6 kbar. These measurements were made at five hydrostatic pressures, namely 1 bar and 1.5, 3.0, 3.3, and 3.6 kbar. The paraelectric-ferroelectric-antiferroelectric triple point occurs at 3.3 kbar and 124 K, approximately. Therefore, we were able to observe the behavior when approaching both the ferroelectric and antiferroelectric phases as well as when approaching the triple point.

The relaxation time (T_1) vs. temperature (T) results are presented in Figure 1 for the above pressures. In general terms, at each pressure T_1 decreases with temperature in a similar way. At higher temperatures the

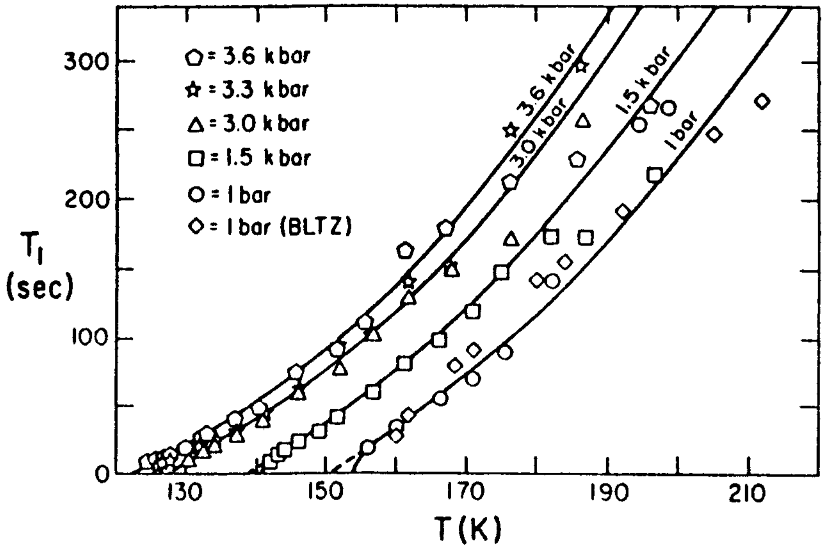

FIGURE 1 Temperature dependence of the critical portion of ^{133}Cs spin-lattice relaxation time T_1 in CsH_2PO_4 for pressures of 1 bar (circles, BLTZ data shown by inverted triangles), 1.5 kbar (squares), 3 kbar (triangles), 3.3 kbar (stars), and 3.6 kbar (pentagons). Predictions of Eqs. (11) and (20) are indicated by solid lines. Dashed line portions correspond to an extrapolation of the 2-d expression of Eq. (14). The line for 3.3 kbar is omitted for clarity.

T_1 behavior corresponds nearly to that expected for proton intrabond fluctuations in a strictly 1-d Ising chain with FE coupling between protons. At lower temperature, T_1 exhibits a Curie-Weiss form extrapolating to zero T_1 at the ordering temperature for the 2-d-coupled hydrogen-bonded planes.

THEORY

The interpretation of these results is made within the framework of a theory presented by Blinc, Lozar, Topic, and Zumer (abbreviated here as BLTZ).[15] In this theory the strongest interaction, which is the FE coupling in the ordering chains, is treated exactly. The intermediate-strength interaction between such chains within a hydrogen-bonded plane, and the weakest interaction which occurs between such planes, are treated in the mean-field approximation. We correct some misprints in the BLTZ equations and expand their mean-field analysis of the two weaker interactions, which were performed numerically in BLTZ without separating the effects of these two interactions. This analysis demonstrates that the intermediate interaction causes Curie-Weiss-type dependence of T_1 on $T-T_{c2-d}$, while the weakest interaction gives a dependence varying as $(T-T_c)^{1/2}$ in a narrow temperature range just above T_c.

The BLTZ theory has its roots in the wave-vector-dependent susceptibility for the pure 1-d Ising model developed by Suzuki and Kubo,[18] and the static behavior including the phase transition for a system of weakly coupled 1-d chains studied by Scalapino et al.[19] Zumer[20] combined those two approaches to obtain the $\hat{q}$-dependent susceptibility for the weakly coupled system. BLTZ introduced anisotropy into the interchain interactions and calculated quadrupolar spin-lattice relaxation from the ac dielectric susceptibility using the fluctuation-dissipation theorem. In each case, the intrachain interactions were treated exactly and interchain interactions in the mean field approximation.

The BLTZ theory begins with the assumption that the dominant mechanism for spin-lattice relaxation is the interaction of the nuclear electric quadrupole moment with the fluctuating electric field gradient (efg). This assumption appears to be correct over the temperature ranges covered in our experiments. It is further assumed that the quadrupolar interaction is small compared to the Zeeman interaction of the nuclear magnetic dipole moment with the applied magnetic field H_0. Under these assumptions the inverse spin-lattice relaxation time $1/T_1$ for quadrupolar relaxation of nuclei having spin I (I=7/2 for ^{133}Cs) and quadrupole moment Q is given by

$$\frac{1}{T_1}=\frac{e^4Q^2}{40\hbar^2}\frac{2I+3}{I^2(2I-1)}[J^{(1)}(\omega)+4J^{(2)}(2\omega)]\,, \tag{1}$$

in which the spectral density of the autocorrelation function for the fluctuating efg tensor at the ^{133}Cs site is

$$J^{(k)}(\omega)=\int_{-\infty}^{\infty}\langle V^{(k)}(0)V^{(-k)}(t)\rangle \exp(ik\omega t)dt\ . \tag{2}$$

Here the following notation is used in terms of efg components for a system with the z axis along the applied magnetic field H_0

$$V^{(\pm1)}=V_{xz}\pm iV_{yz},\quad V^{(\pm2)}=\tfrac{1}{2}(V_{xx}-V_{yy})\pm iV_{xy}. \tag{3}$$

In Eqs. (1) and (2), the average efg components contribute nothing to the relaxation, so in Eq. (3) we need only the magnitudes of the fluctuations about these averages. These fluctuations result mostly from atomic displacements within a "source radius" of perhaps 5 Å around the Cs nucleus, caused by proton motions in the disordered chains. Each Cs nucleus is within 5 Å of two disordered H-bonded chains belonging to the same H-bonded plane. We assume that the fluctuation correlation length is greater than the source radius, so the efg at a given Cs nucleus at a given instant approximates its static value inside a FE domain. (From the neutron scattering study of Frazer et al.,[21] this assumption is good over a wide temperature range for the intrachain $\underline{b}$ correlations, and from their Figure 6 may be good to 5 or 10 K above T_C for the $\underline{c}$ correlations between chains in the same H-bonded plane.) Accordingly, we choose for the magnitude of the fluctuations half of the difference between the two efg's determined by Kanda and Fujimara[14] for the two possible FE phase domains. This assumption differs somewhat from that of BLTZ, who used the difference between the efg for one FE domain type and the efg for the PE phase.

In the BLTZ development, Eq. (2) is then Fourier-transformed, the random phase approximation is made, and the shortness of the efg source radius is invoked so that $V_q^{(i)}=V_0^{(i)}$, which leads to

$$\begin{aligned} J^{(1)}(\omega)&=(V_{xz}^2+V_{yz}^2)j(\omega)\ , \\ J^{(2)}(2\omega)&=[\tfrac{1}{4}(V_{xx}-V_{yy'})^2+V_{xy'}^2]j(2\omega)\ . \end{aligned} \qquad (4)$$

Here $j(\omega)$ is a sum over Fourier components, which following Topic et al.[12] is related to the imaginary part of the pseudo-one-dimensional Ising model wavenumber-dependent susceptibility:

$$j(\omega)=\frac{1}{N}\sum_q j_q(\omega)=\frac{2T}{CN}\sum_q \chi''(\omega,q)\ . \qquad (5)$$

Here C is the Curie-Weiss constant for the dielectric behavior, N is the number of mobile protons, q is the wavevector, and a factor of 2 missing in BLTZ is inserted.

The BLTZ analysis for the susceptibility follows that of Zumer,[20] ignoring tunneling which seems to have no major effect, treating intrachain interactions exactly via the one-dimensional Ising model, and treating the much weaker interchain interactions in mean field. The Hamiltonian for the jth chain with z (z=4 for CDP) adjacent chains then is

$$H_j=-\sum_i \left[J_b p_{i+1,j} p_{i,j}+\sum_{m=1}^{z} J_{p,m}\langle p_{i,j+m}\rangle p_{i,j}\right], \tag{6}$$

where J_b is the $J_{||}$ interaction for nearest proton neighbors in the disordered chains running along b, J_p is the $J_{\perp}$ interaction which is $(J_a+J_c)/2$ (nearly $J_c/2$ because $J_a \ll J_c$),[21] and the p's are pseudospins ±1 representing disordered proton positions.

From the susceptibility expression developed by BLTZ they obtain two expressions for $j(\omega)$ in their Eq. (26). The first is correct but the second should be

$$\begin{aligned} j(\omega)=&\frac{2}{\pi^3}\tau_0 F\sin\gamma \\ &\times\int_0^{\pi}\int_0^{\pi}\int_0^{\pi}\frac{dx\,dy\,dz}{[D(x,y)-E\cos z]^2+(\omega\tau_0)^2}, \end{aligned} \tag{7}$$

where D, E and F are defined below. We also define three new variables, a, b and f, which are more convenient for performing the integrations of Eq. (7).

$$\begin{aligned} D(x,y)&=1-z'\beta J_p F(1+\alpha)^{-1}(\cos x+\alpha\cos y) \\ &=1-b(\cos x+\alpha\cos y), \end{aligned} \tag{8}$$

$$\alpha=J_a/J_c\ll 1,$$

$$E = \tanh(2\beta J_b) = 1 - a, \quad a = 1 - \tanh(2\beta J_b)\ , \tag{9}$$

$$F = 2\exp(-2\beta J_b), \quad f = \tau_0 F \sin\gamma\ ,$$

$$\beta = 1/kT, \quad T > T_C\ , \tag{10}$$

and γ is the monoclinic angle of 72.3°.

Carrying out integrations over z, x and y with some simplifying assumptions produces the general expression for $j(\omega)$

$$j(\omega) \simeq \frac{4fI[2b/(a+b)]}{\pi(2-a)^{3/2}[(a+b)(a-b+b\alpha)(a-b-b\alpha)]^{1/2}}\ . \tag{11}$$

This expression is valid over the entire temperature range above T_C within the approximations listed above. We now examine its predictions in four temperature regimes above T_C. These are the noncritical regime above room temperature, the 1-d regime below room temperature but well above T_C, the 2-d region extending to within a few degrees of T_C, and the 3-d region in the last degree or two above T_C. We note that Morosov and Sigov[22] discussed the importance of the 1-d, 2-d, and 3-d correlation regions for CsH_2PO_4 also, but in connection with dielectric permittivity.

In the noncritical regime the temperature is too high to allow correlations even of the protons in H-bonded chains running along <u>b</u>. In this regime, $1 \gg (1-a) \gg b \gg \alpha b$, the argument of I approaches 0 so I approaches $\pi/2$, and Eq. (11) becomes

$$j(\omega)_{hi-T} \simeq 4\tau_0 \sin\gamma\ . \tag{12}$$

Here $kT \gg J_b \gg J_p \gg J_a$, and there is no significant temperature dependence predicted for $j(\omega)$ or for the spin-lattice relaxation rate T_1.

In the 1-d regime we have 1>>a>>b>> b, which yields

$$j(\omega)_{1D} \simeq \frac{2f}{(2a)^{3/2}} \simeq \tfrac{1}{2}\tau_0 \sin\gamma \exp(4\beta J_b)\ . \tag{13}$$

Physically this implies that relaxation is governed by the Boltzmann factor for populations of (HPO_4,H_3PO_4) defect <u>pairs</u>. The effective diffusion of these defects by means of b-chain proton intrabond transfer causes the relaxation. As the temperature drops, the correlation time becomes longer because the defect population drops, and in the rapid-motion regime this increases the relaxation rate which is proportional to $j(\omega)$. The relaxation rate according to Eq. (13) would become infinite at absolute zero (the ordering temperature for the 1-d Ising model), if Eq. (13) were valid down to that temperature.

In the 2-d regime the inequality order becomes $1 \gg a \gg (a-b) \gg \alpha b$, so the argument of I, and I itself, approach 1 because a+b~2b. Then $j(\omega)$ becomes

$$j(\omega)_{2D} \simeq \frac{f}{\pi b^{1/2}(a-b)}\ , \tag{14}$$

where the critical behavior is in the $(a-b)^{-1}$ factor which can be expanded to give the temperature dependence $(T-T_{c2\text{-}d})^{-1}$. The Curie-Weiss temperature $T_{c2\text{-}d}$ for this 2-d regime is found from the implicit relation

$$2J_b/kT_{C2D} = -\ln[z'J_p/(1+a)kT_{C2D}]\ . \tag{15}$$

This regime is recognized in the data by a straight portion of the T_1 <u>vs</u>. T plot.

Before the temperature drops to $T_{c2\text{-}d}$ the system goes over into the 3-d regime characterized by $1 \gg a \gg (a-b-b) \gg (a-b-\alpha b)$. Then in addition to the approximations made in the 2-d regime, we can also set $a-b+\alpha b \sim 2\alpha b$ and we get

$$j(\omega) \simeq \frac{f}{\pi b[2a(a-b-ab)]^{1/2}} \quad (16)$$

The last factor when expanded gives critical temperature dependence $(T-T_C)^{-1/2}$, where T_C is the actual transition temperature which is slightly above T_{C2-d} and is given by the implicit relation

$$2J_b/kT_C = -\ln(z'J_p/kT_C) \,. \quad (17)$$

Because much of our T_1 data is in crossover regions between the above regimes, we use the general expression in Eq. (11) for $j(\omega)$. Since we are in the fast-motion regime, $j(\omega)$ actually has no dependence on frequency ω, so $j(2\omega)=j(\omega)$ in Eq. (4). Then the spectral density factor in Eq. (1) becomes

$$\begin{aligned}&[J^{(1)}(\omega)+4J^{(2)}(2\omega)] \\ &\qquad = [V_{xz}^2+V_{yz}^2+(V_{xx}-V_{yy})^2+4V_{xy}^2]j(\omega) \,. \end{aligned} \quad (18)$$

According to Kanda and Fujimura,[14] the only efg tensor components at the ^{133}Cs site which change upon domain reversal in the FE phase of CDP are

$$\begin{aligned} eQV_{x'y'}/h &= eQV_{yz}/h = \pm 7.6 \text{ kHz} \,, \\ eQV_{y'z'}/h &= eQV_{xz}/h = \pm 12.5 \text{ kHz} \,, \end{aligned} \quad (19)$$

where the primed coordinates represent crystal axes and the unprimed coordinates represent laboratory system axes for our measurements in which the static magnetic field H_0 was along z, corresponding to the crystal y' or b axis.

From the discussion following Eq. (3), the above numbers divided by eQ/h are squared to provide V_{xz}^2 and

V_{yz}^2 in Eq. (18), and the other V_{ij} in that equation vanish. Then, using I=7/2 for ^{133}Cs, Eq. (1) becomes

$$1/T_1 = 2.87 \times 10^7 s^{-2} j(\omega) . \qquad (20)$$

This is the final expression of T_1 in terms of Eq. (11).

DATA ANALYSIS

There are four fitting parameters which could be used in comparing predictions of Eqs. (11) and (20) to T_1 results. These are the inverse attempt frequency τ_0 which is assumed independent of temperature and pressure, and the three interaction energies J_a, J_b, and J_c which are assumed to have linear dependence on hydrostatic pressure but to be independent of temperature. The fitting process requires Eq. (20) for $1/T_1$, Eq. (11) for $j(\omega)$, the definitions in Eqs. (8) through (10), and the relation $J_p=(J_a+J_c)/2$.

Unfortunately we did not obtain T_1 data close enough to T_c to observe the 3-d regime where T_1 is proportional to $(T-T_c)^{1/2}$. Only in this regime would the relaxation results be sensitive to α , or equivalently to J_a. Accordingly, we use only the τ_0, J_b, and J_c parameters to fit the T_1 data. To find J_a and its pressure dependence, we use the method of Blinc and Sa Barreto[23] which relies on the slopes dT_c/dp of transition temperature vs. pressure both above and below the triple point pressure. Our method differs from theirs only in that we use the pressure dependences of both J_b and J_c determined from the T_1 fit, whereas they implicitly assume no pressure dependence for J_c.

The fit of T_1 for the parameters and their pressure dependences given below is shown in Figure 1. The straight 2-d regime and curved 1-d regime portions of the curves are clearly seen.

The parameters and their pressure dependences found from the T_1 fit and from the T_c vs. pressure curve are

$\tau_0=2.9\times10^{-12}$ s

$J_b/k=225.7$ K - (6.85 K/kbar)p

$J_c/k=3.80$ K - (0.428 K/kbar)p

$J_a/k=0.305$ K - (0.0924 K/kbar)p

$J_p/k=2.05$ K - (0.520 K/kbar)p

$J_b/J_p=110$, $J_c/J_a=12.5$,

$T_c=153.9$ K, $T_{c2-d}=150.9$ K, at 1 bar

These parameters are compared in Table I with some J_b, J_p, and τ_0 values obtained by other workers.

The triple point at which the transition changes from FE to AFE occurs at 3.30 kbar and 124.6 K from the above parameters. At this point J_a becomes negative, so that the ferroelectrically ordered hydrogen-bonded planes have AFE instead of FE stacking, yielding overall AFE order.

Although we did not make any T_1 measurements in the 3-d region above T_c, we did look at the NMR spectrum at 152.4 K and atmospheric pressure. This temperature is between the actual T_c and T_{c2-d} which is the temperature at which the 2-d regime T_1 extrapolates to 0. The NMR spectrum was characteristic of the FE rather than the PE phase, indicating indirectly the presence of the 3-d regime with its square-root dependence of T_1 on temperature.

TABLE I Energy parameters and correlation time from various experiments and theories, for CsH_2PO_4 at atmospheric pressure. Note that some entries differ by factors of 2 or 4 from those appearing in the corresponding references, because of differences in definitions of J_b and J_p.

J_b/k, K	J_p/k, K	τ_0, s	Method$^{Ref.}$
225.7	2.05	2.9×10^{-12}	^{133}Cs NMR
234	3.39	1.9×10^{-13}	dielectric[8]
$J_b/J_p=100$		1.9×10^{-13}	^{31}P chem. shift[10]
305	1.8		dielectric[7]
250			thermal expansion[24]
287	1.9		calorimetric[25]
273	3.0	5.7×10^{-14}	hyper-Raman spec.[26]
265.5	3.0		dc dielectric[27]
		6.7×10^{-14}	ac dielectric[28]
300	3		dielectric[29]
278	2.1		calorimetric[30]

DISCUSSION

From the above parameters and their pressure dependences, we can predict that if the linear pressure dependence approximation holds, there will be another triple point at 8.88 kbar and 76.7 K, where J_c should go to 0. Above this pressure, both J_a and J_c would be negative, so that looking along the b axis the chains would order in a checkerboard AFE pattern rather than a sheet pattern. So far, the existence of this second triple point has not been investigated experimentally.

The phase diagram predicted by this linear pressure dependence assumption appears in Figure 2. The pressure dependence of T_c is predicted to change sign at this higher triple point, so it should be possible to observe it easily by dielectric means. This Figure ends below the pressure of 32.9 kbar where the linear extrapolation of J_b goes to 0, because that is too long an extrapolation to be taken seriously.

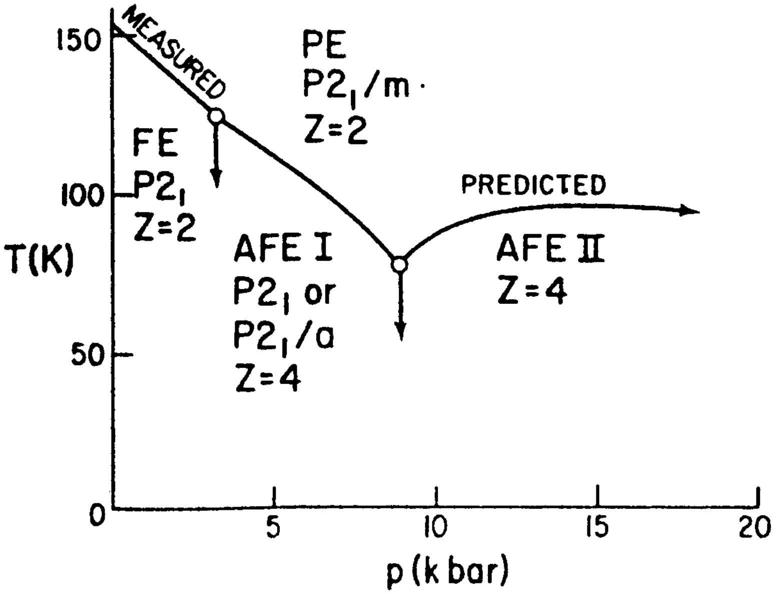

FIGURE 4 Known and proposed phase diagram for CsH_2PO_4 at low temperature and moderate hydrostatic pressure, showing monoclinic space groups and number Z of molecules per unit cell. Known phase boundaries are solid lines, proposed boundaries are dashed lines. Phases shown are paraelectric (PE), ferroelectric (FE), planar antiferroelectric (AFE I), and proposed checkerboard antiferroelectric (AFE II).

We do not attempt a critical evaluation of the various parameters presented in Table I. We simply note that our 1 bar values for J_b and J_p are near the ranges found by other workers. Also, the ratio J_c/J_a=12.5 at 1 bar is near the value of 10 found by other workers.[15] Our large value for τ_0 is troublesome. Perhaps the efg fluctuations are considerably larger than those occurring when a ferroelectric domain reverses, in which case a smaller and more reasonable value of τ_0 would give the correct T_1 magnitudes.

In conclusion, our results are in good accord with the BLTZ theory, and provide a more complete test of that theory than was possible based on the atmospheric pressure data of that paper. We have extended the BLTZ theory to show the specific behaviors associated with the 1-d, 2-d, and 3-d fluctuation regions. Based on these results a second triple point where the PE phase meets both planar and checkerboard AFE phases is predicted. We hope that someone will undertake an experimental search for this triple point.

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