



A study of the two-halide superexchange interaction in the compounds $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{CuX}$ for $n=2, 3, 4$, and 5 and $\text{X}=\text{Cl}_4$ and Cl_2Br_2
by Leslie Orin Snively

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

Results of magnetic susceptibility and magnetization measurements on the eclipsed layered compounds $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{CuX}$ for $n=2$ and 4 with $\text{X}=\text{Cl}_4$ and for $n=2$ with $\text{X}=\text{Cl}_2\text{Br}_2$ are presented. The intralayer and interlayer superexchange values for the three compounds were found to be $J/k=23.0\text{K}+0.5\text{K}$, $J'/k=-13.7\text{K}+0.5\text{K}$; $J/k=13.0\text{K}+0.2\text{K}$, $J'/k=1.5\text{K}+0.2\text{K}$; and $J/k=15.0\text{K}+1.0\text{K}$, $J'/k=31.0\text{K}+1.0\text{K}$ respectively. These values along with those for the $n=3$ and 5 members of the above Cl_4 series were used to obtain the first direct measurement of the two-halide superexchange interaction in a transition metal. Strong evidence is presented that the halide-halide overlap is the primary factor in determining the strength of the superexchange interaction through a two-halide bridge rather than the cation-cation separation as has previously been suggested. A Rayleigh-Schrodinger perturbation calculation is also presented on a four-center, four-electron cluster which represents a linear two-halide superexchange bridge. The results of the calculation support the experimental findings that the critical parameter involved in the two-halide superexchange is the interaction between the intervening diamagnetic anions.

A Study of the Two-Halide Superexchange Interaction in the Compounds

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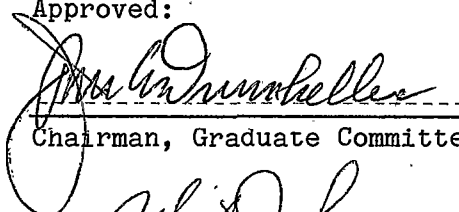
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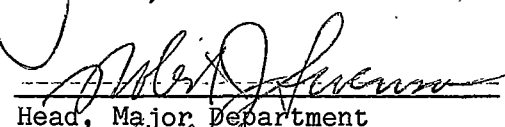
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ABSTRACT

Results of magnetic susceptibility and magnetization measurements on the eclipsed layered compounds $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3) \text{CuX}$ for $n=2$ and 4 with $\text{X}=\text{Cl}_4$ and for $n=2$ with $\text{X}=\text{Cl}_2\text{Br}_2$ are presented. The intralayer and interlayer superexchange values for the three compounds were found to be $J/k=23.0\text{K}\pm 0.5\text{K}$, $J'/k=-13.7\text{K}\pm 0.5\text{K}$; $J/k=13.0\text{K}\pm 0.2\text{K}$, $J'/k=-1.5\text{K}\pm 0.2\text{K}$; and $J/k=15.0\text{K}\pm 1.0\text{K}$, $J'/k=-31.0\text{K}\pm 1.0\text{K}$ respectively. These values along with those for the $n=3$ and 5 members of the above Cl_4 series were used to obtain the first direct measurement of the two-halide superexchange interaction in a transition metal. Strong evidence is presented that the halide-halide overlap is the primary factor in determining the strength of the superexchange interaction through a two-halide bridge rather than the cation-cation separation as has previously been suggested. A Rayleigh-Schrodinger perturbation calculation is also presented on a four-center, four-electron cluster which represents a linear two-halide superexchange bridge. The results of the calculation support the experimental findings that the critical parameter involved in the two-halide superexchange is the interaction between the intervening diamagnetic anions.

CHAPTER I. INTRODUCTION

A. Overview of the Two-Halide Superexchange Interaction

There has been very little experimental or theoretical work on the problem of superexchange through a two-halide bridge. This has been caused by two separate but equally arresting reasons. From an experimental standpoint, the compounds that have a simple crystal structure which would allow an investigation of the two-halide exchange have only recently been synthesized. Theoretically, as is well known, the problem of an a priori superexchange calculation is sufficiently difficult with only a single superexchange anion involved so that extending any theory to a second intervening anion is to some degree 'putting the cart before the horse.' The research reported in this thesis provides a first look into both untrodden areas with the primary emphasis placed on learning the phenomenology of the two-halide interaction by studying the experimental results.

Among the many experimental techniques available (for example, epr, magnetic specific heat, magnetic susceptibility, and linear magnetic birefringence) which would allow a determination of the exchange strength, it was decided that a magnetization and susceptibility investigation would be the most useful. This choice was partly dependent on the equipment available. But to a greater extent, the choice was dic-

tated because the susceptibility data as a function of temperature and applied field provide a clearer and more detailed look at the exchange interaction than any of the other methods.

Prior to the start of the research it was thought that 1-2 ethanediammonium tetrachlorocuprate (EDA) would be similar to the already well studied MA_2 series $(C_{n-2n+1}H_{2n+1}NH_3)_2 MX_4$ where M is Cu^{2+} or Mn^{2+} and X could be Cl^- or Br^- with $n=1,2,\dots,10$. These compounds were found to be nearly 2d ferromagnets and were of interest for that reason. More will be said about the important work done on that series later. It soon became clear, however, that EDA was not behaving as the 2d ferromagnet that it was thought to be.

Analysis of the high temperature data by high temperature series expansions indicated the surprising result that EDA was in fact a nearly 3d antiferromagnet. A review of the crystal structure suggested that the larger interplanar exchange might not be unexpected because of the linear two-halide bridge that exists in EDA which does not occur in the MA_2 series. It became clear that the entire EDA series might offer the unique opportunity to investigate this heretofore poorly studied type of superexchange path. It was thought that changing the interlayer superexchange anion would provide still more information about the behaviour of the magnetic interaction so crystals of the mixed halide compound, EDA $CuCl_2Br_2$ were obtained and studied.

A number of important conclusions were drawn by us from this inves-

tigation. Primarily, the two-halide exchange appears to depend critically on the overlap of the two anions rather than the distance between the metal cations as has been previously suggested. Secondly, it was possible to attempt a first principles calculation of the two-halide superexchange with some hope of success since there was now available for comparison the first experimental evidence of an appropriate system.

Before continuing with the details of the experiments which lead to the above conclusions, the history of the 2d studies that preceded this work will be outlined. Following that a brief review of some of the history associated with the superexchange interaction will be given along with an introductory discussion of the Heisenberg Hamiltonian and its place in the study of the magnetic behavior of EDA.

B. Review of Previous Lower Dimensional Experiments

It will first be helpful to define the word dimensionality because in common usage it has many different meanings. In this thesis it will typically refer to the lattice or the spatial dimensionality of an interaction or of a compound and it will be denoted by a lower case d , i.e., an exchange interaction which takes place primarily between magnetic ions along a chain would be called 1d exchange. A capital D will be used to refer to the model dimensionality. (This kind of dimensionality is

called the spin dimensionality by some authors.) The model refers to the way in which it is possible for the spins to couple in an interaction. For example, a 1D interaction, often called an Ising interaction, means that only the z axes of the spins couple along a direction usually defined by the crystal environment in which they sit. A Heisenberg interaction is represented by the notation 3D which indicates that there is no restriction in the ways the spins can couple to each other. One further dimensionality that is sometimes referred to is that of the spin space. This just denotes the total spin of the interacting electrons with the two limits being $1/2$ for a completely quantum-like system and ∞ for the classical system. Since this thesis reports only on the Cu^{2+} magnetic cation, the spin space dimensionality will be taken as $1/2$ for what follows.

Much of the work done on lower dimensional transition metal ions in the past 12 years has occurred because chemists have learned to make them and because the physics of the interactions is to a large extent easier to understand than for those with higher dimensionality. Further, the lower-d models are the only ones which have been solved exactly. The excellent tour de force by de Jongh and Miedema⁽¹⁾ reviews the experimental and theoretical studies of 1d, 2d and 3d systems primarily of the transition metal cations and also details their own significant contributions to this study. More recently Carlin and van Duijneveldt⁽²⁾ have extended the review of de Jongh and Miedema to include recent experi-

ments on these materials. In particular the extensive and thorough magnetic susceptibility and specific heat investigations of de Jongh and his associates has led to a rather complete understanding of the 2d interactions in the layered MA_2 series of compounds. This series was of great interest to us because of its structural similarities to the EDA series. It was originally thought that the MA_2 series would provide a system in which the 2d coupling could be 'tuned' to any desired level by changing the interlayer spacing by inserting more CH_2 's into the interlayer organic chains. It was found however, that the $n=1$ member of the series was already an excellent 2d ferromagnet. Table I illustrates this by showing the values of the exchange for the series. As will be discussed later, in retrospect this small interlayer exchange is not too surprising.

One of the original motivations behind this work was to investigate the existence of the Stanley-Kaplan⁽³⁾ transition. Stanley and Kaplan showed that while no spontaneous magnetization could occur at nonzero temperature for a 2d Heisenberg system, a result proven by Mermin and Wagner⁽⁴⁾, the susceptibility could diverge at a finite temperature. Using the results of the investigation of the MA_2 series de Jongh and Miedema were able to argue convincingly⁽⁵⁾ that such a phase does exist.

As a result of their study of the 2d systems, de Jongh and Miedema suggested that nothing of significance was left to be learned from a search for new 2d ferromagnetic systems⁽⁶⁾. They concluded that all

TABLE I. Various magnetic and structural values for some of the MA_2 series of compounds^(a). T_c indicates the transition temperature, J/k and J'/J give the in-plane exchange and the ratio of the out-of-plane to the in-plane exchange, and d_{in} and d_{out} are the in- and out-of-plane distances between nearest-neighbor Cu^{2+} ions respectively. Distances are in units of angstroms and the exchange energies are in units of degrees Kelvin.

$(C_nH_{2n+1}NH_3)_2CuCl_4$	T_c	J/k	J'/J	d_{in}	d_{out}
n=1	8.91	19.2	$+5.5 \times 10^{-5}$	5.25	18.3
n=2	10.25	18.6	-8×10^{-4}	5.24	21.2
n=3	7.65	16.0	-6×10^{-5}	5.30	24.1
n=10	7.91	17.9	$+3 \times 10^{-6}$	5.24	50.9

a. L. J. de Jongh, W. D. van Amstel, and A. R. Miedema, J. Phys. (Paris) Suppl. 32, 880 (1971).

remaining fundamental questions could be answered by studying the results of the already known compounds. However, one question which had not been adequately addressed is that of a magnetic dimensionality crossover from 1d to 2d or from 2d to 3d at temperatures not near the transition temperature. (The lattice dimensionality crossovers that occur simply because every system which has long range order must eventually become 3d were discussed at length by de Jongh⁽⁷⁾.) Fortunately, chemists had already synthesized a compound similar to those of the MA_2 series, EDA or $(NH_3(CH_2)_2NH_3) CuCl_4$. Because the structure of the layers in the two series was identical and because the importance of the slight difference in the interlayer orientation had not yet become apparent, this compound was not immediately studied for its magnetic properties since it was thought to be only a repeat of the MA_2 compounds. However, the crystal structure is different in what is now known to be an extremely crucial way, a way that allows the crossover in magnetic dimensionality to be studied.

Figure 0 shows a diagram of the unit cells of the archetypical structures of the two series. The layers as already mentioned are isomorphic and show the usual 'buckling' of the planes that is common in the layered type compounds. But notice that adjacent layers are shifted by a half a unit cell in two directions in EDA which causes the magnetic ions to lie nearly above one another. This effectively brings the nearest neighbor out-of-plane cations 50% closer since they were two

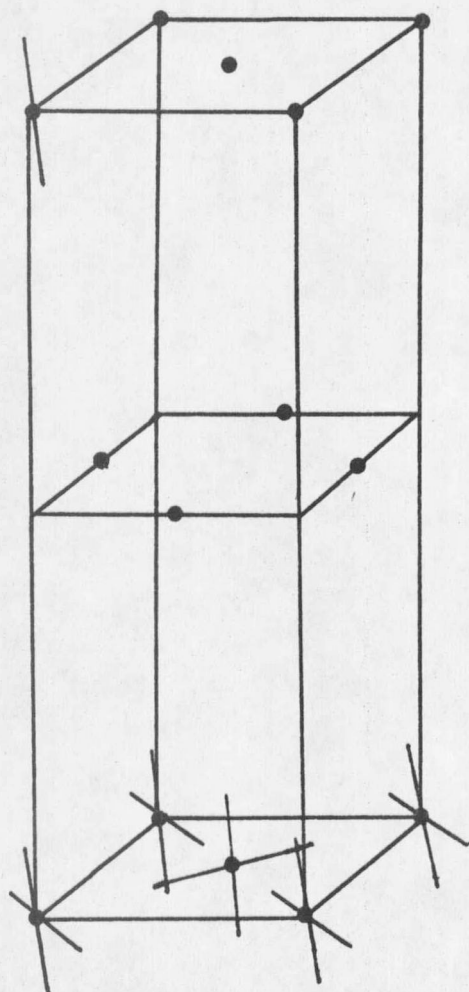
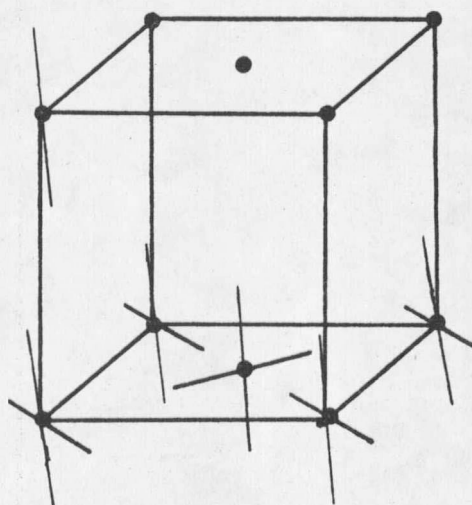

 MA_2

 EDA

FIGURE 0. Diagram of the unit cells of the EDA $CuCl_4$ series compounds and the $MA_2 CuCl_4$ series. The lines through the Cu^{2+} ions indicate the bond directions of the Cl^- anions. The drawing is approximately to scale.

layers apart in the MA_2 compound. As was known 6 or 7 years ago shortly after the crystal structure of EDA was found⁽⁸⁾, that decrease in distance is by itself not sufficient to increase the interlayer exchange appreciably. Again as will be shown in this thesis it is the overlap of the out-of-plane anions that is critical to the increased exchange in that direction.

C. History and Development of Superexchange

Prior to the introduction of quantum mechanics the theoretical basis of magnetism in solids was at least as much a mystery to physicists as the behavior of lodestone was to earlier students of nature. There was no satisfactory way to reconcile what was physically known about solids and their structure and the ability of classical physics to predict magnetic phenomena in them. It took Heisenberg's great insight⁽⁹⁾ in 1926 to point out that the Pauli principle coupled with the ordinary Coulomb interaction could lead to a very strong tendency for spins to align, thus giving rise to ferromagnetic behavior. Dirac soon thereafter expanded that work to define the 'exchange' Hamiltonian⁽¹⁰⁾

$$H_{ex} = - \sum_{i,j} J_{ij} s_i \cdot s_j \quad (1.1)$$

which has since proved to be an extremely useful tool for describing the magnetic interactions of isolated magnetic ions. However, this expres-

sion gives the misleading impression that exchange is dependent upon the properties of spin, which is wholly in error. Dirac only showed that the exchange interaction could be conveniently represented with Eqn. 1.1. The physics of the interaction is contained in the coulombic exchange integral, J_{ab} , which for two electrons in orthogonal orbitals may be written as

$$J_{ab} = \int \psi_a^*(1) \psi_b^*(2) \left| \frac{e^2}{r_1 - r_2} \right| \psi_a(2) \psi_b(1) d\tau_1 d\tau_2 \quad (1.2)$$

The distinction between J_{ij} and J_{ab} is extremely important and is often confused. J_{ij} in general is composed of a sum and difference of integrals, one of which is J_{ab} . This will be made more clear in Chapter IV where a discussion of simple exchange theory is presented.

Not surprisingly, Eqn. 1.1 has been used extensively to predict the behavior of many magnetic systems. Typically a theory is developed using Eqn. 1.1 as part of the Hamiltonian ($\mathbb{H}$) with the exchange constant, J_{ij} , left as an adjustable parameter. In many cases this has led to reasonably consistent values for J_{ij} when two different theories are compared, for example, magnetic susceptibility expansions and epr linewidth calculations. This method has the fault that J_{ij} is found empirically and is not determined from the interaction of the wavefunctions. On the other hand, because of the obvious complications that arise from trying to do an a priori calculation of J_{ij} using real wavefunctions, it is not surprising that there has been very little success in the past following this route. Recently though, as will be discussed in Chapter IV, some

encouraging progress has been made starting from a first principles calculation.

Soon after the idea of exchange between two magnetic ions was proposed and developed it became obvious that many compounds showed magnetic interactions although the magnetic ions in those compounds were much too far apart to interact in the way suggested by Eqn. 1.2. A solution to this anomaly was first offered by Kramers⁽¹¹⁾ in 1934. His hypothesis was that the intervening diamagnetic ligands which occurred in those compounds which had the inexplicable exchange were in some way enhancing the overlap of the magnetic cation wavefunctions. This phenomenon was called superexchange because of the relatively large distances over which it acted. Bequerel, de Hass, and van den Handel⁽¹²⁾ were the first to show experimental evidence for the existence of this 'superexchange' interaction. Twelve years later in 1946 De Klerk⁽¹³⁾ using magnetic specific heat measurements on copper potassium sulfate obtained further results which suggested a superexchange coupling. He showed that the specific heat due to isolated Cu^{2+} ions was too large to involve the usual exchange interaction. Finally, the existence of the superexchange interaction was shown conclusively by Shull⁽¹⁴⁾ and coworkers by use of low temperature neutron diffraction studies on non-conducting solids which showed magnetic ordering of spins on different paramagnetic ions separated by a diamagnetic ligand. The study of magnetic ordering caused by the superexchange interaction has since become a widespread area of

interest. A brief review of the methods used to attempt calculations of it will be presented below.

It should be pointed out that any theory involving superexchange is only applicable to systems in which the magnetic ions are isolated or dilute. Typically, these compounds are electrical insulators or semiconductors rather than conductors. The primary requirement determining this isolation is that the zeroth-order wavefunctions describing the exchange properties may be correctly chosen as those of the non-interacting magnetic ions of the compound. This is referred to as the localized electron approximation and has been shown to be valid for the systems of interest in this thesis. For a more extensive discussion of this criterion the reader is referred to the excellent article of Anderson⁽¹⁵⁾.

Before proceeding a second caveat should be mentioned with regard to the correctness of using a Heisenberg Hamiltonian when discussing transition metal compounds. For almost all copper systems the use of Eqn. 1.1 is justified and it appears to accurately represent the phenomenological interaction. However, that equation is not sufficient to understand the behavior of other iron series ions. In particular, for cobalt and nickel additional terms must be included in the Hamiltonian to appropriately model the magnetic interaction. The interested reader is referred to the detailed discussion of this subject by Wolf⁽¹⁶⁾ for further information.

With those remarks in mind, it is useful to return to the Heisenberg Hamiltonian of Eqn. 1.1 and to rewrite it in a more general fashion:

$$H = - \sum_{i,j} \vec{s}_i \cdot \vec{J}_{ij} \vec{s}_j \quad (1.3)$$

With the exchange in this form a number of traits are immediately apparent. For example, if $\vec{J}$ can be diagonalized by some transformation, ie. if $\vec{J}$ is symmetric, then the anisotropies become obvious. $\vec{J}$ is considered isotropic and 3D if all J_{ii} are equal. For the diagonalized case it is often convenient to further rewrite H as

$$H = -J \sum_{i,j} (a s_i^z s_j^z + b (s_i^x s_j^x + s_i^y s_j^y))$$

where we are assuming only the nearest-neighbor interactions are significant. Notice that for $a=b$ we have the isotropic 3D case which as already mentioned is usually called the Heisenberg model. If $a=1$ and $b=0$ then we obtain the 1D or Ising model: the model with the maximum spin anisotropy. Conversely, if $b=1$ and $a=0$ the model is 2D and it is called X-Y (or planar Heisenberg if the spins are restricted to lie only in the plane).

Finally, if J is not symmetric a further interaction may be important and appropriately enough it is called the antisymmetric exchange. Dzyaloshinsky⁽¹⁷⁾ first suggested that this term could be included in the Hamiltonian and it was later shown by Moriya⁽¹⁸⁾ that it could be explicitly written as $D'(\vec{s}_i \times \vec{s}_j)$. This term is also sometimes called the D-M term or the 'S cross S' interaction. In real compounds it will be

important only if the crystal symmetry is such that a center of inversion does not exist and if there is appreciable spin-orbit coupling.

$$(|D|/J \propto \Delta g/g)$$

CHAPTER II. EQUIPMENT

The equipment used to obtain the data reported in Chapter III may be separated into four distinct components; the magnetometer which measures the magnetic moment of the samples; temperature measurement and control devices; a variable temperature liquid helium cryostat; and the magnet used to apply the variable magnetic field.

A Princeton Applied Research FM-1 vibrating sample magnetometer was used to measure the sample magnetizations as a function of both applied field and temperature. The FM-1 has a rotating head which allows accurate angle dependent measurements to be made on the anisotropic single crystals used. Its theory of operations is based on the technique first suggested by Foner⁽¹⁹⁾. Basically, the sample attached to the end of a long rod is vibrated vertically between a set of coils by an audio coil (speaker) at 82 hertz. The magnetization of the sample induces a voltage in those coils and that voltage is then measured. To give increased sensitivity the induced ac voltage is measured by a phase sensitive detector and the dc voltage output of the detector is then proportional to the magnetization of the sample.

Calibration of the magnetometer was accomplished in two ways. First, a high purity single crystal of MnF_2 weighing 147.8 mg⁽²⁰⁾ was used at room temperature to determine the calibration of the FM-1. This sample was used before each cool-down of the system as it was found that

the calibration changed by a few percent between runs. In calibration runs over many days it was found that the relative accuracy of the magnetometer was on the order of $\pm 3\%$. Absolute accuracy may be a factor of two worse than that.

Second, a powdered sample of 99% pure $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used to check the linearity of the magnetometer from liquid helium temperatures to near 100 K. At higher temperatures the signal was too small to be measured. Since ammonium manganese sulfate is a Curie-law paramagnet until well below 4K, looking at $1/\chi$ vs. T for it is a sensitive test of the linearity of the machine.

The Andonian Dewar used as the variable temperature cryostat was manufactured specifically to couple to the PAR FM-1. A combination of a variable current heater mounted below the sample area and an adjustable gaseous flow rate allows continuous and automatic temperature control from 4.05K up to room temperature. Also, the tail section of the cryostat is designed to fit inside the FM-1 pick-up coils which in turn sit on the pole faces of a magnet. The cryogenic liquid capacity of the dewar is approximately 1.5 liters which allows runs of up to 12 hours per transfer. (The cryostat is a metal design with nitrogen shielding of the inner cryogen well. Both liquid helium and liquid nitrogen may be used as the cryogen. A single vacuum space surrounds both the nitrogen jacket and the inner well. The sample rod of the FM-1 runs through the center of the dewar into a vacuum isolated tail. A small capillary

carries the cryogen to the tail for cooling of the sample as the cold gas 'blows by'.)

Temperature measurement and control were accomplished by two independent systems. The control circuit consists of a Lake Shore Cryotronics Model CSC-400 Cryogenic Capacitance Controller in conjunction with a Lake Shore Cryotronics Model CSC-400 capacitance sensor and a 10 ohm nichrome heater located around the sample area. The controller uses linear, differential, and integral feedback to maintain the temperature (capacitance) at the set point. For the sample sizes we used and with liquid helium as the cryogen, the stability of the temperature could be maintained to better than $\pm 0.005\text{K}$ for temperatures between 4 and 20K and better than $\pm 0.01\text{K}$ between 20 and 40K. Above that temperature stability decreased but was never less than .1K once equilibrium was established. The problem with the higher temperatures is not so much one of control but of the large times necessary for the system to come to equilibrium after a new temperature is set. For low temperatures the time lag was on the order of a few seconds whereas at 100K it was closer to 30 minutes.

The temperature was found by measuring the voltage drop across either a gallium arsenide diode⁽²¹⁾ or a carbon glass resistor⁽²²⁾. The voltage was measured by a Northrop K-5 potentiometer in a circuit in which the polarity could be reversed to average out any thermocouple-like emf's. The K-5 has the capability to measure as little as 0.2 μv .

The excitation current for the sensors was applied by a Lake Shore Cryotronics CCS-EXB Constant Current Source which is stable to $\pm 0.005\%$. The temperature resolution of the gallium arsenide diode was 0.05K in the low T region decreasing to 1K or worse above 100K. It was calibrated in situ against a Scientific Instruments, Inc. Model N2G Calibrated Germanium Resistance thermometer prior to the data runs. Reproducibility was better than 2%. The carbon glass resistor was used for the last three-fourths of the data runs and gave much improved accuracy and reproducibility. It was purchased with calibration as a secondary standard. It has a resolution of better than 0.001K from 4 to 12K, 0.01 from 12 to 30K and no worse than 0.5K at room temperature. Reproducibility also was excellent with the maximum deviation in repeated cyclings to liquid helium temperatures being no more than 0.05K. Besides the outstanding measurement characteristics the primary reason for using a carbon glass resistor (and to a lesser extent the gallium arsenide diode) is that it is not affected by application of large magnetic fields.

A Varian Model 3400 Electromagnet with 8 inch pole faces and a 2.5 inch gap was used to provide a variable field up to 9500 Oe. (For one set of data a Varian 3800 Electromagnet was used to provide a field up to 23,000 Oe thanks to the courtesy of Professor Hugo Schmidt.) The magnet was controlled by a Varian Fielddial Controller and was found to be stable to better than 0.01 Oe. The magnet was calibrated using stan-

dard NMR techniques to better than .1% in the range from 1000 to 5000 Oe. Below and above that a rough calibration using a paramagnetic substance in the magnetometer showed that the calibration was accurate to at least 2% in the remaining range from 100 to 9500 Oe.

A simple schematic diagram of the entire system is shown in Figure 1. The cryostat, magnet and magnetometer are outlined in black while the temperature measurement and control circuits are given in red. The inset is an expanded view of the sample region including the location of the sample, the heater, and the various sensors.

FIGURE 1.

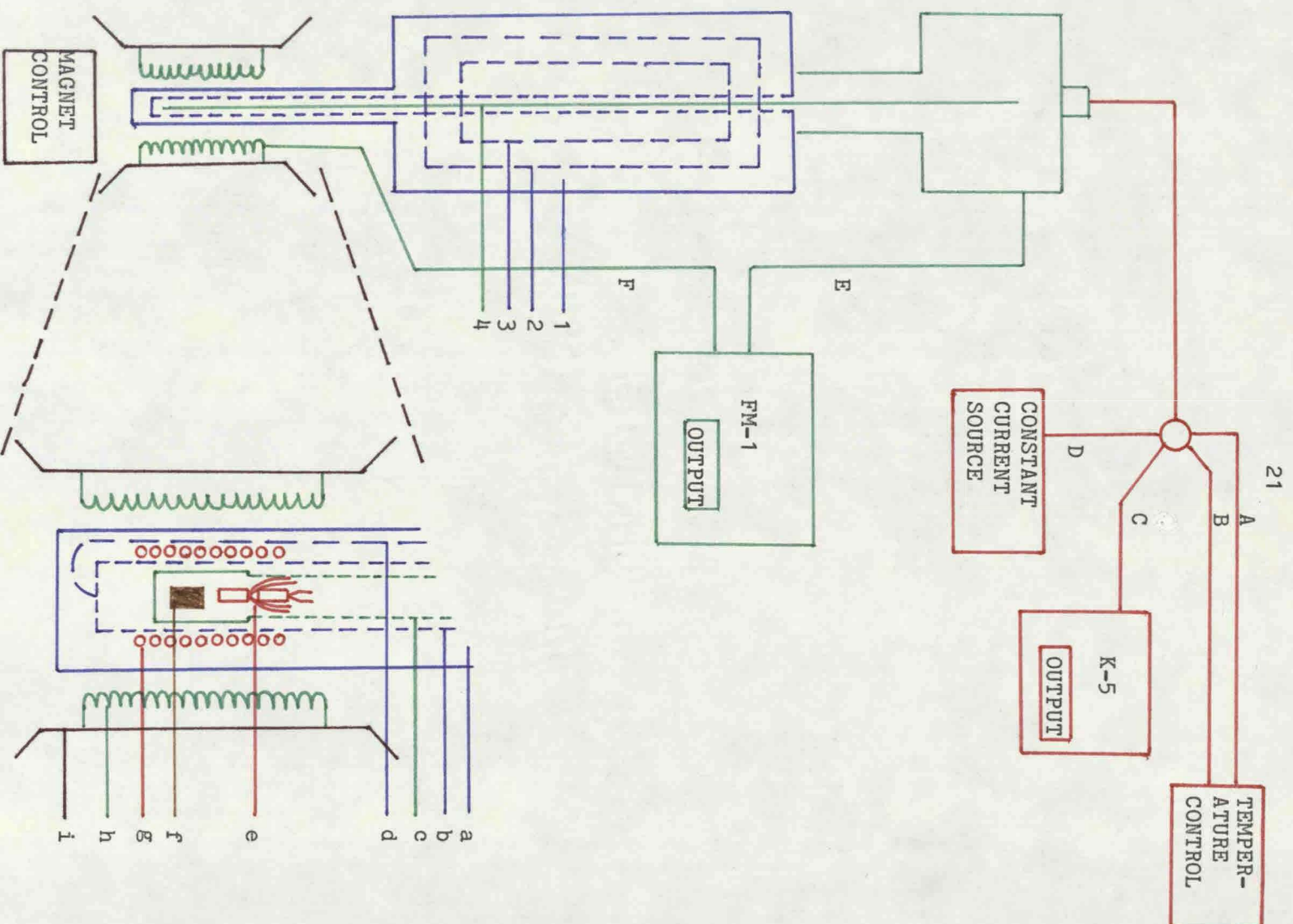
Schematic of the experimental equipment. The four major components are indicated by different colors:

- Black -- magnet**
- Blue -- variable temperature cryostat**
- Green -- vibrating sample magnetometer**
- Red -- temperature measurement and control**

- A -- capacitance sensor leads**
- B -- nichrome heater leads**
- C -- carbon glass resistor leads**
- D -- excitation current leads**
- E -- feedback and drive coil leads**
- F -- pick-up coil leads**

- 1 -- vacuum space**
- 2 -- nitrogen well**
- 3 -- helium reservoir**
- 4 -- sample rod space**

- a -- vacuum space**
- b -- inner tail wall**
- c -- quartz sample rod**
- d -- capillary from helium reservoir**
- e -- capacitance sensor and carbon glass resistor (lower)**
- f -- sample area on plexiglass sample holder**
- g -- nichrome heater windings**
- h -- magnetometer pick-up coils**
- i -- magnet pole face**



CHAPTER III. DATA AND DATA EVALUATION

A. Crystal Structure

The crystal structure of the series of compounds investigated in this thesis is basically that of a metal-halide square planar lattice with planes separated by organic molecules. The length of the organic chains determines the interlayer distance. Table II gives the appropriate cell dimensions and space groups of the members of Cu^{2+} series and also for the Mn^{2+} series for comparison.

Figure 2 shows a diagram of the crystal structure of 1-2 ethanediammonium tetrachlorocuprate (EDA), $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3) \text{CuCl}_4$ with $n=2$ ^(8,23). The structure for the remaining members of the series is very similar. The copper ions sit in sites of distorted octahedral coordination produced by the chlorides. Also, not clearly seen in this diagram but as was shown in Figure 0 the layers are 'puckered' in that each octahedron is tilted with respect to its neighbor along an axis out of the plane. The organic diamine chains are hydrogen bonded to the chlorides in the 'holes' of the square planar network. The interlayer separation is increased by adding CH_2 's to this chain.

As can be seen in Table III, the intralayer distances, d_{in} , remain virtually the same for all members of each magnetic ion's series (The dimensions for the related Mn^{2+} compounds are given for comparison.)

TABLE II. A comparison of the lattice parameters for the EDA CuCl_4 and MnCl_4 series. The distances are in angstroms and the angles in degrees

Compound ($\text{NH}_3(\text{CH}_2)_n\text{NH}_3$) XCl_4		Crystal System	Space Group	a	b	c	γ	Ref.
n=2 (EDA)	X=Cu	Monoclinic	$\text{P2}_1/\text{b}$	8.109	7.158	7.363	92.37	a
				8.10				b
	X=Mn	Monoclinic	$\text{P2}_1/\text{b}$	8.110	7.187	7.366	92.46	c
				8.048	7.319	7.108	91.6(= β)	d
n=3 (PDA)	X=Cu	Orthorhombic	Pnma	8.609	7.130	7.192	92.69	a
	X=Mn	Orthorhombic	Imma	7.200	18.246	7.451	-----	e
					17.88		-----	b
				7.108	18.046	7.466	-----	d
n=4 (BDA)	X=Cu	Monoclinic	$\text{P2}_1/\text{b}$	7.172	19.00	7.361	-----	f
				7.168	7.358	19.004	-----	g
	X=Mn	Monoclinic	$\text{P2}_1/\text{m}$					
				9.094	7.375	7.571	103.1	d
n=5 (Pent DA)	X=Cu	Monoclinic		10.770	7.177	7.307	92.66	f
	X=Mn	Orthorhombic	Imma	11.9	7.152	7.360	23.986	b
							-----	g

* This is the same crystal structure as above, just with different (standard) notation.

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- R. D. Willett and E. F. Riedel, Chem. Phys. **8**, 112 (1975).
- H. Arend, K. Tichý, K. Baberschke, F. Rys, Solid St. Communications **18**, 999 (1976).

FIGURE 2. a). Unit cell of EDA CuCl_4 showing the positions of the ions (except hydrogens). Large circles on the left indicate approximate size of the Cl^- anions. Some of the Cu-Cl bonds are included to help show the 'puckering' of the layers. b). Projection of the structure onto a plane to indicate the assymetric Cu-Cl bond lengths and to show the organic chain locations.

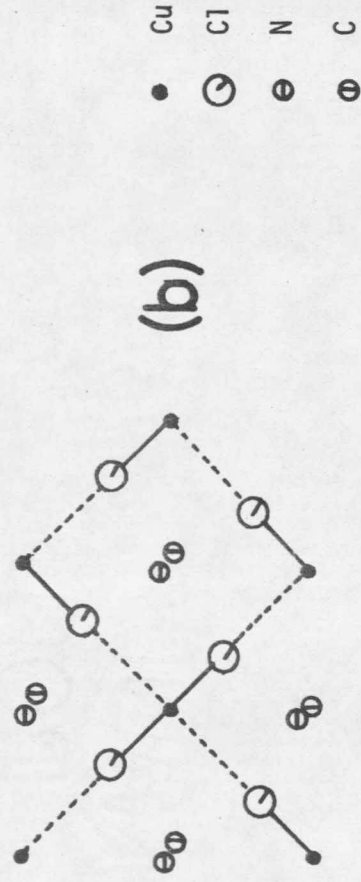
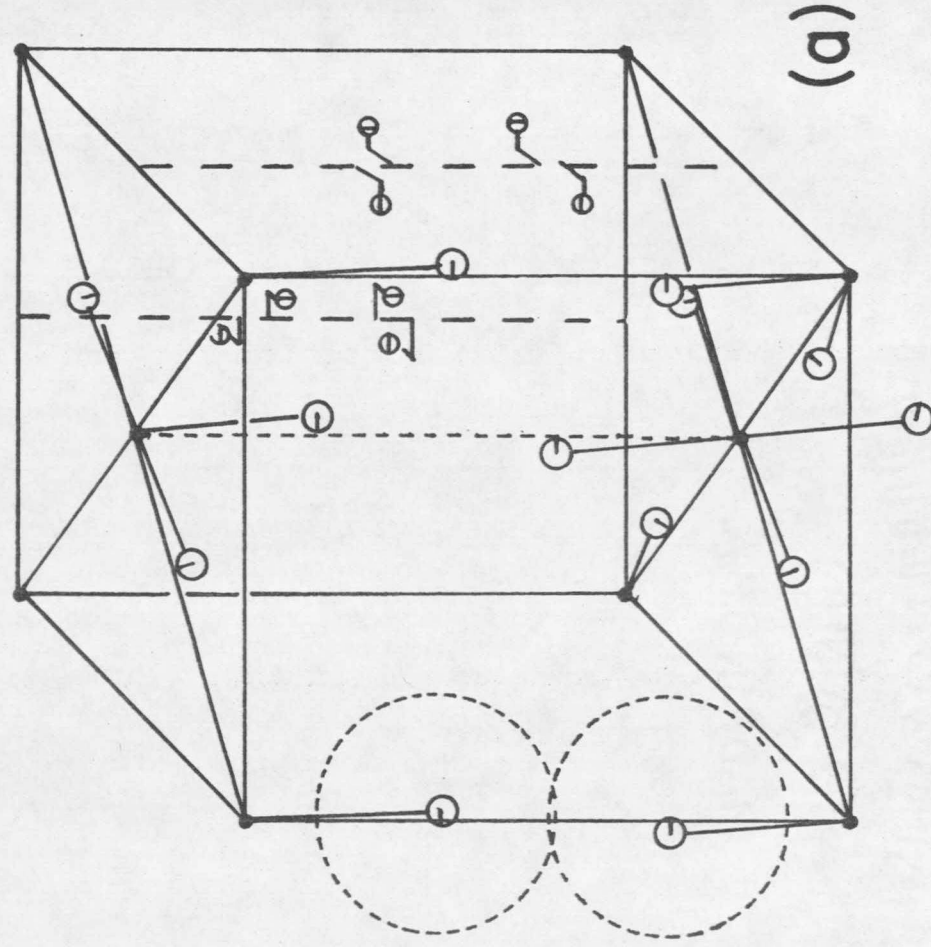


TABLE III. Intralayer, d_{in} , and interlayer, d_{out} , Cu-Cu distances and Cl-Cl distances, d_{Cl} , for the EDA $CuCl_4$ and the $MnCl_4$ series. All distances are in units of angstroms.

$(NH_3(CH_2)_nNH_3) XCl_4$		n=2	n=3	n=4	n=5
Cu	d_{in}	5.20	5.22		
	d_{out}	8.10	9.03	9.04	11.5
	d_{Cl}	3.63	4.6	5.0	7.0
Mn	d_{in}	5.18	5.17		
	d_{out}	8.61	9.5	10.8	12.0
	d_{Cl}	3.5	4.4	5.7	6.9

while the interlayer distances, d_{out} , increases in a smooth fashion with one exception. The interlayer separation is much smaller than would be expected for BDA $CuCl_4$ ($n=4$). It is thought⁽²⁴⁾ that the reason for this owes to a buckling of the organic chain for this compound while in all the other members of the series the chain is nearly linear. This is shown graphically in Figure 3. It is not understood why this should occur but it is fortunate because it allows a distinction to be made between the interlayer exchange strength as a function of cation-cation separation, d_{out} , and as a function of the anion-anion distance, d_{Cl} .

The important feature of the EDA series structure is that the Cu^{2+} ions in adjacent layers are arranged nearly above one another with the out-of-plane Cl^- forming an almost linear superexchange path as shown in Figure 4. This is the only significant difference between this series and the MA_2 series. As was discussed in Chapter I, the adjacent layers in that series are shifted diagonally a half a cell spacing as compared to the layers in the EDA compounds thus causing the nearest-neighbor out-of-plane Cu^{2+} ions to be two layers apart. (Neglecting the 'diagonal' neighbors in the next plane because they do not interact magnetically.) The structure for the EDA series is called eclipsed (ECL) while the latter structure is referred to as staggered (STA). On the basis of this distinction, it might have been expected with 20-20 foresight that the interlayer interaction in the EDA series would be greatly enhanced as we have since shown.

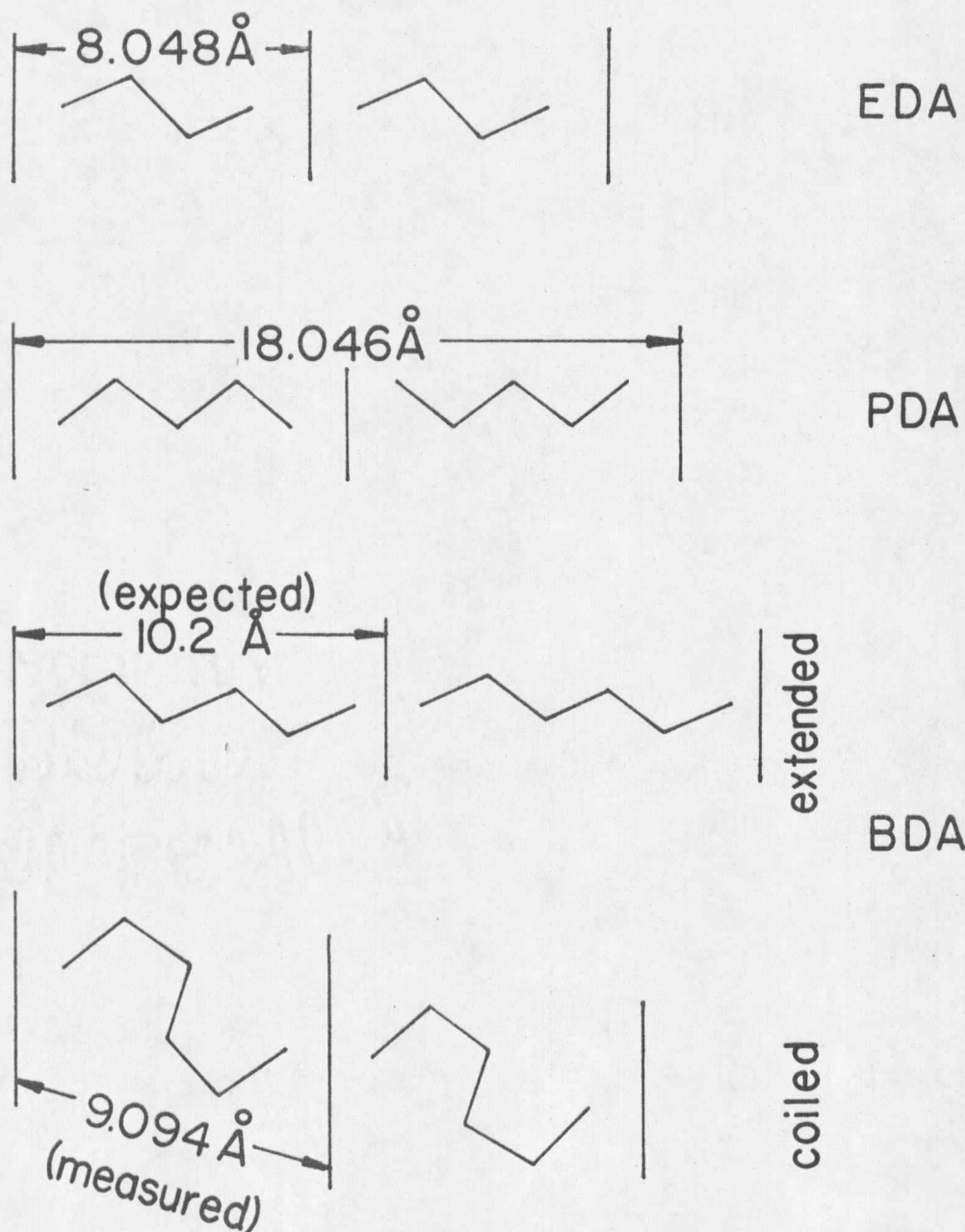


FIGURE 3. Schematic representation of the organic chain structures for $n=2$, 3, and 4. The second diagram for $n=4$ is to indicate a possible coiling of the chain in that compound. Out-of-plane unit cell dimensions are given.

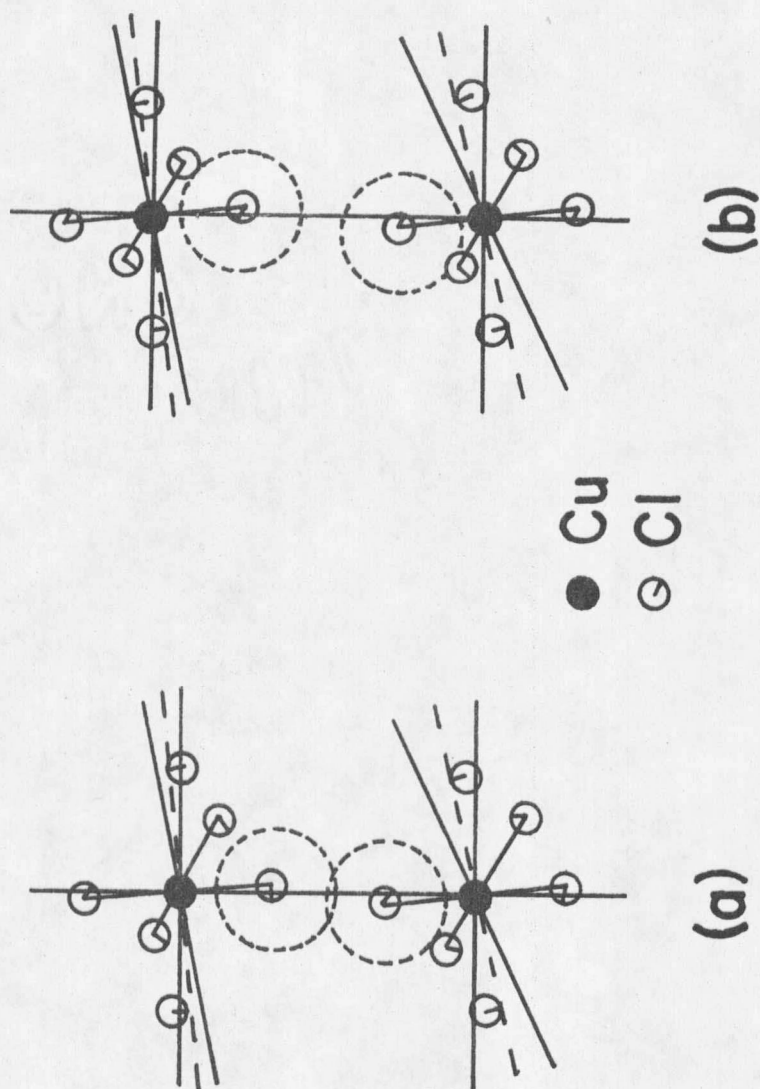


FIGURE 4. Local chlorine environment for the first two members of the EDA series, (a): $n=2$, (b): $n=3$. The circles represent the van der Waals radii of the Cl^- ions. Drawings are to scale.

A variation on the EDA CuCl_4 series was made with the intent being to increase the interlayer exchange still further. It was thought that replacing the interlayer chlorides with bromides would increase the out-of-plane exchange because the Br^- ion is a larger superexchange anion. As will be seen later in this Chapter, that goal was accomplished. At present a partial structural analysis has been done and only some of the unit cell dimensions for EDA CuCl_2Br_2 have been found so it has not yet been confirmed that the bromides do fill the interlayer sites. However, it is known that the bromides do take the interlayer sites in $\text{MA}_2\text{CuCl}_2\text{Br}_2$ ⁽²⁵⁾ and in the related STA compound $\text{Rb}_2\text{CuCl}_2\text{Br}_2$ ⁽²⁶⁾ and since the chemistry is similar between these series it is not unreasonable to expect the bromines would fill the same positions in the EDA compounds. Also, as will be shown in the next section, the susceptibility data seem to support this assumption.

B. Experimental Data

Before we look at the experimental data it might be useful to briefly review magnetic susceptibility units because considerable misunderstanding and confusion seem to surround them. The gaussian unit of magnetic moment (per unit volume) is erg/gauss which is equal to gauss $\cdot\text{cm}^3$ since it can be shown without much difficulty that

gauss²=erg/cm³. Thus the volume susceptibility or the susceptibility per unit volume, χ , has the units of gauss·cm³/oersted since $\chi=M/H$ for dc susceptibility (or $\chi=dM/dH$ for ac susceptibility). χ is usually considered to be dimensionless (ie. 1 gauss=1 oersted), however, it is customary to write χ in terms of emu/cm³ thus effectively making the emu equivalent to cm³. The mass susceptibility, χ_g , is obtained from χ by dividing by the density so the dimensions of χ_g are emu/g. Similarly, the molar susceptibility is obtained by multiplying χ by the molar volume so that χ_M has units of emu/mole (or cm³/mole). Unfortunately there seems to be no consistent use of units in the literature so it is sometimes difficult to compare data from different authors. In this thesis the volume susceptibility, χ , will be used.

In the remainder of this section some of the data taken on the EDA series which illustrate the important features of the magnetic susceptibility and magnetization studies will be presented. For specific details about the experimental conditions and results for EDA and BDA CuCl₄ the reader is referred to the papers by Snively, et al.^(27,24). The results for EDA CuCl₂Br₂ will be presented in this Chapter in their entirety since they have not yet been published elsewhere.

Much about the magnetic behavior of the sample can be seen simply by looking at the shapes of the various kinds of plots of the data. For example, the shape of the χ versus temperature (T) curve quickly points out a number of interesting features. First, if a transition to long

range order occurs it will be seen as either a divergence of the data to a saturation limit (indicated by the data remaining constant as T decreases to zero) for a ferromagnetic transition, or a more or less sharp peak in the data for an antiferromagnetic transition. In the EDA series all compounds have a transition to antiferromagnetic behavior at temperatures below 50K. The transition temperature, T_c ⁽²⁸⁾ is usually defined as the spike in the specific heat curve. However, Fisher⁽²⁹⁾ has shown that for the antiferromagnetic case T_c is given by the point of maximum slope of $\chi_{//}$ on the low T side of the susceptibility peak (χ_{max}). Figure 5 is a plot of χ vs. T for EDA $CuCl_4$. The data were taken on a single crystal and the 3 curves are for each crystallographic axis. The two upper sets of points below χ_{max} are the two $\chi_{\perp}$ showing the expected behavior of the perpendicular susceptibility of an antiferromagnet below T_c . The fact that the curves do not coincide are because of different g -values along those axes as well as anisotropy in the exchange. The set of data that decrease sharply below T_c are those of $\chi_{//}$ and indicate that the spins lie along that direction, the easy axis, which is singled out usually because of the dipole-dipole interaction between the spins. For an ideal antiferromagnet the susceptibility should go to zero along the easy axis ($\chi_{//}$) as T goes to zero for the obvious reason that all the spins are antialigned at $T=0$. This does not occur in this crystal possibly because it was twinned, a state which often exists in the EDA structure⁽⁸⁾, or possibly because of slight misalignment of the easy

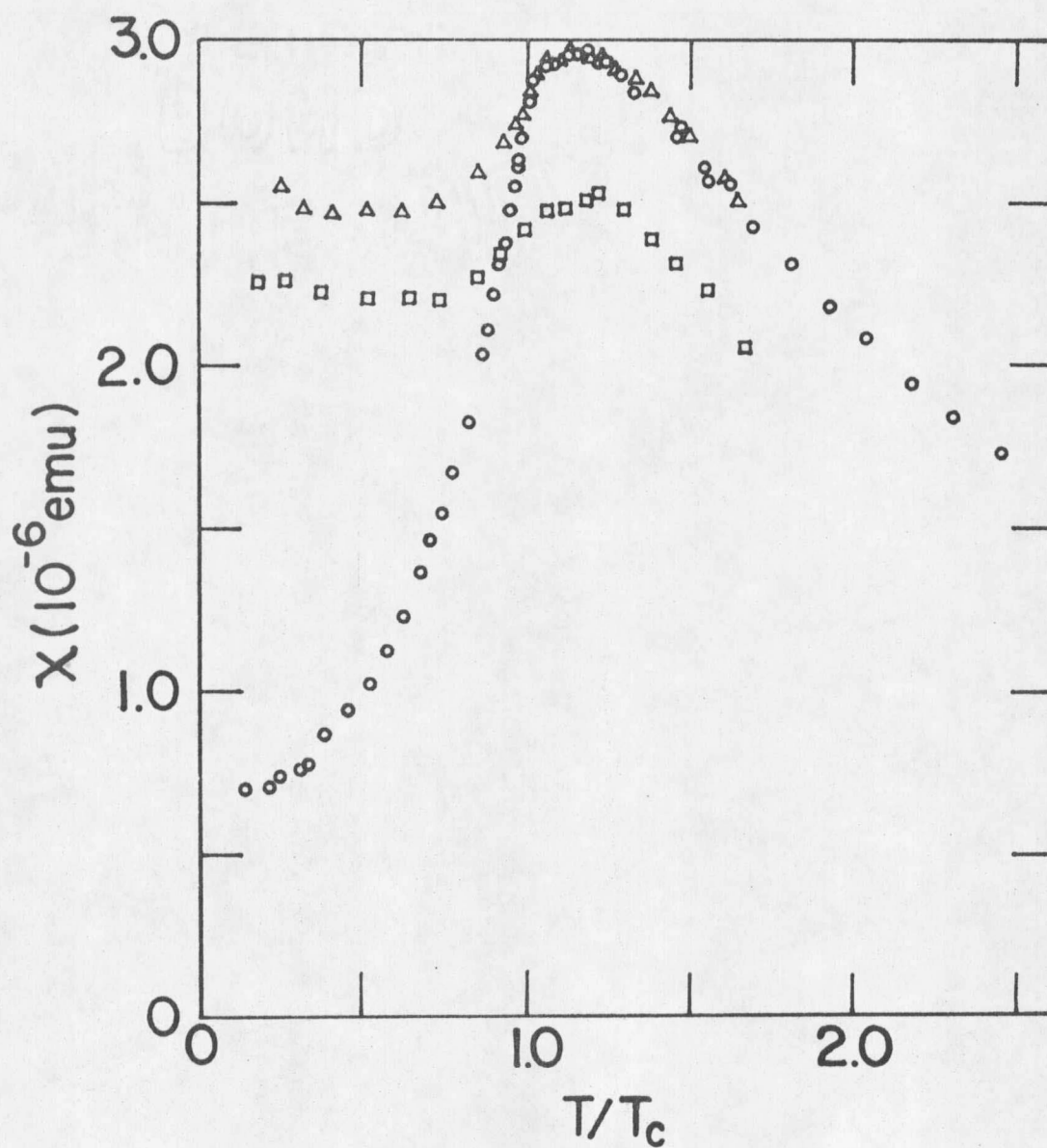


FIGURE 5. Susceptibility of EDA CuCl_4 near the transition temperature for the three axes. $\circ: \chi_a$, $\Delta: \chi_b$, $\square: \chi_c$. $H=5000$ Oe. The error is approximately the size of the circles.

axis and the applied magnetic field.

Figure 6 shows another interesting feature of the susceptibility curves. Notice the difference in the shape of the BDA curve compared to the EDA curve near T_c . A much sharper peak occurs for BDA which is typical of a 2d ferromagnet. The decrease would be sharper on the low temperature side of $\chi_{\max}$ also if this data were from a single crystal. As will be discussed later, EDA is more nearly a 3d antiferromagnet at all temperatures, thus the more rounded appearance of the peak. (Be careful with this nomenclature, the possibility of confusion is great. Remember, in reality all compounds become 3d in their behavior below T_c if they have one. Above T_c all compounds behave as paramagnets. In the sense meant here, 2d refers to the fact that the exchange coupling between spins is equal in a plane. This is the same definition given in Chapter I but it is useful to be reminded of it now.) The 3d nature of EDA is reflected in these curves by the fact that χ increases to $\chi_{\max}$ more gently and is more spread out than it would be if it were a 2d ferromagnet. For a completely 3d antiferromagnet such as MnF_2 the susceptibility above $\chi_{\max}$ is nearly flat. Quantitatively, $[T(\chi_{\max}) - T_c]/T_c$ is approximately 1%⁽³⁰⁾ for a 2d ferromagnet whereas for 3d compounds it is usually 5-15%. For 2d antiferromagnets it is on the order of 50%. While it is not entirely clear from Figure 6 the ratio for EDA is approximately 18% and for BDA it is about 0.6%.

The temperature difference at which T_c occurs is another feature

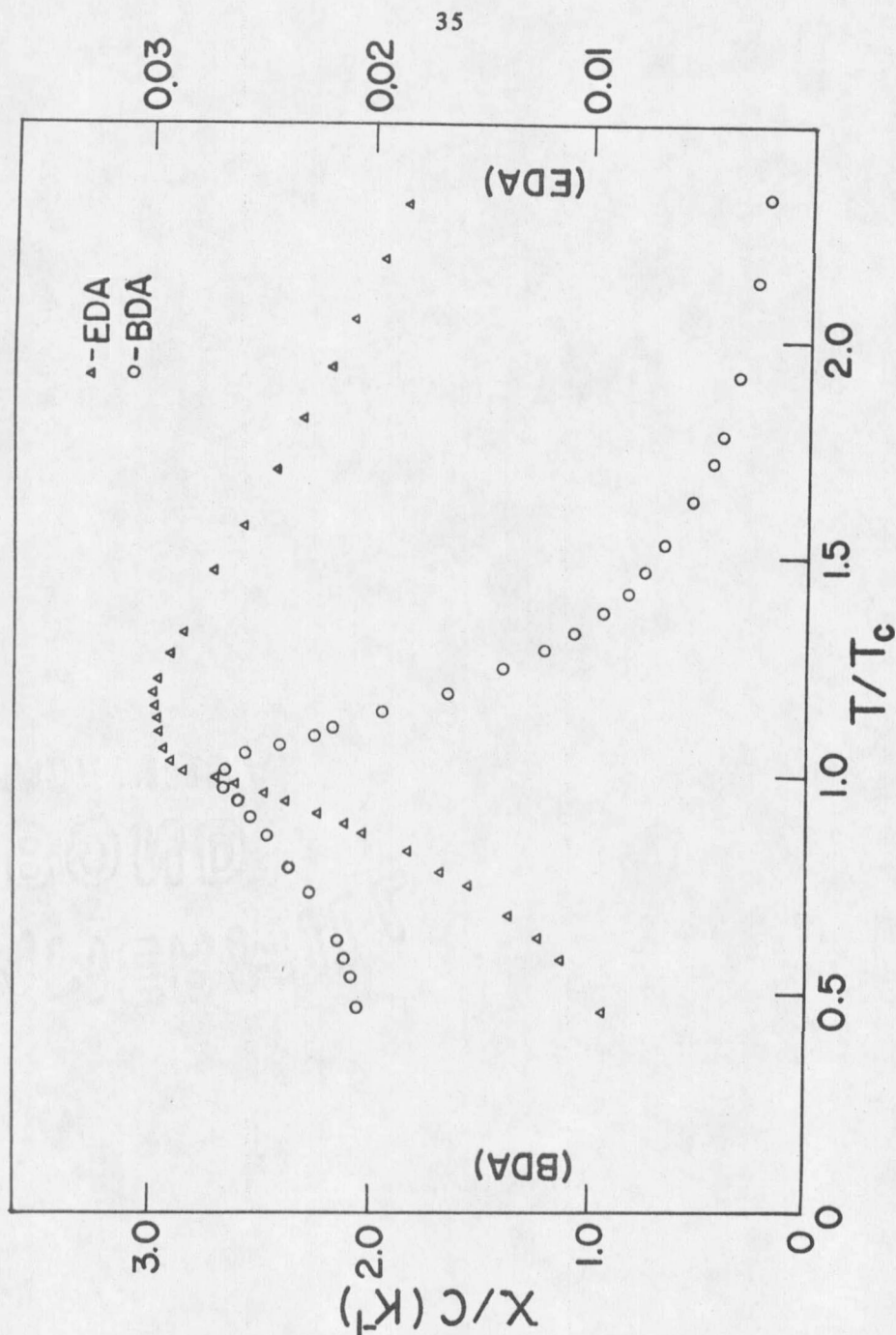


FIGURE 6. Reduced susceptibility vs. the reduced temperature for BDA ($\circ$) and for EDA (Δ). The vertical scales are different for the two sets of data (BDA scale is on the left). $T_c = 31.5\text{K}$ for EDA and $T_c = 8.85\text{K}$ for BDA.

which can be seen from Figure 7. From mean field theory it can be shown that T_c is proportional to the magnitude and sign of the exchange with the near neighbors⁽³¹⁾. For the EDA crystal structure it is expected that T_c should increase with increasing interplanar exchange. Figure 7 clearly shows that BDA should have less out-of-plane exchange than EDA. One other related feature shown in both Figures 6 and 7 is the difference in the maximum value of χ for the two compounds. χ_{max} is much larger for BDA but again this is easily understood. Even though a transition to long range order occurs in EDA it does so at a much higher temperature and thus thermal effects are greater. The ability of the spins to align is greatly hindered by their thermal motion. For this reason the susceptibility cannot be as large.

Another useful method for presenting the data that enhances the differences in dimensionality is to plot C/XT vs. J/kT . (Note that J/k , where k refers to Boltzman's constant, is often used to express the exchange energy since the units are then those of T .) Figures 8 and 9 show examples of this method of looking at the data. In Figure 8 the data for EDA are plotted along with the calculated curves for the following models: a 3d simple cubic compound, a 2d square-planar ferromagnet, mean field, and two, square-planar ferromagnets with strong second nearest-neighbor coupling. The shape of the curves are significantly different and quite clearly EDA is more nearly a 3d antiferromagnet. Figure 9 is the BDA data along with a 2d square-planar ferromagnetic

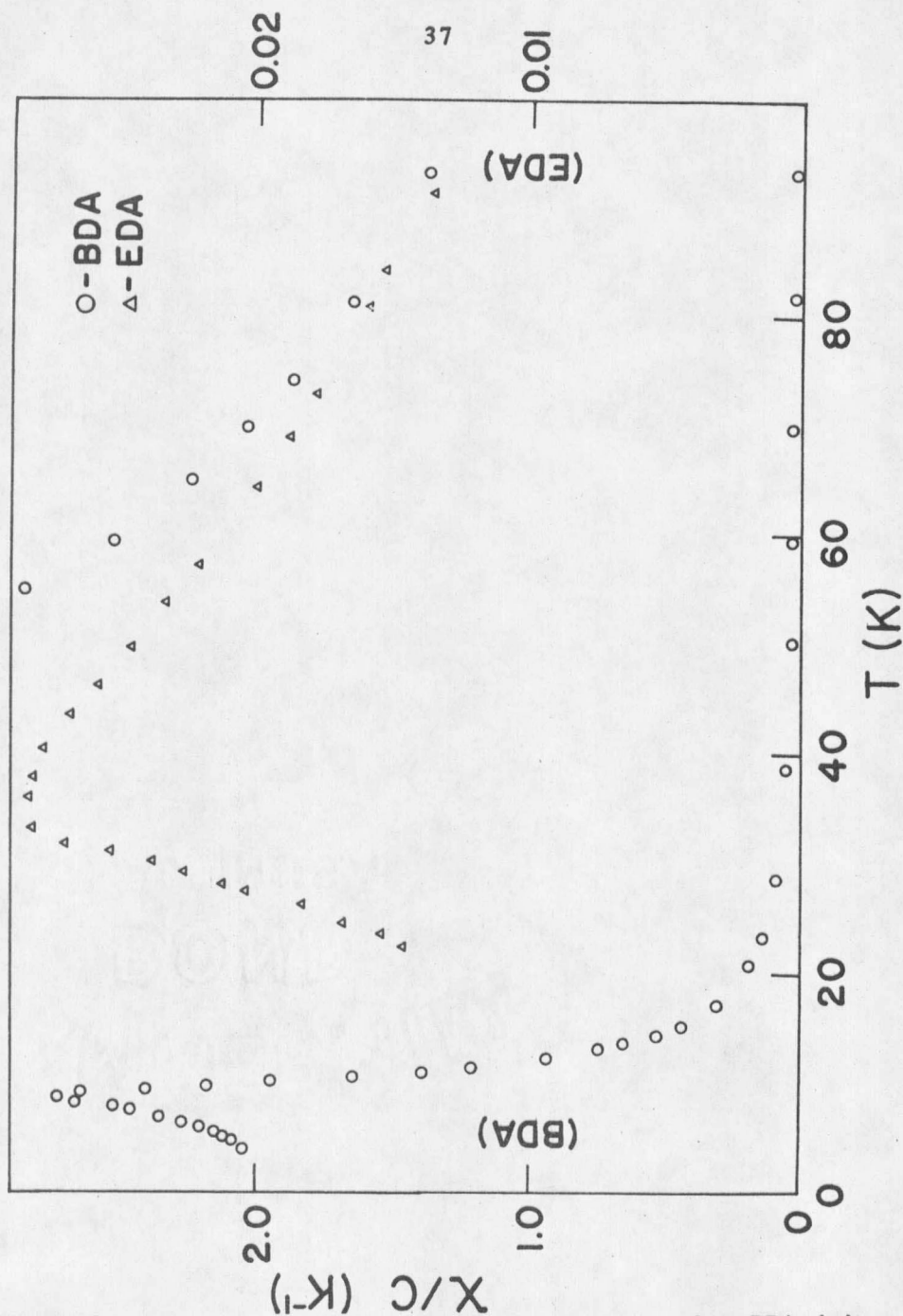


FIGURE 7. Reduced susceptibility vs. temperature for BDA ($\circ$) and EDA (Δ). The vertical scales are different for the two compounds. Circles plotted above and to the right of the EDA data are the BDA points plotted to the expanded right hand (EDA) scale.

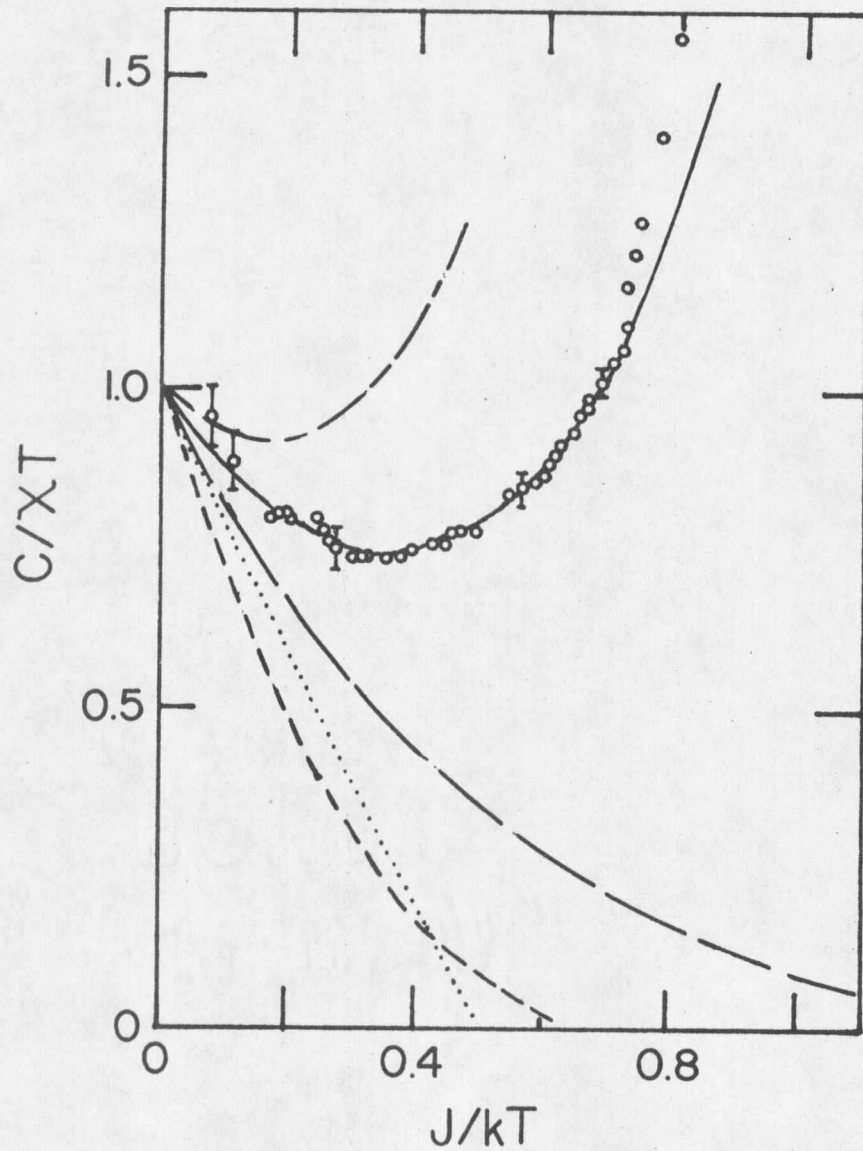


FIGURE 8. High temperature EDA data and series expansion results plotted as C/XT vs. J/kT . $J/kT_c=0.73$, mean field model: ----, simple cubic model: — — — —, square planar model: — — — —, second neighbor model for $J/k=23.0K$ and $J'/k=-13.7K$: — — — —, second neighbor model for $J/k=23.0K$ and $J'/k=-23.0K$.

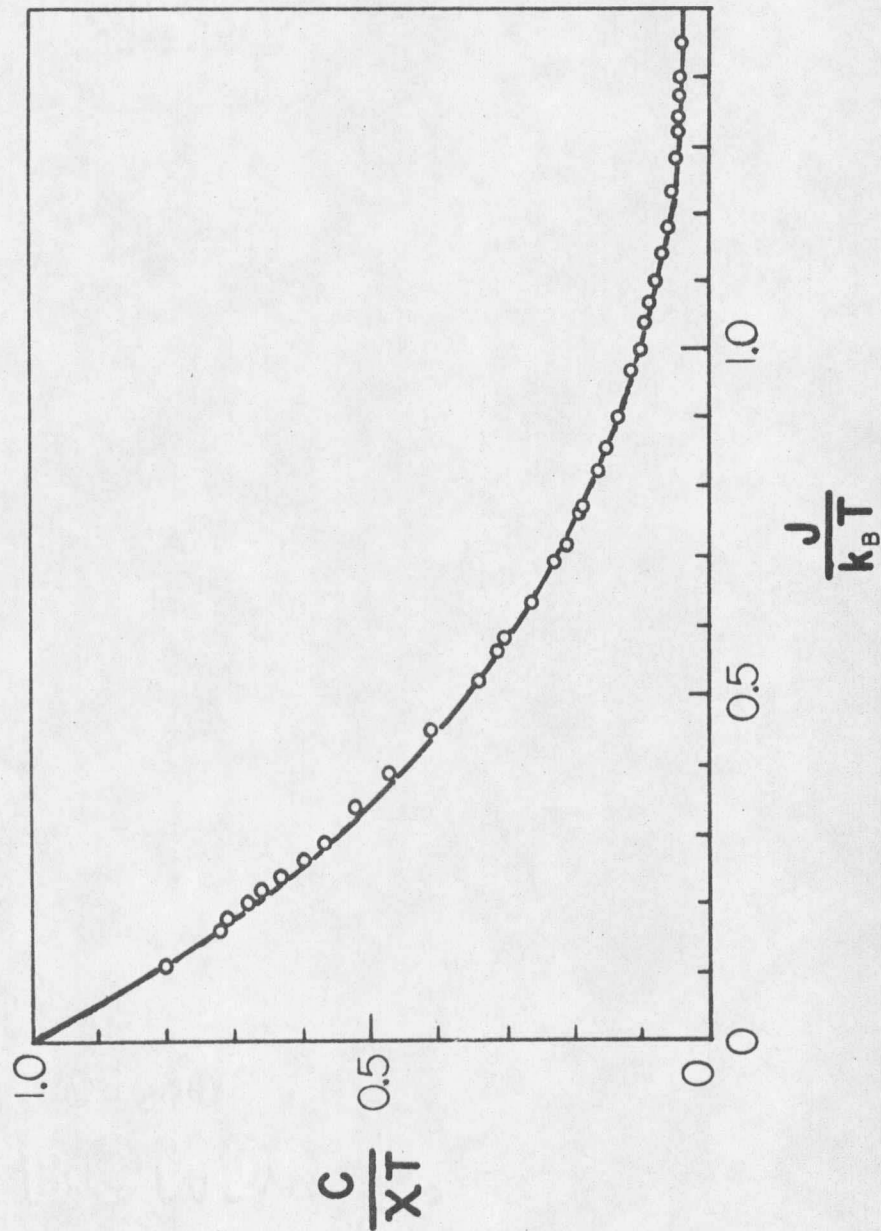


FIGURE 9. High temperature powdered BDA data and the calculated line of a square planar model for $J/k=13.0\text{K}$. The circle size approximates the uncertainty in the measurement.

curve and for that case the coincidence between data and theory is very good indicating that BDA is in fact a 2d ferromagnet.

Finally, Figure 10 shows χ/C vs. T for a powdered sample of EDA CuCl_2Br_2 weighing 0.0687g. (χ/C is used to normalize the data for different weights, for different g -values, and for different spin values.) With the above comments in mind there are a number of general remarks that can immediately be made. From the shape of the curve both above and below χ_{max} , it would not appear that this compound is a 2d ferromagnet. Also the high temperature at which χ_{max} occurs would indicate that there is relatively strong interplanar coupling. (Recall that T_c cannot be found in the usual way from a powdered sample susceptibility measurement because $\chi_{\parallel}$ is not known.) Both of the above observations seem to indicate that the out-of-plane exchange is even stronger in this partially bromated EDA sample than for the tetrachloro compound. As mentioned earlier, this in fact was the result which was anticipated and was the primary reason for investigating this compound. The $C/\chi T$ vs. J/kT plot of Figure 11 also shows a shape reminiscent of those with strong 3d coupling. (An interesting aside concerning the shape of this curve is that in some qualitative ways it looks like that of a 1d magnet, i.e., the curve does not go below a value of $C/\chi T=1.0$. As will be discussed later in this Chapter, the resemblance may not be accidental.) Quantitative values for the intraplane and interplane exchange will be given after a discussion of the fitting procedures.

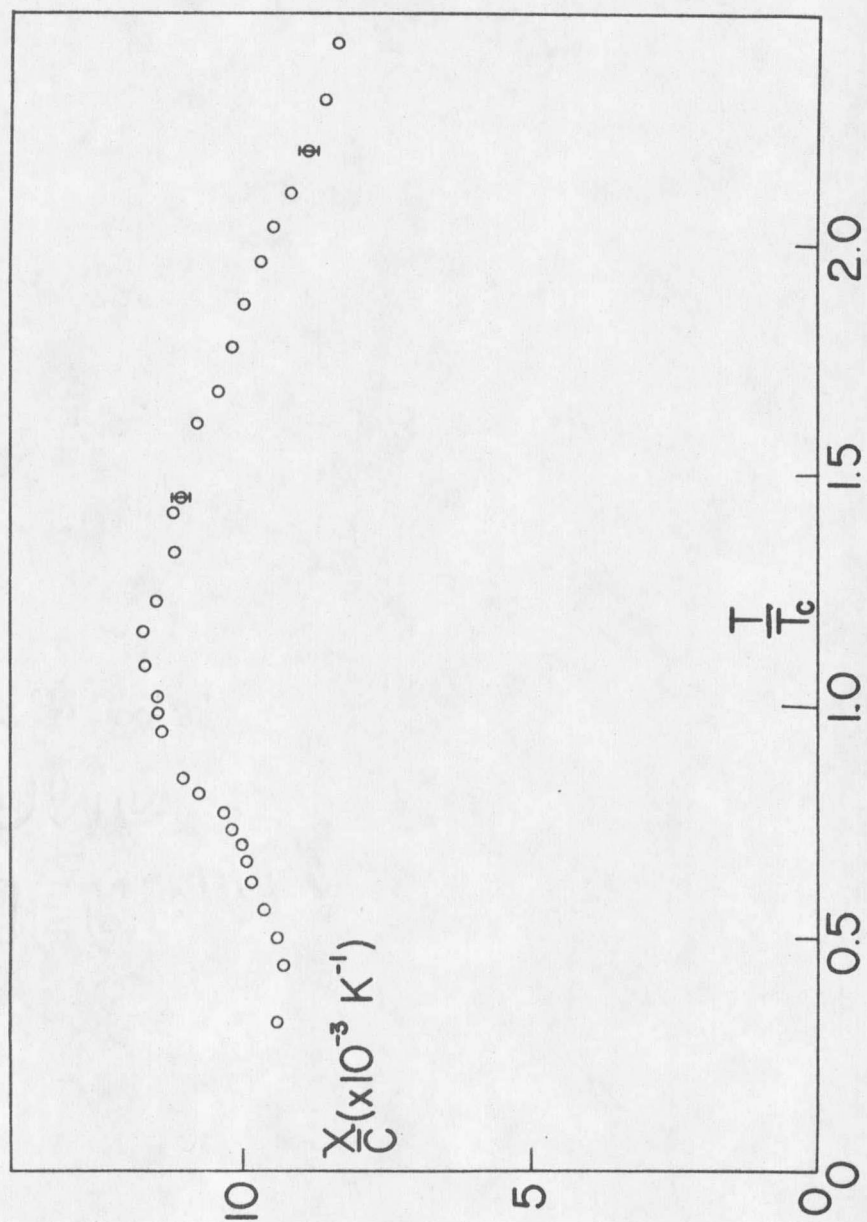


FIGURE 10. Reduced susceptibility vs. reduced temperature for EDA CuCl_2Br_2 . T_C is approximately 45K.

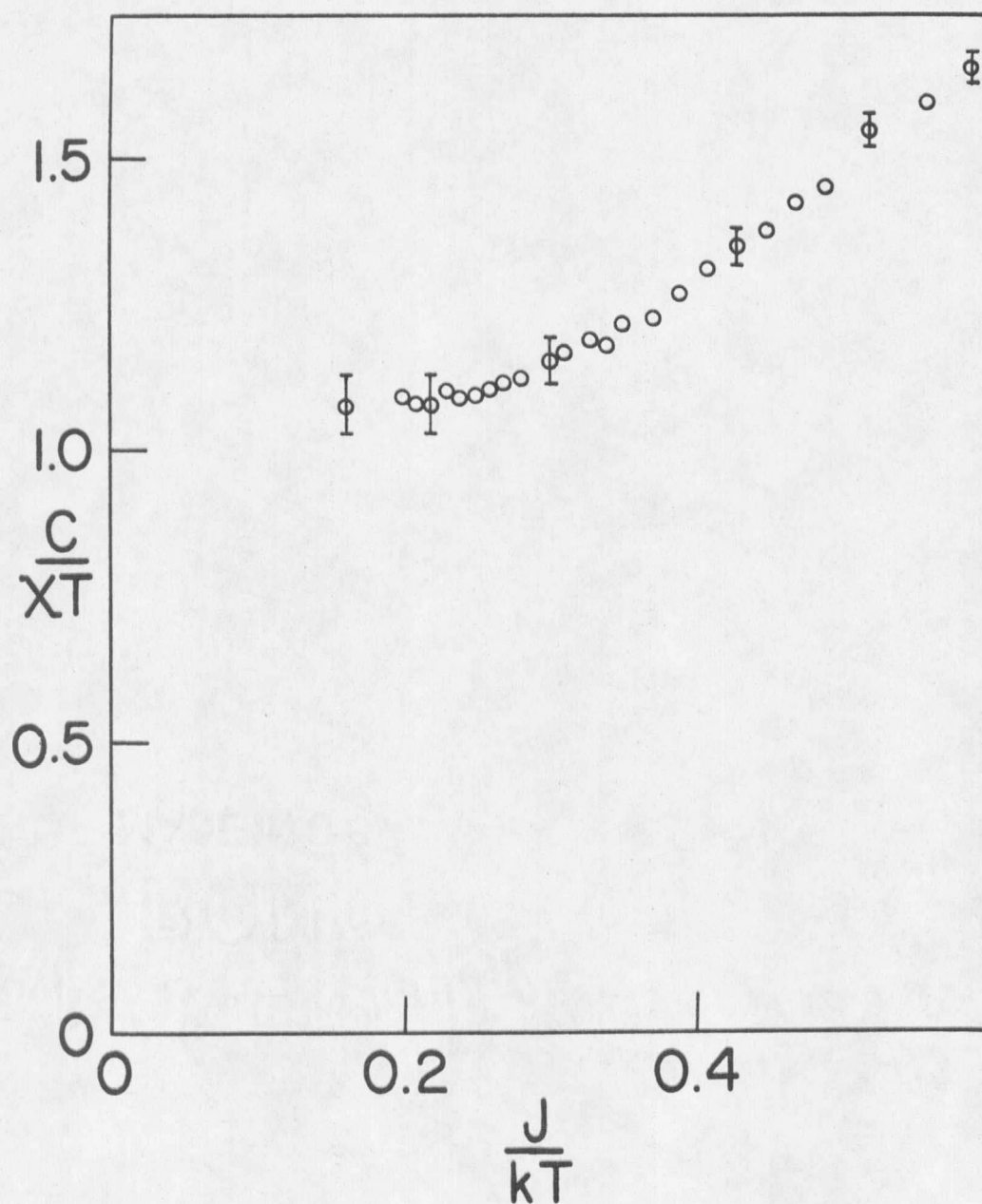


FIGURE 11. Inverse susceptibility vs. J/kT for EDA CuCl_2Br_2 . J/kT_c is 0.69.

Another useful method of presenting the data is that of plotting the magnetization, M , versus the applied field H . This is a particularly important technique when investigating the field dependent behavior of a single crystal. (Recall that with a vibrating sample magnetometer the quantity measured is always M . However, the dc susceptibility is given by $\chi = M/H$. In the cases where χ is plotted against T , H is usually held fixed and M is simply scaled by H to give χ .) In Figure 12 a few isotherms of the M vs. H data for BDA are presented along with a curve showing what the magnetization would look like for $T=0$. The data were taken along the easy axis of the crystal. Because the spins in BDA align antiferromagnetically below T_c the magnetization would ideally remain zero for all fields in that region. The sharp changes in M at H_{SF} and H_p are indications that phase transitions occur in this compound. It is beyond the scope of this thesis to discuss in any detail the vast theory of phase transitions so it will have to suffice to say that the region between H_{SF} and H_p is a region of the spin-flop phase which occurs because of anisotropy in the crystal. The antiferromagnetic phase is below H_{SF} and the usual paramagnetic phase is above H_p . The temperature at which only the paramagnetic phase would exist for all fields is another way of describing the transition temperature. A plot of the critical fields, H_{SF} and H_p , vs. temperature leads to a curve such as that shown in Figure 13 which is a phase diagram in the H - T plane for BDA. As will be shown in the the next section, mean field theory used on

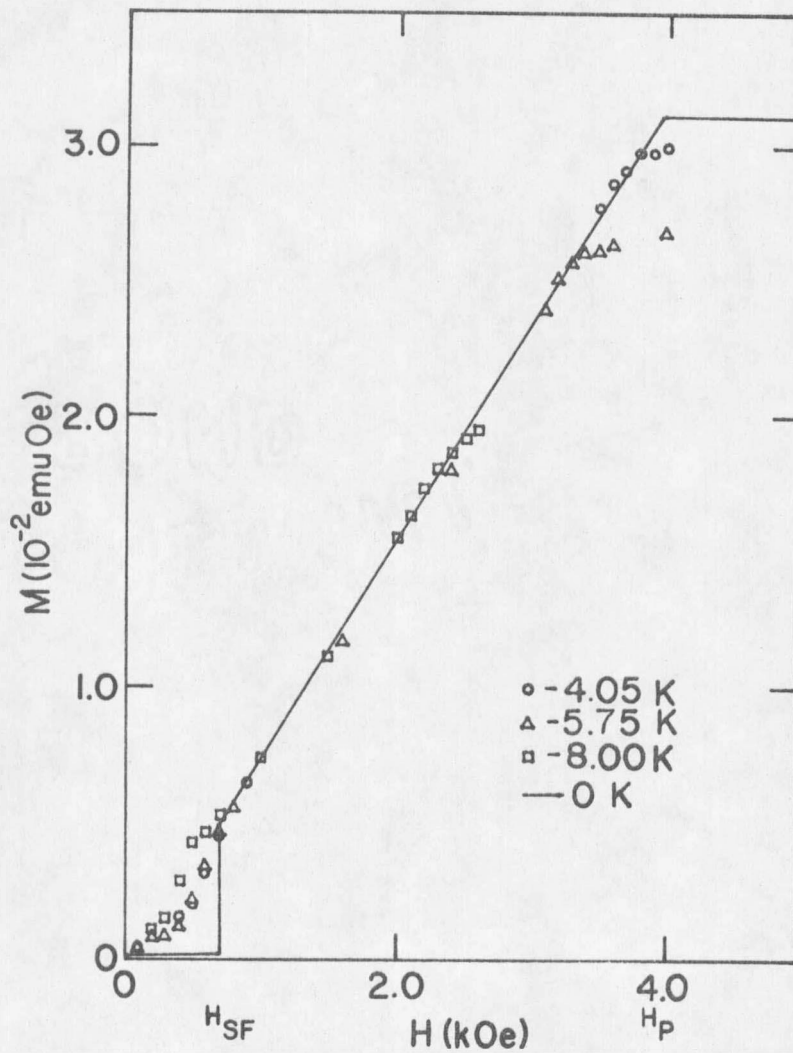


FIGURE 12. Magnetization vs. applied field data of 3 isotherms for BDA CuCl_4 . Solid line represents the ideal behavior at $T=0$. Only some of the data points are shown for clarity. $\circ$ - 4.05K; Δ - 5.75K; $\square$ - 8.00K. The data were taken along the easy-axis.

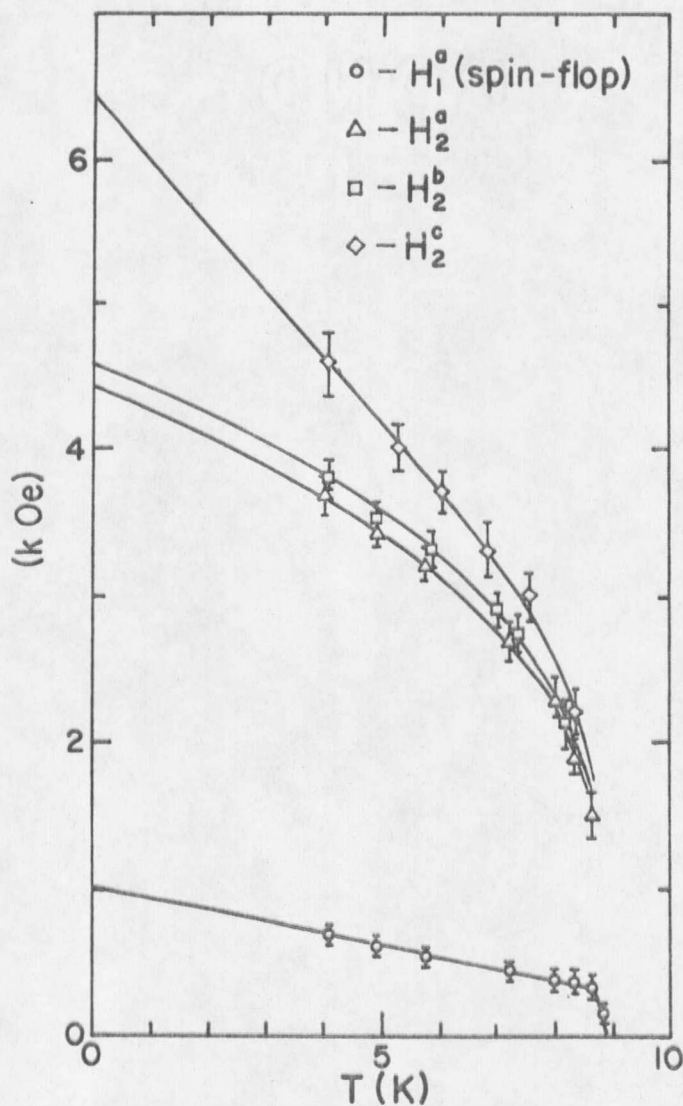


FIGURE 13. Critical field vs. temperature phase diagram. $\circ$ - easy-axis spin-flop fields: Δ - easy-axis flop-to-paramagnetic fields: $\square$ - next-easy-axis antiferromagnetic-to-para fields: $\diamond$ - out-of-plane antiferromagnetic-to-para fields. Lines through the data are aids to the eye only.

the data from the phase diagram provides a different method for calculating the exchange strengths.

Before going on to a discussion of ways to evaluate the data, one other standard method of presenting susceptibility data should be mentioned. Often a plot of $1/\chi$ vs. T is used to investigate the Curie-Weiss behavior of a compound. This technique is particularly useful if the g -value of a sample is not known since the slope of the high temperature portion of the line is proportional to $1/g^2$. (We did not use this method since we have the epr equipment necessary to find g directly.) Also, the $1/\chi$ curve can be used to find a rough estimate of the exchange energy since J is related to the T -axis intercept of a line drawn through the high temperature data.

C. Data Evaluation

Two standard methods for determining the exchange constant from susceptibility and magnetization data will be briefly outlined here because they were the methods used to evaluate the data presented earlier. Fitting to high temperature series expansions (HTSE) is one of the most common and widely used techniques and is particularly useful for compounds which deviate from paramagnetic behavior at temperatures not too near their transition. Another method which in some cases is more

useful is that of using mean field calculations to look at the behavior of critical fields.

A brief review of thermodynamics and statistical mechanics is helpful to outline the development of a HTSE. Recall that χ is given by

$$\chi = (kT/V) \frac{\partial^2}{\partial H^2} (\ln Z)$$

where Z is the partition function and can be written as

$$Z = \exp(-\text{Tr} \mathbb{H} / kT).$$

H refers to the magnetic field and $\mathbb{H}$ (boldface) represents the Hamiltonian of the model chosen, which typically takes one of the forms of Eqn. 1.3. The exponent may be expanded in a power series if the energy associated with $\mathbb{H}$ is small compared with kT , hence the name high temperature series expansion. However, it is somewhat more involved than just that. A second expansion must be done for $\ln Z$, but, a major simplification occurs when it is realized that χ (or M) is an extensive quantity and thus must depend only upon N , the number of magnetic ions in the system, and not N^2 , N^3 , or higher powers. This allows many terms in the expansion to be thrown away immediately leaving something that looks like,

$$\ln Z/N = 1 - E_N/kT + E_N^2/2!(kT)^2 - \dots$$

where E_N is the energy associated with $\mathbb{H}$ and refers to the correct 'configurational' energy. This is the point at which the various possible dimensionalities of the system affect the result since the choice of $\mathbb{H}$ affects both E_N and the way the sums are done. Also, the crystal

structure is involved because it determines the number of 'neighbors' associated with the interaction. An important point to note is that χ must include the Zeeman term, $\mu_B g \sum_i H \cdot s_i$, otherwise there would be no dependence upon H , thus no χ !

Without discussing the details of this calculation explicitly, it is sufficient to recognize that the form of a HTSE looks like,

$$\chi T/C = \sum_{i,n} \frac{a_n}{n!} \left(\frac{J_i}{kT} \right)^n$$

where the a_n contain the structural and model information and J_i is the exchange energy along some given direction. The J_i are the parameters which are varied to achieve a fit of the experimental data. The number of terms which have been calculated depends on the model chosen with the 'fit' extending closer to T_c as more terms are included. For more details about HTSE's, the interested reader is referred to the work of Stanley⁽³²⁾.

The HTSE used to generate the curves shown with the data was of a general nature so that many different models could be used to attempt to fit the data⁽³³⁾. Because it was thought that the main exchange interaction would occur in the planes, the model parameters used enhance the deviation from square-planar behavior. The expansion includes those for a square-planar lattice (10 terms known)⁽³⁴⁾, various second-neighbor models (5 terms)^(35,36), anisotropic⁽³⁷⁾, and Dzyaloshinsky-Moriya⁽³⁸⁾. An example of an explicit form of the HTSE for an eclipsed model with first- and second-neighbor terms included is given in Table IV. It can

Table IV. High temperature series expansion for the ECL model. The lower equations show how the expansion parameter θ and ε are combined to find J and J' for this model.

Eclipsed Model

$$T \ln \frac{X_T}{C} = \theta - \frac{\theta^2}{T} (\varepsilon + 1.5\varepsilon^2) - \frac{1}{2} \frac{\theta^3}{T^2} (\varepsilon + 2\varepsilon^2 + \varepsilon^3) + \frac{5}{192} \frac{\theta^4}{T^3} (1 - 2.4\varepsilon + 6\varepsilon^2 + 36\varepsilon^3 + 37.6\varepsilon^4).$$

$$J = \frac{\theta}{2} (1 + \varepsilon)$$

$$J' = -\theta\varepsilon$$

$$\varepsilon = -1: \text{ ferromagnetic chain}$$

$$\varepsilon = -\frac{1}{3}: \text{ simple cubic ferromagnet}$$

$$\varepsilon = +1: \text{ simple cubic antiferromagnet (planes of alternating spins)}$$

$$\varepsilon = 0.424$$

for EDA

$$\theta = 32.3$$

be seen that if $\epsilon=0$ this expansion would represent a square-planar interaction and in fact it reduces to that of Baker, et al.⁽³⁴⁾. The exact form of the expansion and the definition of Θ and ϵ in terms of J and J' is different for each model. Appendix A contains the complete list of all the expansions used and the appropriate definitions for Θ and ϵ . Since there are only 5 terms in the above series (a leading term of 1 is suppressed by the use of $\ln XT/C$ instead of just XT/C) the expansion is valid only to within approximately $T=2T_c$ of T_c . The fact that there is coincidence between the calculated curves and the data in Figures 8 and 9 below that temperature is interesting but probably only fortuitous.

Two methods were used to obtain best fit values for J and J' . The first involved a least squares fitting procedure in which the coefficients of the series were generated by a best fit to the data and then were compared to coefficients calculated from the expansion models using the F distribution test. By finding values of J and J' which could not be rejected at the 99% confidence level, reasonably good agreement with the data was found. The computer program used to do the fitting is printed in Appendix B.

The second method basically involved a 'plot and see' approach in which the various curves could be plotted along with the data and the parameters of the expansion models could be adjusted to find an 'eyeball' fit. The graphics program developed for this (also given in Appen-

dix B) allowed both the data and the calculated curves to be displayed in any of the three ways mentioned earlier, χ/C vs. T , C/χ vs. T , or $C/\chi T$ vs. J/kT , which helped in separating accidental fits from those which appeared to be more realistic. This also enabled a qualitative study of just what happens when the various parameters are varied over physically possible ranges.

Table V shows the derived values for J and J' for all the investigated members of the EDA series including those given by other authors. The value listed for PDA ($n=3$) as our value was obtained by using the HTSE already presented on the data given by Phelps, et al.⁽³⁹⁾ since they apparently did not investigate the possibility of interplane exchange. The 2d fit they gave appears reasonable, however, when the F test statistics were applied to their data it was found that the 2d ($J'=0$) fit could be rejected at the 99% confidence level whereas the values we derived could not. Since von Känel⁽⁴⁰⁾ obtained an identical result to ours for PDA using a different technique, and the epr linewidth analysis by Kite⁽⁴¹⁾ indicates at least some 3d behavior, we have used our value for J' in the discussion in Chapter V.

A mean field calculation was necessary to determine J' for BDA. This was because of the very small value of the interlayer exchange which was too low to be distinguished from a strictly 2d model with our HTSE. The molecular field method differs from the HTSE technique in that it uses the values of various critical fields near or below the transi-

TABLE V. The magnetic properties of the EDA CuCl_4 series and of EDA CuCl_2Br_2 . The exchange and temperature values are in units of degrees Kelvin while the fields are in units of oersteds.

$(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{CuCl}_x\text{Br}_y$	T_c	J/k	J'/k	H_A^{in}	H_A^{out}	Ref.
n=2 x=2 y=2	45	15	-31			This work
n=2 x=4 y=0	31.5	23.0	-13.7			a.
	34.0	20	12	140	2000	b.
n=3 x=4 y=0		20	2			c.
	14.9	16.5	-1.6	170	4700	b.
	13.5	15.4	0			d.
n=4 x=4 y=0	8.85	13.0	-0.15	200	2050	e.
n=5 x=4 y=0	7.6	14.1	-0.04	31	1400	b.

a. L. O. Snively, P. L. Seifert, K. Emerson, and J. E. Drumheller, Phys. Rev. B20, 2101 (1979).

b. H. von Känel, Physica 96B, 167 (1979).

c. Approximate values using our ECL HTSE on the data of ref. d.

d. D. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. 15, 3147 (1976).

e. L.O. Snively, K. Emerson, and J.E. Drumheller, Phys. Rev., in press.

tion temperature rather than high temperature susceptibility data. Conversely, the reason a mean field calculation was not done for EDA was because we could not generate sufficiently large magnetic fields to be able to detect the critical values. (The values for the critical fields increase with increasing exchange as will be seen. Von Känel⁽⁴⁰⁾ used this method to find the values referenced to him in Table V.) The question arises of comparing the results obtained from two different temperature regimes. However, as indicated above and as may be seen in Table V, the values found by the two methods for EDA and PDA agree to within experimental error. Therefore, while it may not be appropriate to compare such results in all cases, the evidence suggests that it is satisfactory to do so for the EDA series.

The equations used to determine the various critical fields at $T=0$ are obtained by minimizing the free energy of classical spin vectors in an applied magnetic field. After de Jongh⁽³⁰⁾ we may write,

$$(H_{SF}^a)^2 = 2H_A^{\text{in}}H_{af}^{\text{in}} - (H_A^{\text{in}})^2 \quad (3.2)$$

$$H_P^a = 2H_{af}^{\text{in}} - H_A^{\text{in}} \quad (3.3)$$

$$H_P^b = 2H_{af}^{\text{in}} + H_A^{\text{in}} \quad (3.4)$$

$$H_P^c = 2H_{af}^{\text{out}} + H_A^{\text{out}} \quad (3.5)$$

where a denotes the easy-axis, b the other in-plane axis, and c the out-of-plane axis. The subscripts SF and P refer to the spin-flop and paramagnetic transitions respectively. H_{af} and H_A refer to the in- and out-of-plane antiferromagnetic and anisotropy effective fields depending on

the superscript. A simple molecular field model relates the effective field, H_{af} , to J' by $H_{af}^{in} = 2z|J'|S/g_{in}\mu_B$ and $H_{af}^{out} = 2z|J'|S/g_{out}\mu_B$ where z is the number of nearest neighbors and S is the spin quantum number. The critical fields at $T=0$ are estimated from a phase diagram such as Figure 13 and then Eqns. 3.2 through 3.5 are solved to find H_{af} and H_A , which in turn determines J' .

A second approach can be used to check these values starting with the molecular field expressions,

$$\chi_1 = \chi_1^0 (1 + H_A/2H_{af})^{-1}$$

and

$$\chi_1^0 = Ng\mu_B S/2H_{af}$$

where χ_1^0 denotes the perpendicular susceptibility corrected for anisotropy effects. The values for $\chi_1(T=0)$ are estimated from the χ vs. T plots such as figure 5. The details of both this and the critical field calculations for BDA are given by Snively, et al.⁽²⁴⁾ elsewhere.

Recalling the discussion of the qualitative features of the mixed halide data from earlier in the Chapter, the results of the analysis of the EDA CuCl_2Br_2 data will now be presented. Various HTSE's were used to attempt to fit the powdered sample data. Unfortunately, sufficiently good, large single crystals have not yet been available to do single crystal measurements. The best fit of the data occurred for the values of $J=15\text{K}\pm 1\text{K}$ and $J'=-31\text{K}\pm 1\text{K}$. Because of the very high transition temperature which can only be estimated to be near 45K (again because of the

powdered sample), the data used to fit to the expansion were also taken at temperatures at which large errors occur in the magnetization measurements. (Recall that the series expansion for 5 terms is typically only valid to a temperature of approximately $2T_c$.) Nevertheless, the values given from the ECL model were the only ones which could not be rejected at the 99% confidence level of the F test. Figure 14 is a plot of the data of Figure 11 with the best fit curve drawn through it. Again, surprisingly, the agreement is much better than would be expected for temperatures well below $2T_c$.

Besides the large experimental error involved in these data, another question is raised in the analysis. As stated earlier the expansions used were based on the concept that the compounds had predominantly square-planar behavior. The parameter used to measure the deviations was not designed to be large. However, as can be seen from the values for J and J' , EDA CuCl_2Br_2 appears to be in some sense a strong 1d antiferromagnet with weaker ferromagnetic planar coupling between 'chains'. It is not entirely clear that our expansions are valid for this kind of behavior. On the other hand, the value obtained for J is certainly within the range expected for copper chloride planes, and as was discussed previously, the higher transition temperature found is indicative of stronger interplanar coupling. This, along with the fact that the Br^- ions are typically stronger superexchange anions than are Cl^- ions, supports the observed increase in the out-of-plane exchange. With this

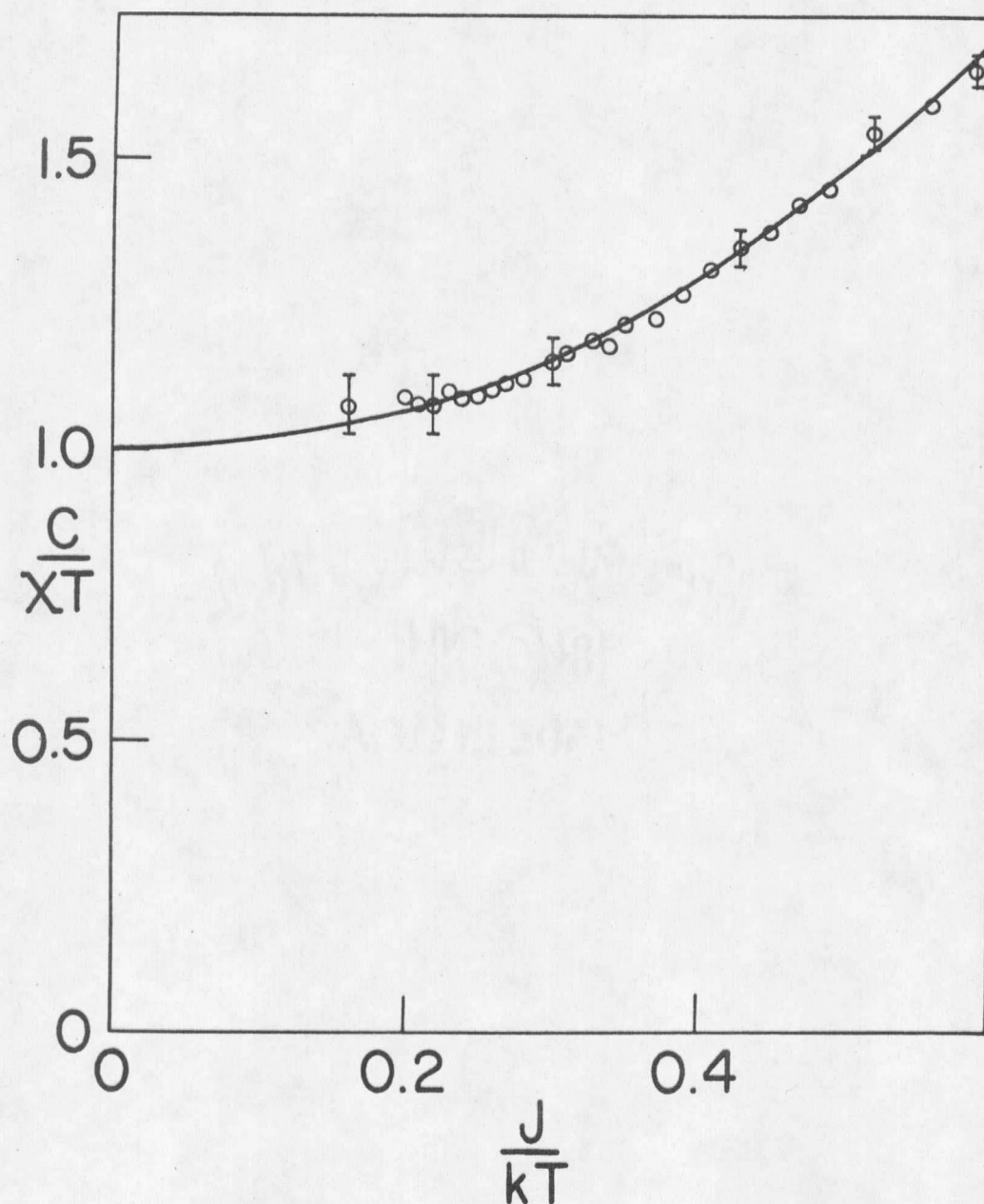


FIGURE 14. Inverse susceptibility vs. J/kT for EDA CuCl_2Br_2 . Solid curve represents the ECL HTSE for $J/k=15.0\text{K}$ and $J'/k=-31.0\text{K}$.

evidence in mind, we feel that the values given for J and J' are reasonable.

CHAPTER IV. THEORY OF THE TWO-HALIDE SUPEREXCHANGE

A. History of Superexchange Theory

Before outlining the basic two-halide calculation it might be helpful to briefly review the various approaches used to calculate the superexchange energy from first principles. For more than just a summary of this complicated and still poorly understood topic the reader is referred to the complete and excellent reviews by Anderson^(15,42) and, for some of the more recent works, that by van Kalker et al.⁽⁴³⁾. Also, a short article by Newman⁽⁴⁴⁾ details the attempts at a priori calculations. The intent in this section is to only point out the important differences of the major methods as a preview of the two-halide calculation presented later in this Chapter.

As stated in Chapter I, it was Kramers⁽¹¹⁾ that first attempted to do a calculation involving a superexchange anion separating two magnetic cations. He took as his basic unit a three-center, four-electron cluster with 1 unpaired electron on each cation and two spin-paired electrons on the diamagnetic ligand. He assumed that in zeroth order the wavefunctions could be taken as those of isolated, well separated ions. In the next step he chose as his basis functions the correct orthonormalized linear combination of the atomic wavefunctions. Then a standard perturbation calculation was done to determine the energies. The problem with

this approach is that because of the orthogonal orbitals the superexchange interaction does not appear until third order. This is not only complicated but masks the true exchange effects because of other unrelated terms which show up due to the high order of the calculation. An improvement can be made on this as will be discussed later by using the fact that the unperturbed wavefunctions are not orthogonal so that the influence of the diamagnetic ligand on the paramagnetic cations shows up in first order. Because of the difficulties involved with the calculation of Kramers, only qualitative results were obtained. Later authors have attempted to correct some of the inconsistencies of this basic approach, most notably Keffer and Oguchi⁽⁴⁵⁾ and Huang and Orbach⁽⁴⁶⁾, and have for individual compounds achieved relatively good results.

Anderson⁽⁴⁷⁾ has taken a different approach which can be separated into two steps involving the evaluation of what are called the potential- and the kinetic-exchange. The first step requires constructing the localized Hartree-Fock wavefunctions (Wannier functions) for a magnetic electron on one cation in the field produced by all other cations and ligands without considering exchange effects between the magnetic electrons. The second step takes into account the exchange between two magnetic electrons on different cations with the modified wavefunctions. This separation of operations causes two types of exchange to show up, one is called 'ionic' or 'non-transfer' and the other is the 'transfer' exchange. The first is just a consequence of the Pauli principle and

because the Wannier functions are orthogonal it favors parallel alignment of spins (potential exchange). The transfer-exchange term favors antiparallel spin alignment (kinetic exchange). Thus one of the advantages of Anderson's method is that it involves a simple balancing of opposite aligning tendencies. As he points out, for nonconducting, ionic solids the larger superexchange interaction is almost always antiferromagnetic, i.e., the kinetic term dominates. This is opposed to the case of direct exchange where, according to Anderson's theory the potential term dominates thus giving ferromagnetic alignment. The problem, however, is that the complete use of this theory is never possible because of the complexities of calculating the Wannier functions. Therefore, in practice important terms are left out which cause the results to be unsatisfactory.

A number of semi-empirical rules have been developed which are based at least partially on the suggestions in the original paper by Anderson⁽⁴⁸⁾ on superexchange. The most successful of these are those referred to as the Kanamori-Goodenough rules^(49,50,51). These rules suggest the sign and the relative magnitude of the exchange depending on the physical orientation of the magnetic orbitals of the cations and the orbitals of the ligands. While these rules have enjoyed reasonable success for the majority of the 3d shell ions they do not give a good quantitative estimate for the strength of the exchange.

Recently, two groups have independently developed a technique for

calculating superexchange magnitudes, which while based on the approach of Kramers, give much better results with less complicated calculations. The discussion in this Chapter will be based on and taken from that of Jansen and his coworkers⁽⁵²⁾ because of their emphasis on insulating, Cu^{2+} -like (unfilled 3d orbitals) compounds. However, Matsen and his group⁽⁵³⁾ have developed nearly the same formalism.

As with Kramers, the basic unit used by Jansen is the three-center, four-electron cluster with the zeroth-order wavefunctions being those of the individual isolated ions. By choosing correctly symmetrized but not orthogonal basis functions the exchange interaction shows up in the first order of a Rayleigh-Schrodinger perturbation calculation. Their technique automatically includes not only the superexchange between the cation electrons through the diamagnetic ligand but also the direct exchange between cations. It may further include the indirect exchange between magnetic electrons on the cation with the valence shell electrons of that cation and then the valence shell-valence shell direct exchange between neighboring cations. This last term has been shown to be important in the exchange for 4f shell cations^(52c). For 3d shell ions their work has indicated that the indirect valence shell exchange is not important nor is it necessary to include terms in the perturbation expansion higher than first order.

This method has been shown to have wide applicability for many different cations and has successfully predicted the magnitude of the

superexchange interaction better than any previous theory. (For a complete list of its applications see reference 12 in reference 43 of this thesis.) Of particular importance to the work reported herein are the results of de Jongh and Block⁽⁵⁴⁾ which detail the results of a linear M-X-M superexchange configuration calculation where $M = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+} and $X = \text{F}^-$ and Cl^- . Using the technique of Jansen they were able to obtain not only the experimentally known cation-cation distance dependence of the superexchange and the correct ratio of the exchange strengths between the various cations, but also, they accurately reproduced the known values for the superexchange interaction within a few percent for many compounds which have the above configuration.

B. The Two-Halide Superexchange Calculation

Basically, the approach is to use a Rayleigh-Schrodinger exchange perturbation technique on an appropriate cluster of magnetic and diamagnetic ions. The zeroth-order wavefunctions are those of the isolated ions and are represented by 1s Slater orbitals. Because these functions are not orthogonal, the exchange effect is seen in first order rather than third order as in the approach of Kramers. This greatly simplifies the calculation and also eliminates some of the errors associated with carrying the calculation to higher orders⁽⁴³⁾. An effective electron

model is used which is also a major simplification.

The main assumptions on which this theory is based are:

1) The exchange interaction is assumed to be weak so that a perturbation calculation can be used and the unperturbed free-ion wavefunctions can be assumed as the zeroth-order approximation.

2) The essential characteristics of the exchange are contained in the permutation symmetry of the Hamiltonian while the spatial symmetries are of lesser importance.

3) The magnetic properties are not dependent on the number of unpaired electrons, so long as there is at least one, but rather on the 'size' of the ions. This allows the replacement of the unpaired electrons on the magnetic ion by a single 'effective' electron. Likewise, on the diamagnetic ligand a spin-pair of electrons represents the closed shell orbitals. The orbital extension parameter of the Slater orbital partially reflects the number of electrons by representing the size of the ions.

4) It is assumed that the exchange interactions are of sufficiently short range such that a small number of ions can be used as a cluster to represent the overall interaction. This, along with assumption 3), form the basis of the often used three-center, four-electron model. For our purposes we extend this to a four-center, four-electron model.

5) Finally, we assume for these compounds that the exchange interactions in one direction of the crystal do not influence the exchange in

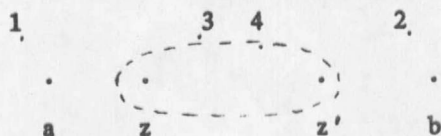
another direction.

With these assumptions in mind we start as usual for a Rayleigh-Schrodinger perturbation calculation by dividing the total Hamiltonian, H , into a zeroth-order part, H_0 , and an interaction term, V . The potential term contains all interionic coulomb interactions including those between electrons on different centers, the electrons on one center and the nuclei of a different center, and the nucleus-nucleus interactions. For the case of four electrons on four centers, V looks like:

$$V = e^2 \left[r_{13} + r_{14} + r_{23} + r_{24} + r_{12} - (r_{1b} + r_{2a} + r_{3a} + r_{4a} + r_{3b} + r_{4b} + r_{1z} + r_{1z'} + r_{2z} + r_{2z'}) + r_{ab} + r_{az} + r_{az'} + r_{bz} + r_{bz'} \right] \quad (4.1)$$

where r_{ij} means $1/r_{ij}$ for this equation.

a and b refer to the two magnetic ions each with one electron and z and z' refer to the centers of the diamagnetic ligand which has a spin-pair of electrons. Diagrammatically this looks like the following:



The numbers refer to the electrons. For the four-center case the ligand is represented as a molecular orbital. The zeroth-order wavefunctions corresponding to the isolated ions are given by the 1s Slater orbitals:

$$a=(\lambda^3/\pi)^{1/2}\exp(-\lambda r_a)$$

$$z=(\mu^3/\pi)^{1/2}\exp(-\mu r_z)$$

$$b=(\lambda^3/\pi)^{1/2}\exp(-\lambda r_b)$$

$$z'=(\mu^3/\pi)^{1/2}\exp(-\mu r_z')$$

where the letters are as before. The molecular orbital (MO) of the diamagnetic ligand is formed in one of three ways in an effort to study the effects of the different combinations. The three MO's are as follows:

$$\xi_{+}^{(1)} = ZK_1^2 \cdot [z(3) + z'(3)] \cdot [z'(4) + z(4)]$$

$$\xi^{(2)} = ZK_2 \cdot [z(3)z'(4) + z'(3)z(4)]$$

$$\xi^{(3)} = ZK_3 \cdot [z(3)z(4) + z'(3)z'(4)]$$

where the ZK's refer to the appropriate normalizing factor for each. The first MO is the usual formulation and both the bonding (+) and the antibonding (-) orbitals were used. The second orbital is called the 'covalent' orbital because it stresses the sharing of the electrons by both of the nuclei of the anions. The last orbital listed is referred to as 'ionic' since it enhances the separation of the two anions. The orbital extension parameters λ and μ are determined from the self-consistent field (SCF) calculations of $\langle r^2 \rangle$ by Herman and Skillman⁽⁵⁵⁾ and the diamagnetic susceptibilities of the closed and open shells of the ions. This procedure is outlined more fully in Appendix C. 1s Slater orbitals were chosen because it has been shown that⁽⁵⁶⁾ higher order orbitals yielded very similar results. Next, if we ignore initially the

exchange effects we can write the groundstate of the subsystems as a simple product function of the isolated orbitals,

$$\phi_0 = a(1)b(2)\xi_i, \quad (4.2)$$

where $i=1, 2$, or 3 . Taking into consideration the Pauli principle for the isolated ions the groundstate eigenfunctions become the simple product functions times a spin function $\phi_0\sigma$. (σ is an eigenfunction of the spin operator S^2 and since H neglects spin-dependent terms, S^2 commutes with H and H_0 .) Because we have chosen $1s$ orbitals, l is 0 for all subsystems, thus L equal 0 and the eigenfunction $\phi_0\sigma$ is non-degenerate.

The Pauli principle requires that the total wavefunction of the system be antisymmetric. The groundstate eigenfunctions can be used to form this correctly symmetrized basis state by application of the antisymmetrizer of Eqn. 4.5. However, the Hamiltonian is now no longer of the same symmetry as the new basis functions. This can be corrected by transforming the operators H_0 and V into permutation invariant operators by using the antisymmetrizer and the operator A which, when acting on the projected eigenfunctions of H_0 , $A\phi_k\sigma$, gives back the original $\phi_k\sigma$. A is given by the expression,

$$A = \frac{1}{N!} \sum \epsilon P_{nn'n''n'''\dots}$$

where $P_{nn'}$ is a permutation operator of the symmetric group S_N and ϵ is the usual function which has the value ± 1 depending on whether an even or odd number of permutations are made. Thus we have

$$\tilde{H}_0 = A H_0 A$$

and

$$\tilde{V} = A V A.$$

This transformation is spectrum conserving which means that the projected eigenfunctions

$$\Psi_{k,\sigma} = A \phi_{k,\sigma} / \langle A \phi_{k,\sigma} | A \phi_{k,\sigma} \rangle, \quad (4.3)$$

which are now eigenfunctions of $\tilde{H}$, have the same eigenvalues as the original eigenfunctions, $\phi_{k,\sigma}$, of H_0 .

This then gives the first order interaction energy as

$$E_{0,\sigma}^{(1)} = \langle A \phi_{0,\sigma} | A V A | A \phi_{0,\sigma} \rangle / \langle A \phi_{0,\sigma} | A \phi_{0,\sigma} \rangle, \quad (4.4)$$

a formidable looking equation. This can be simplified however to the following expression which involves the singlet or triplet projection operator $P_{S,T}$:

$$E_0^{(1)} = \langle \phi_0 | P_{S,T} V | \phi_0 \rangle / \langle \phi_0 | P_{S,T} | \phi_0 \rangle, \quad (4.5)$$

The details of how to get from the Eqn. 4.9 to Eqn. 4.10 are given in Appendix D. With this expression we can now calculate the exchange energy. First, recall that for the magnetic case of one unpaired elec-

tron per magnetic center there can only be two possible spin states, a singlet (S) and a triplet (T), for a cluster with only two cations. As shown in Appendix D, P for these two states is:

$$P_S = (I - P_{13} - P_{23} - P_{13,24})(I + P_{12})$$

$$P_T = (I - P_{13} - P_{23})(I - P_{12})$$

where the individual permutation operators have the usual meaning, i.e., I is the identity permutation, P_{12} exchanges electrons 1 and 2, and $P_{13,24}$ exchanges electrons 1 and 3 then exchanges electrons 2 and 4, etc. In first order then we have, from Eqn. 4.3

$$2J = (1/n^2)(E_S - E_T)$$

$$= (1/n^2)(\langle \phi_0 | P_S V | \phi_0 \rangle / \langle \phi_0 | P_S | \phi_0 \rangle - \langle \phi_0 | P_T V | \phi_0 \rangle / \langle \phi_0 | P_T | \phi_0 \rangle) \quad (4.6)$$

Recall that the zeroth-order energies are equal, i.e. $E_S^{(0)} = E_T^{(0)}$ and that it has been shown that first order theory is sufficient^(28b,30). Also notice that n refers to the number of unpaired electrons on the magnetic ions. This renormalizes the calculation to the actual number of magnetic electrons on the cations.

The last equation allows us to evaluate the exchange energy to first order for a given cluster. The explicit form of all of the individual integrals which appear in Eqn. 4.6 are given in Appendix E. Then in Appendix F the computer program used to calculate J is printed. The

results of these calculations using the three molecular orbitals given earlier are presented and discussed in the next Chapter.

CHAPTER V. DISCUSSION AND CONCLUSIONS

Table VI gives the important values for the intraplane and the interplane structural and exchange parameters. Notice that the values of J are all relatively constant throughout the series, not varying by more than about 10K. That amount of variation is somewhat larger than that found in the MA_2 series and there is no satisfactory explanation of that fact. It is not unreasonable to consider that there may be at least a weak coupling between the intraplane and the interplane exchange in these compounds, thus perhaps explaining the wider variation of the intraplanar exchange in the EDA series. More will be suggested later about how to investigate this possibility.

As has been mentioned, the interesting and at least initially surprising result of studying this series is the large interplane interaction found. The exchange effectively goes from a 1d antiferromagnet to a 3d antiferromagnet then to a 2d ferromagnet as first the anion is changed (Br^- to Cl^-) and then the interlayer distance is increased. A more useful method of viewing this for the $CuCl_4$ compounds is to compare the natural logarithm of J' to the natural logarithm of the distance between the interlayer copper ions, d_{out} , as in Figure 15a. Except for BDA a straight line may be drawn through the data with a slope of -16 ± 2 . This value represents the first direct measurement of the linear two-halide bridge and should be compared to the empirical suggestion of de Jongh et al.^(54,57) that each additional superexchange anion will de-

TABLE VI. Out-of-plane distances ($\text{\AA}$) and exchange values (K) for the EDA series.

$(\text{NH}_3(\text{CH}_2)_n\text{NH}_3) \text{CuX}$		d_{out}	d_{Cl}	T_c	J/k_B	$R=J'/J$	Ref.
n=2	X= Cl_2Br_2	8.3 ± 0.1	3.7 ± 0.1	45.0 ± 4.0	15.0 ± 1.0	-2.1	this work
n=2	X= Cl_4	8.11	3.63	34.0 ± 1.0	20.0 ± 2.0	-0.3 to 1	a).
				31.5 ± 0.5	23.0 ± 1.0	-0.6	b).
n=3	X= Cl_4	8.94	4.60	14.9 ± 0.2	16.5	-0.1	a).
		9.12		13.5	15.4	0	c).
						-0.1	this work
n=4	X= Cl_4	9.04	5.00	8.85 ± 0.1	13.0 ± 1.0	-0.012	d).
n=5	X= Cl_4	11.5 ± 0.4	6.6 ± 0.4	7.6 ± 0.2	14.1	-0.0028	a).

a). H. von Känel, Physica 96B, 167 (1979).

b). L. O. Snively, P. L. Seifert, K. Emerson, and J. E. Drumheller, Phys. Rev. B20, 2101 (1979).

c). D. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. 15, 3147 (1976).

d). L. O. Snively, J. E. Drumheller, and K. Emerson, Phys. Rev. B23, 1 (1981).

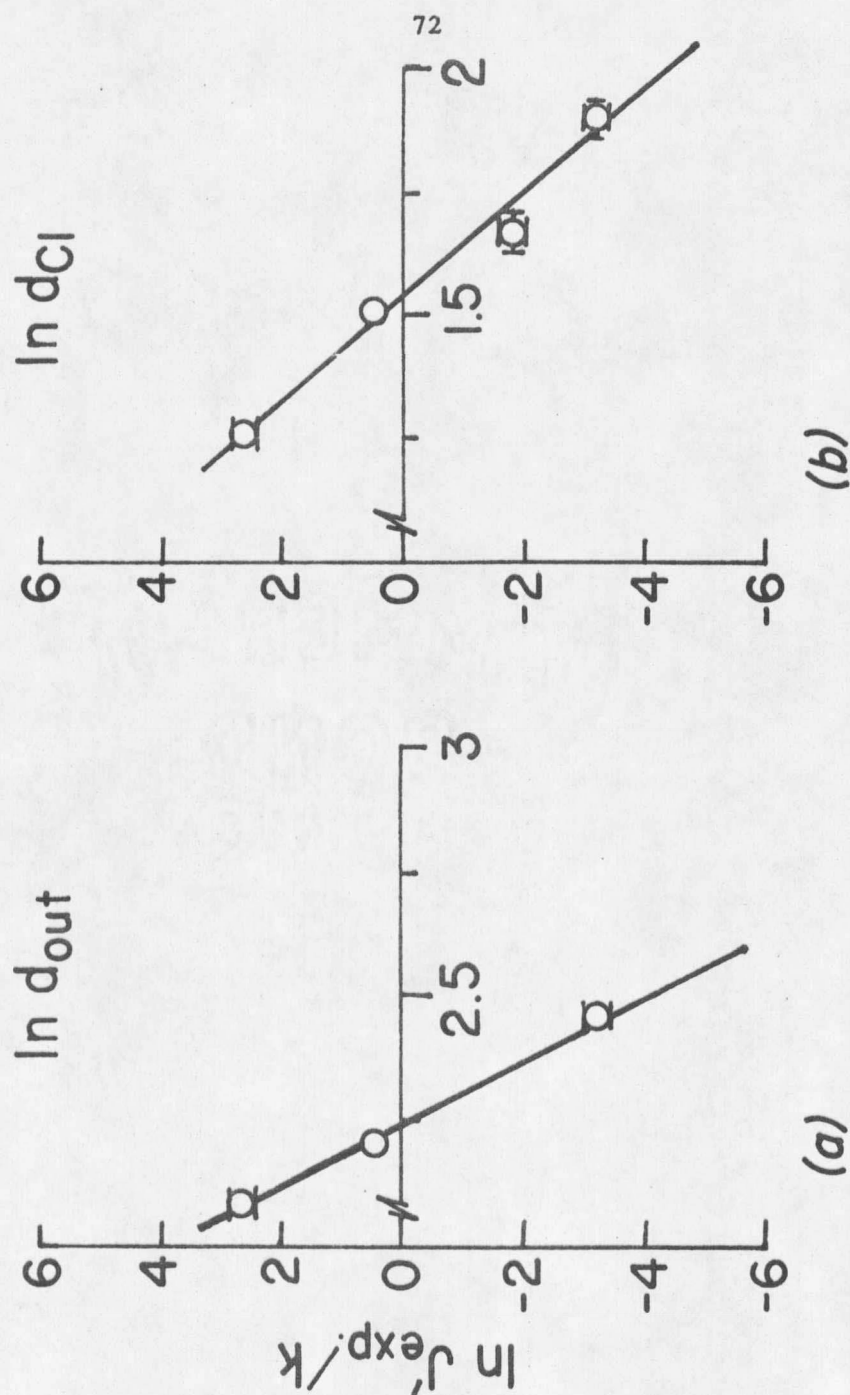


FIGURE 15. a). natural logarithm of J'_{exp} vs. natural logarithm of d_{out} for the EDA CuCl_4 series. Slope of the line is -16 ± 2 .
 b). $\ln J'_{\text{exp}}$ vs. $\ln d_{\text{Cl}}$ for the same series. Slope of the line through the data is -10 ± 2 .

crease the magnitude of the single-halide interaction by a factor of 10^{-2} . Thus, our result appears to require a revision of the estimate that the exchange through a two anion path goes as $r^{-12} \cdot 10^{-2}$. However, it is not a matter of simply redefining the constant that multiplies the single anion exchange behavior of r^{-12} since, as will be discussed, d_{out} (The notation is not standardized. d_{out} and r refer to the same distance in this case.) may not be the appropriate distance to consider for two-halide superexchange in the first place.

Strong evidence for this last statement is found from the failure of BDA to fall on the straight line through the data. As was seen in the structural data, BDA does not have an expected increase in its inter-layer distance. We believe as mentioned earlier⁽²⁴⁾ that this is because the organic chain buckles. Regardless of the reason for that buckling, the question must be asked as to why the magnetic interaction decreases as though the separation were larger.

One possible explanation is that the exchange path in BDA is not exactly linear because of the 13° shearing of the adjacent layers. There is evidence from the superexchange calculations of van Kalker et al.⁽⁴³⁾ that the exchange does weaken in nonlinear exchange paths. However, it would not be expected to decrease the interaction by as large an amount as the data shows it does.

A better explanation seems to be that it is not the cation distance that is critical to the strength of the superexchange but rather the

halide-halide separation, d_{Cl} . Figure 15b shows a plot similar to that of 15a except that the important distance is now the $Cl^- - Cl^-$ spacing. Notice that all 4 data points lie nearly on a line indicating that in fact it may be the anion-anion overlap that is the primary parameter dictating the superexchange strength. Remember that even though the layers shear in BDA, the Cu^{2+} octahedra retain their orientation with respect to the plane. Thus, d_{Cl} increases in this compound compared to PDA whereas d_{out} does not. Now, the fact that BDA shows only slightly weaker exchange than its separation would indicate may be explained by its nonlinear exchange path as was suggested above.

Other authors have not totally ignored the importance of the anion-anion interaction. Von Känel⁽⁴⁰⁾ presents one of the strongest statements where he calls the overlap of the Cl^- anions crucial to the magnitude of the exchange for the EDA series. However, he basically makes only that one comment. Evidence is given by Algra et al.⁽⁵⁸⁾ that the anion-anion overlap is important in the Co-Cl-Cl-Co path in Cs_2CoCl_4 . However, that bridge is far from being linear and thus it introduces considerable complications when trying to assign a specific path to the exchange. Because of that they only make the claim that the anion-anion overlap plays a role in the overall exchange interaction, new quantitative estimates for its strength were not presented. Algra et al.⁽⁵⁹⁾ make a similar statement concerning the importance of the anion-anion overlap in the more nearly linear path of Co-O-O-Co in the com-

pound $(C_5H_5NO)_6Co(ClO_4)_2$. Unfortunately, in neither case are they able to compare directly the effects of varying the anion-anion separation as we have done. Also, van Kalker et al.^(52d) attempted to calculate the behavior of manganese pyrites using a nonlinear two-halide bridge, although their efforts were not entirely successful.

One further conclusion which is tempting to draw, but probably erroneous, is that the superexchange through a two-halide bridge can be stronger than it is for a single-halide bridge. The data from EDA $CuCl_2Br_2$ seem to support this. However, it should be mentioned that the ferromagnetic superexchange that occurs in the planes of the Cu^{2+} series is somewhat misleading. Experimental^(1,30) and theoretical^(15,18,19) evidence abound which show that 180° superexchange interactions are and should be antiferromagnetic. The fact that the copper chloride layers are ferromagnetic is a rare exception. Kugel and Khomskii⁽⁶⁰⁾ have shown that the ferromagnetic interaction in those planes is due to the Jahn-Teller distortion of the Cu-Cl bonds. Recall that this asymmetry was pictured in Figure 2. Without the distortion the expected value for J would be on the order of $-200K$ ⁽⁶¹⁾!

Now we will turn briefly to the results of the theoretical calculation of Chapter IV. It was anticipated before the calculation was attempted that the approach of using a four-center, four-electron model was not the best possible choice. However, considering the much greater computational problems involved in doing the four-center, six-electron

cluster it was thought wisest to begin on a more modest scale. Table VII presents the results obtained from the model calculations along with the extension parameters used and the appropriate distances for EDA, PDA, PentDA, and for the mixed chloride-bromide EDA. Because the calculation is only valid for a 180° exchange path, J' was not found for BDA since the bridge is not sufficiently linear. Clearly, the results are completely unacceptable for the usual molecular orbital and for the 'covalent' orbital. While a much more extensive investigation would be necessary to show this conclusively, it appears as though this indicates that the anions are not bonding to each other in any significant way. Thus, the suggestion made earlier by this author⁽²⁷⁾ that the anions were behaving as a single superexchange anion does not seem to be supported by this simple theory.

As can also be seen in Table VII the results for the ionic case are not acceptable either as far as the absolute values for the exchange. However, this orbital does reproduce the qualitative behavior of the series. First, the magnitude of the exchange for the Br^- ion is larger than that for the Cl^- ion by a ratio of 2.1:1. The ratio for the measured values is also 2.1:1. Second, the exchange does decrease in going through the series from EDA to PentDA as shown in Figure 16a. The format is the same as the previous $\ln\text{-}\ln$ plot of the exchange values vs. distances. The slope of the line in Figure 16a is approximately -19 which is relatively far from that found from the data for the $\text{Cu}^{2+}\text{-Cu}^{2+}$

TABLE VII. Experimental and calculated interplane superexchange values for the EDA series compounds. The orbital extension parameters used for the calculation were: $\lambda(\text{Cu}^{2+})=1.0 \text{ au}^{-1}$, $\mu(\text{Cl}^-)=0.7 \text{ au}^{-1}$, and $\mu(\text{Br}^-)=0.6 \text{ au}^{-1}$. The four calculated values for each compound correspond to the molecular orbitals: (1) $a(1)b(1)[z(3)+z(4)]$ (two values for bonding (+) and antibonding (-)), (2) $a(1)b(2)[z(3)z'(4)+z'(3)z(4)]$, and (3) $a(1)b(2)[z(3)z(4)+z'(3)z'(4)]$. $1 \text{ au} = 0.529 \text{ \AA}$. Distances are in angstroms and exchange constants are in degrees Kelvin.

$(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{CuCl}_x\text{Br}_y$	d_{out}	d_{Cl}	$J'_{\text{cal.}}/\text{k}$	$J'_{\text{exp.}}/\text{k}$
n=2 x=2 y=2	15.7	7.0	(1) + -198 - -288 (2) +23 (3) -2.3	-31
n=2 x=4 y=0	15.3	6.9	(1) + -176 - -217 (2) -171 (3) -1.1	-13.7
n=3 x=4 y=0	17.1	8.7	(1) + -195 - -205 (2) -540 (3) -0.15	-1.6
n=5 x=4 y=0	21.0	12.5	(1) + -190 - -182 (2) -662 (3) -0.003	-0.04

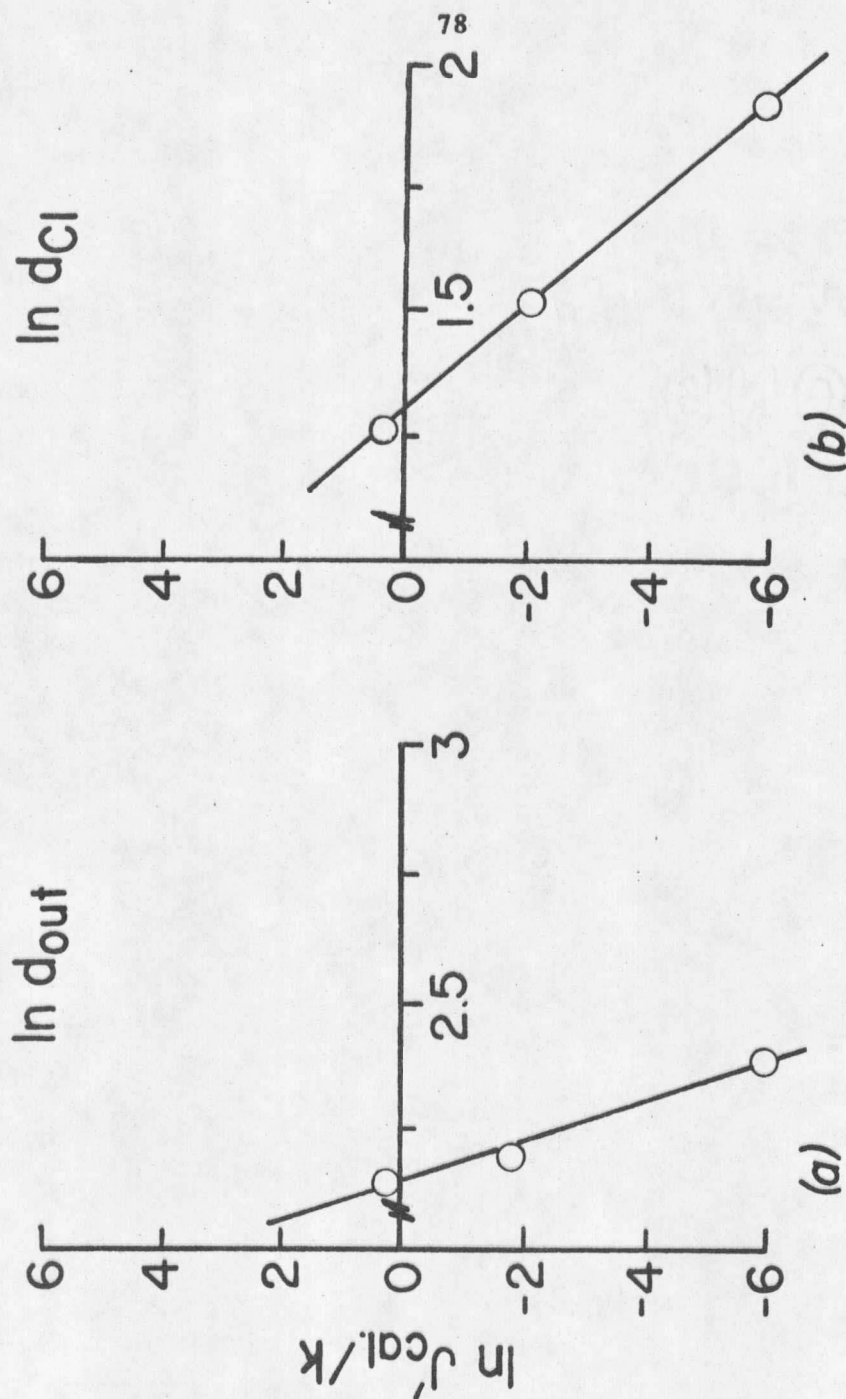


FIGURE 16. a). natural logarithm of $J'_{\text{cal.}}$ vs. natural logarithm of d_{out} for the EDA CuCl_4 series. Slope of the line is -19. b). $\ln J'_{\text{cal.}}$ vs. $\ln d_{\text{Cl}}$ for the same series. Slope of the line through the points is -10.

separation. Contrariwise, the slope of the line through the data in Figure 16b for the $\text{Cl}^- - \text{Cl}^-$ distance is approximately -10 which is exactly the same as the value for the slope of the line for the experimental data in Figure 15b, -10 ± 2 . Obviously, this analysis is not sufficient to support the contention that the anion-anion overlap is the critical parameter in the two-halide exchange. On the other hand, it is an encouraging indication that perhaps the results for the 'ionic' orbital offers the promise that further calculations with this technique are warranted.

With regard to that last statement one interesting point to note from the above calculations is that the orbital which gives the correct qualitative behaviour is also the one which is closest to the concept of a four-center, six-electron cluster. A simpleminded idea may be used to explain why that is the case. As mentioned in Chapter IV the reason for the name 'ionic' is because that orbital in some sense 'localizes' both electrons of the spin-pair on either one or the other anion, whereas, the remaining two orbitals enhance the 'sharing' of the two electrons by the anions. In the case of the four-center, six-electron cluster each anion would be represented by its own spin-pair of electrons, thus making the separation of the two anions even more complete than is done by using the ionic orbital.

B. Possible Future Research

The work which has been presented in this thesis suggests a number of possible directions for future research. One of the main areas of research needed is not related to the physics of the two-halide interaction but rather to the more complete determination of the crystal structure of the mixed halide series compounds. When the structures are known better the magnetics of the mixed series will presumably lead to another set of data with which the 'statistics' of the present results can be improved upon simply because of additional data points.

However, as hinted at previously in this Chapter, a more interesting and possibly useful study involving both the mixed series and the related fully bromated series might be that of understanding the coupling which may or may not occur between the intralayer and the interlayer exchange interactions. Extending the measurements already made to include these two series would give a wide range of exchange ratios with which to look at the effects of any coupling between the two exchange directions using a 'one parameter' at a time approach.

Another interesting problem has recently presented itself with the synthesis of the isostructural compound, EDA NiCl_4 , by Skarup and Berg⁽⁶²⁾. Besides determining the crystal structure of the compound they also made susceptibility measurements of it in the temperature region from 45K to room temperature, although they did not carry through with

an analysis of the magnetic properties. Typically, Ni^{2+} behaves as an antiferromagnet and may be either 2d or 3d depending upon the structure it resides in. From the shape of their rather sketchy data, however, it seems that the Ni^{2+} in EDA NiCl_4 is behaving in a manner significantly different from that usually expected of an antiferromagnet. Besides simply completing the study of another isostructural cation in the EDA series (as mentioned previously Mn^{2+} and Fe^{2+} (63) have been studied also) this fact warrants a more careful investigation of the magnetic properties of this compound.

Finally, as mentioned earlier, further first principle calculations using the method outlined in Chapter IV would be quite useful. Even with the massive bookkeeping difficulties associated with the four-center, six-electron problem, the results presented earlier make proceeding with the calculation appear to be worthwhile. If appropriate simplifications are made, the problem could become tractable and its successful completion would add significantly to the understanding of two-halide superexchange in insulators.

SUMMARY

Presented in this thesis is the first thorough, experimental investigation of a simple, two-halide superexchange bridge in transition metal with the primary emphasis on the behavior of the exchange as a function of the cation-cation distance and separately as a function of the anion-anion separation. It is shown that the strength of the superexchange through a two-halide bridge appears to depend more critically on the overlap of the anions rather than on the simple cation-cation distance as has been previously suggested. Specifically, the interaction is shown to go as the 10^{th} power of the halide-halide separation. An attempt is made to calculate the magnitude of the superexchange using an extension of a relatively simple technique. While the method gives poor quantitative results it does reproduce the measured anion-anion distance dependence of the superexchange.

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APPENDICES

APPENDIX A. COEFFICIENTS OF VARIOUS HIGH TEMPERATURE SERIES EXPANSIONS

The following tables contain the coefficients for a number of HTSE's. The parameters Θ and ϵ were chosen because they enhance the differences between a square-planar Heisenberg interaction and various other interactions including 1-d, 3-d, Ising, and X-Y like behavior. Θ is the usual Curie-Weiss parameter and ϵ is a measure of the deviation from square-planar behavior. Table A.I. contains the usual $\chi T/C$ expansions. Table A.II. gives the coefficients for the $T \ln(\chi T/C)$ HTSE's which are more useful in this case because that form is especially sensitive to the departure from a square-planar model.

The form of the expansions are as follows:

$$\chi T/C = \sum_i a_i[\epsilon](\Theta/T)^i$$

and

$$T \ln(\chi T/C) = \sum_i b_i[\epsilon](\Theta^i/T^{i-1}) .$$

The coefficients a_i and b_i are functions of ϵ and are given in the tables as such. For example a coefficient of $a_2 = 1 - 9\epsilon - 15\epsilon^2 - 7\epsilon^3$ is written as -9, -15, -7 where $\epsilon^0 = 1$ has been suppressed since it occurs in all terms. If a particular power of ϵ is zero with a nonzero power later it is explicitly given to avoid confusion. Otherwise, the entry is left blank. Leading coefficients which are the same for all models are given with the column heading. A '?' indicates that the remaining fourth order

terms were too complex to generate in a finite amount of time. Note, however, that the leading term of $\varepsilon^0=1$ still remains.

The direction of $\underline{H}$, the magnetic field, and the sign of ε are also given for each model. The designation DM refers to a Dzyaloshinsky-Moriya model with the number indicating which particular DM model. (See ref. 38 for more details.) AH means 'anisotropic Heisenberg' with Z implying that the $\hat{z}$ direction is the unique direction, and R implying that it is the $\hat{r}^{ij}$ direction that is favored. SQU, DIA, and REC refer to a square-planar (no second-neighbor), a diagonal second-neighbor, and a rectangular second-neighbor lattice respectively implying the obvious additional interaction direction. Similarly, ECL and STA refer to models in which the lattices are either eclipsed or staggered as discussed in Chapter III, again including second-neighbor interactions.

In the case of SQU the remaining 6 terms of the expansion have been calculated by Baker et al.⁽³⁴⁾ and have been rewritten for the TlnXT/C form as follows: a_5 through a_{10} 0.08333, -0.57916, 0.08888, 0.71716, -3.73442, 1.85941.

All expansions were generated or derived by Ms. Patton Seifert from her work or from the appropriate sources referenced earlier in Chapter III.

TABLE A.I. Coefficients for the XT/C expansions. Note that for all models $a_0=a_1=1$. N means normal to the plane and IN means in the plane.

Model	Sign of ε	Direction of $\underline{H}$	$(1/2)a_2$	$(1/6)a_3$	$(13/192)a_4$
SQU	$\varepsilon=0$	N			
ECL	ANY	ANY	-2,-3	-9,-15,-7	-15.7,-16.15,27.8,31.2
STA	ANY	ANY	-2,-1.5	-9,-7.875,1.125	-15.7,-6.7,7.6,3.14
REC	+	ANY	-2	-6	-2.77,13.85
DIA	ANY	ANY	-2,-2	-5.25,-1.5,3.75	-1.845,19.4,27.8,7.38
AHZ	ANY	N	-2	-9	6.77,12.3
AHZ	ANY	IN	-2	-9,-14	?
AHR	ANY	N	-2,-2.67	-9,-14	?
AHR	ANY	IN	-2,-13.33	-9,-76,-32	?
DMO	+	N	-2	-6.375	?
DMO	+	IN	-2	-7.5	?
DM1	+	N	-2	-9	6.77,12.3

TABLE A.I. (continued)

Model	Sign of ε	Direction of H	$(1/2)a_2$	$(1/6)a_3$	$(13/192)a_4$
DM1	-	IN	-2	-3.75	?
DM2	+	N	-2	-9	11.7, 12.3
DM2	+	IN	-2	-22.5	?
DM4	+	N	-2	-9	16.6, 12.3
DM4	+	IN	-2	-9.75	?
DM5	+	N	-2	-9	9.24, 22.2
DM5	-	IN	-2	6	?
DM6	+	IN	-2	-4.5	?
DM8	-	IN	-2	-15	?

TABLE A.II. Coefficients for the TlnXT/C expansions. For these models $b_0=0$ and $b_1=1$. The sign of ε and the direction of H are the same for each model as the previous Table A.I.

Model	$(-)b_2[\varepsilon, \varepsilon^2]$	$(-1/2)b_3[\varepsilon, \varepsilon^2, \varepsilon^3]$	$(5/192)b_4[1, \varepsilon, \varepsilon^2, \varepsilon^3, \varepsilon^4]$
SQU	0,0	0,0,0	0,0,0,0
ECL	1,1.5	1,2,1	-2.4,6,36,37.8
STA	1,0.75	1,1.125,0.375	-2.4,-0.6,-1.8,-2.67
REC	1,0	0,0,0	12,16.8
DIA	1,1	-0.25,-1.5,-1.25	-19.2,79.2,120
AHZ	1,0	1,0,0	56,12.8
AHZ	1,1.33	1,2,0	?
AHR	1,1.33	1,2	?
AHR	1,6.67	1,12,2.67	?
DMO	1,0	0.125,0	?
DMO	1,0	0.5,0,0	?

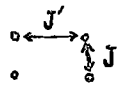
TABLE A.II. (continued)

Model	$(-)b_2[\varepsilon, \varepsilon^2]$	$(-1/2)b_3[\varepsilon, \varepsilon^2, \varepsilon^3]$	$(5/192)b_4[1, \varepsilon, \varepsilon^2, \varepsilon^3, \varepsilon^4]$
DM1	1,0	1,0,0	56,12.8
DM1	1,0	-2.875,0	?
DM2	1,0	1,0,0	68.8,12.8
DM2	1,0	5.5,0,0	?
DM4	1,0	1,0,0	81.6,12.8
DM4	1,0	1.25,0,0	?
DM5	1,0	1,0,0	62.4,38.4
DM5	1,0	-4,0,0	?
DM6	1,0	-2,0,0	?
DM8	1,0	3,0,0	?

The following table describes how J , J' , and D^2 depend on θ and ε .

If useful a clarifying statement or picture accompanies the entry. For both of the AHZ and AHR models J , corresponds to $J_{//}$ and J' to $J_{\perp}$. Also, as indicated in the heading, only the coefficient is given for D^2 when the whole term is the coefficient times $\theta^2\varepsilon$.

TABLE A.III. Relationship between the parameters Θ and ε and the exchange energies J , J' , and D^2 .

Model	J	J'	$D^2 [\Theta^2 \varepsilon]$	Comments
SQU	$\Theta/2$	0	0	
ECL	$(\Theta/2)(1+\varepsilon)$	$-\Theta\varepsilon$	0	
STA	$(\Theta/2)(1+\varepsilon)$	$(-1/4)\Theta\varepsilon$	0	
REC	$(\Theta/2)(1+\sqrt{2\varepsilon})$	$(\Theta/2)(1-\sqrt{2\varepsilon})$	0	
DIA	$(\Theta/2)(1+\varepsilon)$	$(-1/2)\Theta\varepsilon$	0	
AHZ	$(\Theta/2)(1+4\varepsilon)$	$\Theta/2$	0	$J=J_{ }$, $J'=J_{\perp}$ $\varepsilon=-1/4$: X-Y
AHZ	$\Theta/2$	$(\Theta/2)(1+4\varepsilon)^{1/2}$	0	$\varepsilon=-1/4$: Ising
AHR	$(\Theta/2)(1+4\varepsilon)$	$(\Theta/2)(1-4\varepsilon)$	0	$\varepsilon=1/4$: X-Y; $\varepsilon=-1/4$: Ising
AHR				same as AHZ with $H_{ }\hat{z}$
DM0	0	0	6/7	
DM0	0	0	3/4	
DM1	0	0	-3/8	
DM1	0	0	1	same for all with $H_{ }\hat{z}$
DM2	0	0	3	same for DM6
DM4	0	0	3/4	
DM5	0	0	-3/2	same for DM8

APPENDIX B. HP9825A PROGRAMS FOR DATA REDUCTION

The two HP9825A programs which were used to reduce and manipulate the magnetization and susceptibility data are given in this appendix. The first program, JFIT, determines by the method of least squares and the Fisher F test the parameters which produce a best fit to the corrected magnetization data. It is important that the data read by the program contain all corrections such as empty sample holder offset and the diamagnetic corrections for that particular sample.

The second program, the susceptibility data plotting routine, also includes the data loading program which puts the data on tape in the proper format for use by both this program and JFIT and at the same time does the appropriate corrections to the raw data after querying the user for the necessary information. The other options available in this program are for plotting the data on the CRT, printing the data on the thermal printer, calculating and displaying a HTSE model curve, and correcting errors in the input data. The plot option further allows the user to display both the data and the generated curve in one of three formats: χ/C vs. T , C/χ vs. T , and $C/\chi T$ vs. J/kT . The program prompts the user for all necessary inputs.

Finally, the last page of printout is a listing of the special function keys and their definitions. These are used for the plotting routine and must be loaded into key memory before using that program.

```

0: "JFIT improve
ment":
1: ent "Enter
order polynomia
l.",M
2: dim T[100],
A[M],Z[100,M],
Y[100],B[M],
C[M],P[M,M],
Q[M,M],D[M],
E[4,2]
3: dim F[1],H#[6
0],X#[402],A#[1
],G[100],X[M,
100],H[1,M]
4: 2÷D[1];0÷D[2]
÷D[3];.416667÷D
[4]
5: trk 1;ent
"Which file
are the data
in?",r2
6: ldf r2,H#,X#;
itf(X#[1,2])÷N;
trk 0
7: prt "Data
for";prt H#[18,
29];spc
8: prt "taken
on";prt H#[30,
38];spc
9: if M>4;for
I=5 to M;ent
D[I];next I
10: ent "A guess
at Theta",r6;
stf(H#[10,13])÷
G;stf(H#[2,5])*
1e6÷C
11: dsp "The
value of a is",
G;wait 3000
12: ent "Another
value of a?(y
or n)",A#;if
A#="n";jmp 2
13: "G":ent "New
a?",r3;r3r3C/
GG÷C
14: stf(H#[14,
17])÷H
15: prt "Guess
at theta=",E;
prt "C=",C;prt
"Field was",H;
spc 2
16: for I=3 to
4N-1 by 4;J+1÷J
17: itf(X#[I+2,
I+3])/100÷T[J];
itf(X#[I,I+1])/
100÷G[J]
18: next I
19: for V=1 to N
20: V÷I;1/T[V]÷X
;1÷Z[I,1]
21: for J=2 to M
22: Z[I,J-1]*
X÷Z[I,J];next
J;r6*X÷W;Xr4÷X
23: G[V]T[V]/C+
((1+4W+7.25WW)X
X-(.4+3.4W)X^4)
/3÷r11
24: T[V]*ln(r11)
÷Y[I];next V
25: trn Z÷X;mat
XZ÷P
26: inv P÷Q
27: mat XY÷C;
mat QC÷B
28: 0÷S
29: mat ZB÷G;
ara Y-G÷Y
30: for I=1 to
N;S+Y[I]Y[I]÷S;
next I
31: N-M÷r13;S/
r13÷S;M-1÷r14
32: prt "Fitting
Tln(XT/C) to",
r14,"order poly
nomial in 1/T
gives coefs.:"
33: aprt B
34: ent "Enter
T value for
desired level
of confidence",
W;1÷H
35: for J=1 to
2;2J-1÷L;S÷Q[J,
J]÷X
36: (B[J]-W*rX)*
H÷C[L];(B[J]+W*
rX)*H÷C[L+1]
37: -1/B[1]B[1]÷
H;next J
38: B[2]*H÷r12
39: dsp "From
intercept,theta
is between",
C[1],C[2];wait
5000
40: dsp "From
slope, epsilon
is between",
C[3],"and",C[4]
;wait 5000;.5*
B[1]÷E
41: "FIFTY":
42: for J=1 to
M;D[J]*E÷J-B[J]
÷C[J];next J
43: trn C÷H;mat
PC÷A;mat HA÷F
44: F[1]/S/M÷F[1
]

```

```

45: prt "Using
J=",E,"K gives
F(",M,r13,")=",
F[1];spc 2
46: ent "Type
in another J.
To quit, type
J>900.",E
47: if E<900;
sto "FIFTY"
48: ent "Another
a value?(y or
n)",A$;if A$="y
"sto "G"
49: "TWO":ent
"Enter coef of
(Theta**3)*Epsi
lon in B[3].",
r7
50: if r7>10;
sto "4-TERM"
51: B[1]r7+E
52: (Q[3,3]+Q[2,
3]*E*2+Q[2,2]*
E*E)*2+X
53: (B[3]+B[2]*
E)/rX+G
54: prt "This
model gives
T(",r13,")=",G;
spc 2
55: if abs(G)>W;
jmp -6
56: dsp "Can
not reject this
hypothesis.";
wait 5000
57: ent "Enter
specific value
of Epsilon;>1;
test skipped",H
58: if H>1;jmp -
9
59: B[1]→E
60: "FOUR":B[1]-
E→C[1]
61: "THREE":B[2]
-r7*H*E*E→C[2];
B[3]-r7*H*E↑3→C
[3]
62: trn C→X;mat
PC→A;mat XA→F
63: F[1]/S/3→F[1]
64: F[1]→F
65: prt "With
Theta=",E,"K,
Epsilon=",H,"
model gives
F(",M,r13,")=",
F;spc 2
66: ent "Want
to try another
E?",H
67: if H<1;sto
"THREE"
68: r12→H;ent
"How about anot
her Theta?",E
69: sto "TWO";
if E<=900;sto
"FOUR"
70: "4-TERM":
71: ent "To cont
inue with 4-
term fit,type
<=1",A
72: if A>1;sto
"END"
73: 4→M
74: "EIGHT":ent
"Enter coef.
of E**2 in -
B[2]",E[1,1]
75: ent "E**(1
thru 3) in -
2B[3]",E[2,1],
E[3,1],E[4,1]
76: ent "E**(1
thru 4) in 192/
5*B[4]",E[1,2],
E[2,2],E[3,2],
E[4,2]
77: B[1]→E;r12→H
78: "SEVEN":E-
B[1]→C[1]
79: "SIX":-(H+
E[1,1]*H*H)→C[2]
1;0→C[3]
80: for I=1 to
3;C[3]-.5*E[I+
1,1]*H↑I→C[3];
next I
81: 1→C[4]
82: for I=1 to
4;C[4]+E[I,2]*
H↑I→C[4];next I
83: C[4]/38.4→C[
4]
84: for I=2 to
4;C[I]*E↑I-B[I]
→C[I];next I
85: trn C→H;mat
PC→A;mat HA→F
86: F[1]→F;.25*
F/S→F;prt "For
Theta=",E,"Epsi
lon=",H;spc 2
87: prt "then
F(",M,r13,")=",
F;spc 2
88: ent "Want
to try another
E?",H
89: if H<2;sto
"SIX"
90: r12→H;ent
"How about anot
her Theta?",E
91: if E<900;
sto "SEVEN"

```

```
92: ent "Another  
    model:0=YES?"  
    ,A  
93: if A=0:sto  
    "EIGHT"  
94: ent "Another  
    value for a?(y  
    or n)",A$;if  
    A$="y":sto "G"  
95: "END":prt  
    "THE END":end  
*18
```

0: "Susceptibili
ty Data and
HTSE Plotter":

1:
2: "LOS : May,
1980, Rev. A":

3: "This program
will store
new or print
old magnetizati
on or":

4: "susceptibili
ty vs. temperat
ure data. It
can also then
plot the data":

5: "in either a
X/C or C/XT
format. Various
HTSE or exact
expressions
can":

6: "be used to
generate curves
to compare
with the data."
:

7:
8: "EXEC":

9: "This portion
of the program
initializes
the system and
directs it.":

10: "Initialize"
:dim C,E,G,H,N,
M,T

11: dim B\$(11),
E\$(11),A\$(5),
B(4),C(4,2),
D(4)

12: dim H\$(60),
M\$(402)

13: 0→r11

14: wtb 718,3,
20,13,10,"em::e
n::ex::sn::um::
ux::"

15: fmt 1,/,16"-
",/

16: "List option
s.":spc 2

17: prt "
OPTIONS "

18: wrt 16.1

19: prt "STORE
NEW DATA-0"

20: prt "PRINT
OLD DATA-1"

21: prt "PLOT
DATA -2"

22: prt "CALC.
NEW HTSE-3"

23: prt "RECORD
DATA -4"

24: prt "MODIFY
DATA -5"

25: wrt 16.1

26:

27:

28:

29: "CHOOSE":

30: dsp "Select
a special funct
ion key."istp

31:

32:

33:

34: "STORE":

35: "LOS : May,
1980 ;Rev. A":

36: "This subro
utine will stor
e and/or print
magnetization,
":

37: "susceptibil
ty, and tempera
ture data from
raw magnetomete
r results.":

38: "Also, the
Curie constant,
field, and
other pertinent
values can
be":

39: "stored.
All data are
stored in strin
gs in either
split or intese
r":

40: "precision.
Up to 100 data
pairs can be
stored with
each compound.
HTSE":

41: "values can
also be stored
for future use
with this progr
am.":

42: fmt 1,/,16"-
",/

43: fmt 2,x,f6.2
,3x,f6.2

44: fmt 4,c8,
f8.4

45: fmt 5,c6,
e10.3

46:

47: "Print":

48: ent "Print
data from which
file?",r1,trk

1

```

49: ldf r1,H$,
M$;sps ;wrt
16.1;sps ;trk 0
50: prt "This
compound is";
prt H$[18,29];
sps
51: prt "Data
were taken";
prt H$[30,37];
sps
52: prt H$[38,
60];sps
53: wrt 16.5,"
C= ",stf(H$[2,
5]);sps
54: wrt 16.4,
"SIZE(a):",stf(
H$[6,9]);sps
55: wrt 16.4,"
a= ",stf(H$[10
,13]);sps
56: wrt 16.5,
"H(G)= ",stf(H$
[14,17]);sps
57: itf(M$[1,
2])>N
58: wrt 16.1;
sps
59: if H$[1,1]="
X";prt " X(*
10-6) T(K) ";
sps ;jmp 2
60: prt " M(*10-
2) T(K) ";sps
61: for I=3 to
4N-1 by 4
62: wrt 16.2,
itf(M$[I,I+1])/
100,itf(M$[I+2,
I+3])/100
63: next I;sps 2
64: sto "CHOOSE"
65:
66:
67:
68:
69:
70:
71:
72: "NEW":
73: "Fileheader"
:"hhhhhhhhhhhh">H
$[1,10]
74: dsp "First,
input the exp.
conditions";
wait 5000
75: ent "a=?",G;
ent "H=?",H;
fts (G)>H$[10,
13];fts (H)>H$[
14,17]
76: ent "Number
of millimoles=?
",M
77: ent "Sample
size in grams=?
",S;fts (S)>H$[
6,9]
78: ent "Is this
X (X) or Mas.
(M) data?",H$[1
,1]
79: ent "Type
in the compound
name(<12c).",
H$[18,29]
80: ent "Date
of data run?(mm
/dd/yy)",H$[30,
37]
81: ent "Descrip
tion, ie. powde
r (<23c)",H$[38
,60]
82: 9.383e-5*
GGM>C;fts (C)>H
$[2,5]
83: "Now store
the data after
corrections
for empty sampl
e holder,";
84: "diamagnetis
m, and of cours
e the calibrati
on cconstant
have been made.
";
85: dsp "Input
data in magneto
meter units";
wait 5000
86: ent "What
is the calibrat
ion constant?",
K
87: ent "What
is the diamag.
correction?(in
e(-6) units)";D
88: ent "How
many data pairs
?",N;fti (N)>M$
[1,2]
89: if H$[1,1]="M"
;jmp 6
90: for I=3 to
4N-1 by 4
91: ent "T=",T;
ent "M=",M
92: (M+.001383T†
(-.49)H)K/H*
1e6+D>X;fti
(100X)>M$[I,I+
1]
93: fti (100T)>M
$[I+2,I+3]
94: next I;jmp 6

```

```

95: for I=3 to 4N-1 by 4
96: ent "M=?",M;
   ent "T=?",T
97: (M+.001383T+
   (-.49)H)100K+
   HD/100→M;fti
   (100M)→M#[I,I+
   1]
98: fti (100T)→M
   #[I+2,I+3]
99: next I
100: sto "CHOOSE"
101:
102:
103:
104:
105: "RECORD":
106: "LOS : Max,
   1980":
107: "This porti
   on of the progr
   am will record
   on the designat
   ed file the":
108: "fileheader
   , the corrected
   data, and the
   results from
   the HTSE.":
109:
110: trk 1
111: ent "Store
   in which file?"
   ,r2
112: fdf r2;idf
   r3,r3,r3
113: if r3=0;
   rcf r2,H$,M$;
   jmp 4
114: ent "Data
   in file! Record
   over(y or n)?"
   ,B$
115: if B$="n";
   jmp -4
116: rcf r2,H$,
   M$
117: trk 0;sto
   "CHOOSE"
118:
119:
120:
121: "PLOT":
122: "LOS : Max,
   1980":
123: "This subro
   utine will plot
   X/C vs. T, C/
   X vs. T, or C/
   XT vs. J/kT
   data.":
124: "It will
   automatically
   scale the CRT
   display and
   label it.":
125: fnt 6,f4.0,
   ",",f4.0,";"
126: "First,
   the scale param
   eters and the
   format.....":
127: ent "From
   tape?(y or n)",
   E$;if E$#"y";
   jmp 3
128: esb "LOAD"
129: itf(M#[1,
   2])→N;stf(H#[2,
   5])→C;stf(H#[10
   ,13])→G
130: "G":ent "A
   different value
   of a?(y or
   n)",E$;if E$="n"
   ;jmp 2
131: ent "a(new)
   =?",r12;r12*
   r12C/GG+C
132: esb "AXIS"
133: esb "Format"
134: "Find min.
   and max. X valu
   e within T
   range.":
135: ent "Autosc
   ale?(y or n)",
   E$;if E$="y";
   jmp 6
136: ent "Choose
   upper value
   for y-axis?",r5
137: 0→r6;if
   r4>1;.01→r6
138: if L=0;.01→
   L+r10
139: esb "TScale"
140: jmp 10
141: 0→r5;1000→r
   6
142: for I=3 to
   4N-1 by 4
143: itf(M#[I,I+
   1])/100/C/1e6→X
   ;itf(M#[I+2,I+
   3])/100→T
144: if L<T and
   T<U;jmp 2
145: jmp 3
146: if X>r5;
   X→r5;T→r9
147: if X<r6;
   X→r6

```

```

148: next I
149: asb "SCALE"
150: "Now to
    plot the data..
    ....":
151: wrt 718,
    "ef3,::f1200,
    ::nf3,::"
152: for I=3 to
    4N-1 by 4
153: itf(M$[I,I+
    1])/100+X;itf(M
    $[I+2,I+3])/
    100+T
154: if r10<T
    and T<r7;jmp 2
155: jmp 5
156: X/C/1e6+X;
    if r4=1;jmp 3
157: 1/X+X;if
    r4=2;jmp 2
158: X/T+X;J/T+T
159: cll 'Plot' (
    X,T,S,V,L,r6)
160: next I
161: wrt 718,
    "sn"
162: sto "CHOOSE"
163:
164: "SCALE":
165: if r4=2;
    r5+r8;1/r6+r5;
    1/r8+r6
166: if r4=3;
    r5+r8;1/r6/U+r5
    ;1/r8/r9+r6
167: if r6>r5;
    r5+r1;r6+r5;
    r1+r6
168: "TScale":if
    r4=3;J/L+U;J/
    r7+L
169: U-L+S;r5-
    r6+V
170: cll 'LABEL'
    (L,U,r6,r5,r4)
171: ret
172:
173: "LABEL":
174: fmt 8,f6.2,
    1b
175: wrt 718,
    "f1500,::nf2,
    ::"
176: wrt 718,
    "pe0,::pa500,
    40;"
177: if p5=3;
    jmp 3
178: wrt 718,
    "pe1,::cs1,::tx
    T(K)",char(3)
179: jmp 2
180: wrt 718,
    "pe1,::cs1,::tx
    J/kT",char(3)
181: wrt 718,
    "pe0,::pa60,
    480;"
182: " X/C "+A$;
    if p5>1;" C/X
    "+A$;if p5>2;"
    C/XT"+A$
183: wrt 718,
    "pe1,::cs5,::tx
    ",A$,char(3)
184: wrt 718,
    "pe0,::pa16,0;"
185: wrt 718.8,
    "pe1,::cs0,::tx
    ",p1,3
186: wrt 718,
    "pe0,::pa950,0;"
187: wrt 718.8,
    "pe1,::tx",p2,3
188: wrt 718,
    "pe0,::pa10,16;"
189: wrt 718.8,
    "pe1,::cs4,::tx
    ",p3,3
190: wrt 718,
    "pe0,::pa10,
    950;"
191: wrt 718.8,
    "pe1,::tx",p4,3
192: wrt 718,
    "pe0,::sn,::"
193: ret
194:
195:
196:
197: "Plot":
198: "This is
    the actual plot
    ting routine.":
199: wrt 718,
    "pe0,::"
200: wrt 718.6,
    "pa",1000(p2-
    p5)/p3+20,1000(
    p1-p6)/p4+20
201: wtb 718,
    "pe1,::tx",30,
    3,13,10
202: wrt 718,
    "pe0,::"
203: ret
204:
205:
206: "AXIS":
207: wrt 718,
    "f10000,::nf1,
    ::"
208: wrt 718,
    "pa20,1020;"
209: wrt 718,
    "cs1,::pe1,::pa
    20,20;1020,20;"

```

```

210: wrt 718,
    "pe0,::"
211: for I=20
    to 1020 by 100
212: wrt 718.6,
    "pa",20,I
213: wtb 718,
    "pe1,::tx",12,
    3,13,10
214: wrt 718,
    "pe0,::"
215: next I
216: for I=20
    to 1020 by 100
217: wrt 718.6,
    "pa",I,20
218: wtb 718,
    "pe1,::tx",11,
    3,13,10
219: wrt 718,
    "pe0,::"
220: next I
221: wrt 718,
    "sn:."
222: ret
223:
224: "LOAD":
225: ent "Which
    file are the
    data in?";r11
226: trk 1;ldf
    r11,H$,M$;trk 0
227: ret
228:
229: "CALC":
230: "LOS : May,
    1980":
231: "This subro
    utine will
    calculate, plot
    and/or print
    values for X
    vs. T":
232: "To shorten
    this program
    the models are
    stored in their
    own files.":
233: fnt 1,/,
    16"-",/
234: fnt 6,f4.0,
    ",",f4.0,";"
235: if fls4=0;
    sfs 4;jmp 2
236: jmp 10
237: spc 2;prt
    "      MODELS
    ";wrt 16.1
238: prt "PAT'S
    HTSE      -1"
239: prt "BAKER'
    S 2D HTE-2"
240: prt "EXACT
    1D ISING-3"
241: prt "1D
    HEISENBERG -4"
242: wrt 16.1
243:
244:
245:
246: ent "Do
    you want the
    same model?(y,
    n)";E$;if E$="y.
    ";jmp 4
247: ent "Which
    model do you
    want?";r0
248: 11+F;if
    r0>1;10+F;if
    r0>2;12+F;if
    r0>3;13+F
249: ldf F,302,
    250
251: ent "Plot(p
    ) or print(w)
    the results?",
    B$;if B$="w";
    sto "Cprt"
252: cfs 3;ent
    "Plot with data
    (d) or alone(a)
    ?";B$;if B$="d"
    ;jmp 7
253: asb "AXIS"
254: ent "C=?";
    C,"for a=?";G
255: ent "Choose
    upper value
    for y-axis?";r5
256: 0+r6;if
    r4>1;.01+r6
257: asb "TScale"
    "
258: asb "MODEL"
259:
260:
261: sto "CHOOSE"
    "
262:
263:
264: "CPlot":
265: wrt 718.6,
    "pa",1000(p2-
    p5)/p3+20,1000(
    p1-p6)/p4+20
266: if fls2=0;
    sfs 2;wrt 718,
    "pe1,::"
267: ret
268:
269: "Format":
270: fnt 1,/,
    16"-",/

```

```

271: if f1=0;      288: if F=12;
    sfa 1;jmp 2      prt "1D HTSE"
272: jmp 4          289: if r4=1;
273: wrt 16.1        prt " X/C(1/K)
274: prt " X/C      T(K)";jmp 3
    vs. T -1";      290: if r4=2;
    prt " C/X vs.   prt " C/X(K)
    T -2";prt "C/    T(K)";jmp 2
    XT vs. J/kT -3" 291: prt " C/XT
275: spc ;wrt        vs. J/kT
    16.1;spc 2       292: spc ;asb
276: ent "Which     "MODEL"
    format?";r4      293: if F=11;
277: dsp "What      wrt 16.4,"C=";
    T range do you   C;wrt 16.4,"for
    want to see?";   a=";G
    wait 2000        294: if F=11;
278: ent "Low       wrt 16.4,"Theta
    T=?";L;ent "His  =" ;D;wrt 16.4;
    h T=?";U;U+r7;   "Epsilon=";E
    L+r10            295: if F=10;
279: if r4=3;        wrt 16.4;"J/
    ent "What value  k=";J
    for J/k?";J;     296:
    if L=0;1+L+r10   297:
280: ret            298:
281:                299: wrt 16.1
282: "Cprt":4+0      300: sto "CHOOSE
283: fmt 3,f9.3,     "
    f7.2;fmt 4,c8;   301:
    e8.3;sfa 3;wrt   *13488
    16.1
284: asb "Format
"
285: prt " The
    model is "
286: if F=11;
    prt "PAT'S HTSE
"
287: if F=10;
    prt "BAKER'S
    HTSE"

```

```

f0: *cont "NEW"
f1: *cont "STORE"
f2: *cont "PLOT"
f3: *cont "CALC"
f4: *cont "RECOR
D"
f5: *ldf 13,274,
274
f6: *wtb 718,3,2
0,13,10,"em:en
::ex::sh::um::"
f7: *wrt 718,"pa
0,1000;"
f8: *wrt 718,"pe
1,::cs0,::tx"
f9: dsp "Load pr
ogram to be dis
played.";stp
f10: list#718.1
f11: *wtb 718,3,
13,10,"pe0,::"

```

APPENDIX C. DETERMINATION OF ORBITAL EXTENSION PARAMETERS

De Jongh and Block⁽³⁰⁾ have determined the orbital extension parameters for Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , F^- , and Cl^- . In our analysis we have simply used their values for (Cu^{2+}) of 1.00 au^{-1} and for (Cl^-) of 0.70 au^{-1} . However, it is appropriate to outline the details of how these numbers were derived and to derive the value we used for Br^- . To illustrate the technique the values of Mn^{2+} , Cu^{2+} , F^- , Cl^- , and Br^- will be found.

In their method they gave primary importance to determining the ratios of the other extension parameters to that of F^- . This allowed the values to be consistent and necessitates choosing only one absolute value for the orbital extension parameter for F^- . The ratios are determined by comparing the contributions to the diamagnetic susceptibility of the open shells for the cations and the valence shell for the anions of the SCF expectation values of r^2 , $\langle r^2 \rangle$. The $\langle r^2 \rangle$ values are taken from the SCF calculations of Herman and Skillman⁽⁵⁶⁾. The following relation is used to accomplish the above,

$$\chi_{\text{dia}}^{\text{open}} = (\Sigma \langle r^2 \rangle_{\text{open}} / \Sigma \langle r^2 \rangle_{\text{total}}) \cdot \chi_{\text{dia}}$$

and for the anions, 'valence' replaces 'open'. The χ_{dia} values are taken from the Landolt-Bornstein tables⁽⁶⁴⁾. Now, since for 1s Slater functions it is known that,

$$\langle r^2 \rangle = 3/\lambda^2$$

we then have

$$(\lambda_a/\lambda_b)^2 = \chi_b^{\text{open}}/\chi_a^{\text{open}}.$$

In the case of an anion compared with a cation a factor of 1/2 must appear with χ^{valence} because there are two effective electrons on the anion.

Using the $\langle r^2 \rangle$ values from Table C.I the ratio of $\lambda(\text{Mn}^{2+}) : \lambda(\text{Cu}^{2+})$ is 1:0.90 and for $\mu(\text{F}^-) : \mu(\text{Cl}^-)$ we have 1:0.63. From the Landolt-Bornstein tables they obtain -13.0×10^{-6} for χ_{dia} of F^- and -14.0×10^{-6} for χ_{dia} of Mn^{2+} . Thus $\lambda(\text{Mn}^{2+})/\mu(\text{F}^-) = 0.97$ and the remaining ratios may be obtained trivially. At this point it becomes necessary to assign a particular value to $\mu(\text{F}^-)$ and they chose 1.10 au^{-1} because it gives the best fit to their data. That being the case we have

$$\lambda(\text{Mn}^{2+}) = 1.08 \text{ au}^{-1}$$

$$\lambda(\text{Cu}^{2+}) = 1.00 \text{ au}^{-1}$$

$$\mu(\text{Cl}^-) = 0.70 \text{ au}^{-1}$$

$$\mu(\text{Br}^-) = 0.60 \text{ au}^{-1}$$

where $1 \text{ au} = 0.529 \text{ \AA}$.

TABLE C.I. SCF calculations of the expectation values of $\langle r^2 \rangle$ for the open- and closed-shell electrons of the various cations and anions considered. ($\langle r^2 \rangle$ values are in atomic units.)

	Mn ²⁺	Cu ²⁺	F ⁻	Cl ⁻	Br ⁻
$\langle r_{1s}^2 \rangle$	0.00505	0.00373	0.04	0.011	0.0026
$\langle r_{2s}^2 \rangle$	0.09250	0.06620	1.153	0.230	0.0443
$\langle r_{2p}^2 \rangle$	0.07378	0.05183	1.369	0.197	0.0341
$\langle r_{3s}^2 \rangle$	0.82626	0.58361		2.578	0.3601
$\langle r_{3p}^2 \rangle$	0.92207	0.63675		3.538	0.3751
$\langle r_{3d}^2 \rangle$	1.49209	0.98227			0.4095
$\langle r_{4s}^2 \rangle$					3.1258
$\langle r_{4p}^2 \rangle$					4.8922
$\langle r^2 \rangle$ (3d ⁿ)	7.46	8.84			
$\langle r^2 \rangle$ (val. shell)			10.52	26.38	35.60
$\langle r^2 \rangle$ (total)	15.28	14.28	10.60	28.05	42.97

APPENDIX D. THE SYMMETRIC DOUBLE COSET DECOMPOSITION

Starting with expression 4.4 we can immediately rewrite it as

$$E_{0,\sigma}^{(1)} = \langle \phi_{0,\sigma} | \Delta V | \phi_{0,\sigma} \rangle / \langle \phi_{0,\sigma} | \Delta | \phi_{0,\sigma} \rangle \quad (D.1)$$

because of relation 4.3 and the fact that the transformations used are spectrum conserving. To get from that form of the expression to that of 4.5 the denominator of D.1 will be used as an example since the presence of V does not effect the final result.

Writing out the denominator using the explicit form for Δ we get,

$$(N!)^{-1/2} \sum_{P \in S_N} \epsilon_P \langle \phi_{0,\sigma} | P | \phi_{0,\sigma} \rangle = (N!)^{-1/2} \sum_{P \in S_N} \epsilon_P \langle \phi_0 | P | \phi_0 \rangle \langle \epsilon | P | \epsilon \rangle \quad (D.2)$$

Now, this can be simplified by a symmetric double coset decomposition⁽⁶⁵⁾ of the elements, P , which basically means that the elements can be grouped together in a clever way which makes the calculation much easier.

First, a few definitions might be helpful:

A left coset of a subgroup S of the group G is the set formed by taking any element of G not in S and operating on S from the left, i.e., if $p \in G$ not in S then a left coset of S is pS . (Vice versa for the right coset.)

A double coset of S and T generated by $p \in G$ not in S or T , is

the set SpT .

A symmetric double coset (SDC) generated by P then is the set given by SpS .

For the case of a four-electron problem, S_4 consists of 24 elements, $S_4 = \{I, P_{12}, P_{13}, P_{14}, P_{23}, P_{12,34}, \dots\}$. Let this be broken into a few important subgroups; the main criterion for the subgroups being that they contain the permutation operators of 'like' centers. For example, let

$$S_\alpha = \{I, P_{12}\}, \text{ ie. magnetic ions a and b}$$

$$S_\beta = \{I, P_{34}\}, \text{ ie. diamagnetic ions z and z'}$$

Now form the subgroup which is the direct product of these,

$$H = S_\alpha \circ S_\beta = \{I, P_{12}, P_{34}, P_{12,34}\}.$$

We can look at the SDC's of H by picking a few elements of S_4 . For example, use I , P_{13} , and $P_{13,24}$. (These are then called the generators of the SDC's.) These three are chosen because they involve the interchange of 0, 1, and 2 electrons between the two different subgroups of ions. For I we get,

$$HIH = \{I, P_{12}, P_{34}, P_{12,34}\} = H.$$

Actually, H is generated four times from HIH . The same sort of result occurs for the other two generators,

$$HP_{13,24}H = \{P_{13,24}, P_{14,23}, P_{1423}, P_{1324}\}$$

and

$$HP_{13}H = \{P_{13}, P_{23}, P_{14}, P_{24}, P_{123}, P_{132}, P_{234}, P_{243}, \\ P_{134}, P_{143}, P_{124}, P_{142}, P_{1234}, P_{1432}, P_{1243}, P_{1342}\}.$$

The notation was changed slightly in the above to the usual cyclic form. It should be noticed that every element of S_4 can be generated by those 3 SDC's.

If we now let p represent an element of H (from the left) and q represent an element of H (from the right) then any element of S_4 can be written in the form $p\pi_i q$ where $\pi_i = I, P_{13,24},$ or P_{13} . This can be expressed by the operator identity,

$$\sum_{p \in S_N} \varepsilon_p P = \sum_{p, q \in H} \varepsilon_p p(\pi_1/4 + \pi_2/4 + \pi_3)q$$

Since the effect of $p\pi_i q$ on ϕ_0 and ∇ is easy to determine we can simplify the evaluation of the integral.

Returning to the singlet state of Eqn. D.2 for π_1 (SDC generator I) we have

$$= (1/4)(4!)^{-1/2} \sum_{p, q \in H} \varepsilon \langle \phi_0 | pq | \phi_0 \rangle \langle \sigma | pq | \sigma \rangle$$

where the $1/4$ comes from the fact that the SDC is generated 4 times over and where $\varepsilon = (-1)^{p+q}$. Since the singlet state must be antisymmetric in

the interchange of 1 and 2 and it must be antisymmetric on 3 and 4 (spin-paired orbital)

$$\langle \sigma | pq | \sigma \rangle = (-1)^{p+q} \langle \sigma | \sigma \rangle = (-1)^{p+q}.$$

Also, since ϕ_0 is symmetric in 3 and 4 ($\phi_0 = a(1)b(2)(z(3)z(4) + z'(3)z'(4))$)

$P_{34}\phi_0 = \phi_0$ and $P_{12,34}\phi_0 = P_{12}\phi_0$. The end result is

$$\begin{aligned} & (1/4)(4!)^{-1/2} \cdot 4 \cdot \sum_{p,q \in H} (-1)^{p+q} (\langle \phi_0 | \phi_0 \rangle + \langle \phi_0 | P_{12} | \phi_0 \rangle) ((-1)^{p+q}) \\ & = (3!)^{-1/2} \langle \phi_0 | I + P_{12} | \phi_0 \rangle. \end{aligned}$$

Similar arguments may be used for the remaining two generators (the algebra becomes longer but no more difficult conceptually) and the final result may be written as

$$(4!)^{-1/2} \sum_{p \in S_N} \varepsilon \langle \phi_0 | P | \phi_0 \rangle \langle \sigma | p | \sigma \rangle = \langle \phi_0 | P_S | \phi_0 \rangle$$

where

$$P_S = (6!)^{-1/2} (I - P_{13} - P_{23} + P_{13,24}) (I + P_{12}).$$

The triplet case is nearly the same except that the spin function

is symmetric in 1 and 2 while it is still antisymmetric in 3 and 4. When all of the dust settles from the cranking the triplet projector is

$$P_T = (6!)^{-1/2} (I - P_{13} - P_{23}) (I - P_{12}).$$

For a more detailed discussion of the double coset decomposition and its application to this problem see the more complete development by Block⁽⁶⁵⁾.

APPENDIX E. TWO-CENTER SUPEREXCHANGE INTEGRALS

This appendix contains the explicit exact forms (except for C2) of the two-center exchange integrals used in the two-halide superexchange calculation. It also lists the 3 three-center integrals J4, J5, T1, T2, T3, and T4 which were calculated numerically (along with C2) as well as the four-center integrals F1 and F2. The numerical integrals were done by rewriting the potential in terms of a Neumann expansion and then carrying out the infinite series to an order high enough not to cause an error in the exchange calculation.

A helpful reference which describes many of the techniques used to write the integrals in closed form is the book by J. C. Slater, Quantum Theory of Molecules and Solids, Vol. I, (McGraw-Hill, New York, 1963), p. 22. It describes in detail the transformations needed to simplify the calculations.

The names given to the following integrals are used in the Fortran program EXCHANGE listed in Appendix F where the closed form expressions for them may be found. The wavefunctions a, b, z, and z' refer to the individual wavefunctions described in Chapter IV with the electron numbers 1 through 4 left off since they would be superfluous. The letters in parentheses under the name column are the appropriate intercenter distances involved in the integral and refer to the designations of those distances in the program. Also included in that column are the CALL statements with the parameters which are passed to

the subroutines for the numerical integrations. S=metal-halide distance;
SX=halide-halide distance; R=metal-metal distance; XL= λ and XM= μ .

Integral	Name
$\int ab \, d\tau$ (the 3-d spatial element, $d\tau$,	S1
$\int az = \int bz'$ is implied in all of the following)	S2(S)
$\int az' = \int bz$	S2(S+SX)
$\int a^2/r_b = \int b^2/r_a$	K1
$\int a^2/r_z = \int b^2/r_z'$	K2(S)
$\int b^2/r_z = \int a^2/r_z'$	K2(S+SX)
$\int z^2/r_a = \int z'^2/r_b$	K3(S)
$\int z^2/r_b = \int z'^2/r_a$	K3(S+SX)
$\int ab/r_a = \int ab/r_b$	J1
$\int az/r_a = \int bz'/r_b$	J2(S)
$\int bz/r_b = \int az'/r_a$	J2(S+SX)
$\int az/r_z = \int bz'/r_z'$	J3(S)
$\int bz/r_z = \int az'/r_z'$	J3(S+SX)
$\int az/r_b = \int bz'/r_a$	J ₄ ^a NUMIN1 (XL,XL,XM,S,S+SX)
$\int bz/r_a = \int az'/r_b$	J ₄ ^b NUMIN1 (XL,XL,XM,S+SX,S)
$\int zz'/r_a = \int zz'/r_b$	J ₄ ^z NUMIN1 (XM,XL,XM,SX,S)

$\int az/r_z = \int bz'/r_z$	J_4^z	NUMIN1 (XL, XM, XM, S, SX)
$\int ab/r_z = \int ab'/r_z$	J_5^a	NUMIN1 (XL, XL, XM, S, S+SX)
$\int az'/r_z = \int bz/r_z$	J_5^z	NUMIN1 (XL, XM, XM, S, SX)
$\int a_1^2 b_2^2 d\tau_1 d\tau_2$	(The first two letters are the	D1
$\int a^2 z^2 = \int b^2 z'^2$	first integration, the second	D2(S)
$\int b^2 z^2 = \int a^2 z'^2$	two are the second integration.)	D2(S+SX)
$\int abab$		C1
$\int azaz = \int bz'bz'$	C_2^a	NUMIN2 (XL, XL, XM, S, S+SX)
$\int bzbz = \int az'az'$	C_2^b	NUMIN2 (XL, XL, XM, S+SX, S)
$\int azz^2 = \int bz'^3$		AL(S)
$\int bzz^2 = \int az'^3$		AL(S+SX)
$\int azb^2 = \int a^2 bz'$	T_1^a	NUMIN1 (XL, XL, XM, S, S+SX)
$\int a^2 bz = \int az'b^2$	T_1^b	NUMIN1 (XL, XL, XM, S+SX, S)
$\int azz'^2 = \int bz'z^2$	T_1^z	NUMIN1 (XL, XM, XM, S, SX)
$\int b^2 zz' = \int a^2 zz'$	$T_1^{z'}$	NUMIN1 (XM, XL, XM, SX, S)
$\int abz^2 = \int abz'^2$	T_2^a	NUMIN1 (XL, XL, XM, S, S+SX)
$\int az'z^2 = \int bzz'^2$	T_2^z	NUMIN1 (XL, XM, XM, S, SX)
$\int azbz = \int az'bz'$	T_3^a	NUMIN2 (XL, XL, XM, S, S+SX)

$$\int azz'z = \int bz'zz'$$

$$T_3^z \quad \text{NUMIN2} (XL, XM, XM, S, SX)$$

$$\int abbz = abaz'$$

$$T_4^a \quad \text{NUMIN2} (XL, XL, XM, S+SX, S)$$

$$\int abbz' = abaz$$

$$T_4^b \quad \text{NUMIN2} (XL, XL, XM, S, S+SX)$$

$$\int az'zz' = \int bzz'z$$

$$T_4^z \quad \text{NUMIN2} (XM, XL, XM, SX, S)$$

$$\int azaz' = \int bz'bz$$

$$T_4^{z'} \quad \text{NUMIN2} (XL, XM, XM, S, SX)$$

$$\int abzz'$$

$$F_1 \quad \text{NUMIN3} (XL, XL, XM, XM, 2^\circ S+SX, SX)$$

$$\int azbz'$$

$$F_2^a \quad \text{NUMIN3} (XL, XM, XM, XL, S, S)$$

$$\int az'bz$$

$$F_2^z \quad \text{NUMIN3} (XL, XM, XM, XL, S+SX, S+SX)$$

APPENDIX F. TWO-HALIDE SUPEREXCHANGE PROGRAM

The following Fortran 4+ program was used to calculate the single- and two-halide superexchange interactions given in Chapter V using the theory described in Chapter IV. It was designed specifically to run on the MSU Scientific Subsystem VAX 11/780 computer, however, it should be adaptable to any system which has the capability to utilize double precision variables and functions.

The program will calculate either the single-halide, three-center, four-electron superexchange (by setting the halide-halide distance to zero) or J' for all three two-halide, four-center, four-electron molecular orbitals discussed in Chapters IV and V. The information required consists of the orbital extension parameters λ and μ , the cation-cation and anion-anion separation distances, and the integration grid dimensions. The output consists of the superexchange energy J'/k in units of K. Also, the various subparts of the calculation are given including the values for the integrals (calculated in the three subroutines NUMIN1, 2, and 3 listed following EXCH.FOR), the individual values for the permutation operators, and the values for the energy denominators; all in units of the square of the elementary electron charge, e^2 .

PROGRAM EXCHANGE

C THIS PROGRAM WILL CALCULATE THE EXCHANGE INTEGRAL FOLLOWING THE
 C METHOD OF HANSEN, ET.AL. INPUT REQUIRED ARE THE ORBITAL
 C EXTENSION PARAMETERS AND THE INTER-ION SEPARATIONS. THIS
 C PROGRAM MAY BE USED FOR ONE- OR TWO-HALIDE EXCHANGE.

C The output from this program gives H for all three MO's, the
 C usual, the covalent, and the ionic. It also gives the values
 C for the individual permutation operators and the energy
 C denominators.

IMPLICIT DOUBLE PRECISION (A-H,I,K,O-Z)

COMMON J4,J5,T1,T2,T3,T4,C2,NA,NB,AMX

DIMENSION P(8)

C Following are the initial function definitions.

X0(D)=D*XM

A0(D)=D*(XL+XM)/2.0

B0(D)=D*(XL-XM)/2.0

A1(D)=D*(XL+3.0*XM)/2.0

B1(D)=D*(XL-3.0*XM)/2.0

Z(A)=DEXP(A)-DEXP(-A)

Y(A)=DEXP(A)+DEXP(-A)

EI(X)=-DEXP(X)*(1.+1./X+2./X/X+6./X/X/X+24./X/X/X/X+

C 120./X/X/X/X/X)/X

C FOLLOWING ARE THE INTEGRALS DEFINED AS FCNS. THE TERMS DO
 C NOT INCLUDE NUCLEAR-NUCLEAR INTERACTIONS.

S2(D)=(D**3.0)*XLM*DEXP(-A0(D))*(Z(B0(D))*(1./A0(D)+

C 1./A0(D)/A0(D)-1./B0(D)/B0(D))+Y(B0(D))/B0(D))

C /A0(D)/B0(D)/2.0

K2(D)=(1.-DEXP(-2.*XL*D))*(1.+XL*D))/D

K3(D)=(1.0-DEXP(-2.0*X0(D))*(1.0+X0(D)))/D

J2(D)=0.5*D*D*XLM*DEXP(-A0(D))*(Z(B0(D))*(1./A0(D)-

C 1./B0(D))+2.*DEXP(B0(D)))/A0(D)/B0(D)

J3(D)=D*D*XLM*DEXP(-A0(D))*(Z(B0(D))*(1./A0(D)+1./B0(D))

C -2.*DEXP(-B0(D)))/2.0/A0(D)/B0(D)

D2(D)= D*D*(XM**3.0)*0.5*((2.0*DEXP(-X0(D))/(X0(D)**3.0))

C *(DEXP(X0(D))-DEXP(-X0(D))*(1.0+X0(D)))

C -(DEXP(-2.0*A0(D))/8.0/A0(D)/B0(D))*(Z(2.*B0(D))*(1./A0(D)

C -1./B0(D))+4.*DEXP(2.*B0(D))+D*XL*(Z(2.*B0(D))*(1./A0(D)

C +0.5/A0(D)/A0(D)-0.5/B0(D)/B0(D))+Y(2.*B0(D))/B0(D)))

AL(D)=.5*D*D*XLM*((DEXP(-A0(D))/A0(D)/B0(D))*(Z(B0(D))*(1./A0(D)

C +1./B0(D))-2.*DEXP(-B0(D)))

C -(DEXP(-A1(D))/A1(D)/B1(D))*(Z(B1(D))*(1./A1(D)+1./B1(D))

C -2.*DEXP(-B1(D))+D*XM*(Z(B1(D))*((1./A1(D)

C +1./A1(D)/A1(D)-1./B1(D)/B1(D))+Y(B1(D))/B1(D)))

C The units for the following inputs are, lambda and mu- inverse au;
C distances- au.

WRITE (6,10)

10 FORMAT (' LAMBDA,MU,A-B SEPARATION,CL-CL SEPARATION')

READ (5,20) XL,XM,R,SX

20 FORMAT (4F6.3)

WRITE (6,30)

30 FORMAT (' THE NUMBER OF UNPAIRED ELECTRONS?')

READ (5,40) N

40 FORMAT (I2)

C The next statement asks for the integration grid sizes and the upper

C limit for the alpha integration. Typical values are 300,200, and 9.0.

WRITE (6,42)

42 FORMAT (' ALPHA GRID, BETA GRID, MAX ALPHA)

READ (5,44) NA,NB,AMX

44 FORMAT (2I4,F4.1)

S0=R/2.0

S=S0-SX/2.0

XL=(XL*XM)**1.5

X=R*XL

INDEX=0

GI=1.0

Z0=DEXP(-SX*XM)*(1.+SX*XM+SX(SX*XM*XM/3.))

C NOW DEFINE THE REMAINING EXACT 1 AND 2 CENTER INTEGRALS.

S1=(1.+X+X*X/3.)*DEXP(-X)

S1X=(1.+X+X*X/3.)*DEXP(X)

K1=(1.-DEXP(-2.*X)*(1.+X))/R

J1=XL*(1.+X)*DEXP(-X)

D1=0.5*DEXP(-X)*(2.*Z(X)-X*DEXP(-X)*(2.75+1.5*X+X*X/3.))/R

C1=6.*(S1*S1*(0.57722+DLOG(X))+S1X*S1X*EI(-4.*X)

C -2.*S1*S1X*EI(-2.*X))/X

C1=(-DEXP(-2.*X)*(-3.125+5.75*X+3.*X*X+X*X*X/3.))+C1)/5.

C THE NEXT SECTION CALLS THE APPROPRIATE SUBROUTINES TO

C CALCULATE THE REMAINING INTEGRALS.

CALL NUMIN1 (XL,XL,XM,S,SX+S)

J4S=J4

J5S=J5

T1S=T1

T2S=T2

CALL NUMIN2 (XL,XL,XM,S,S+SX)

T3S=T3

T4S=T4

C2S=C2

CALL NUMIN1 (XL,XL,XM,S+SX,S)

J4SX=J4

T1SX=T1

CALL NUMIN2 (XL,XL,XM,S+SX,S)

T4SX=T4

C2SX=C2

IF (SX .EQ. 0.0) GO TO 1000

C THIS SECTION DEFINES AND GENERATES THE ODDBALL INTEGRALS
C THAT SHOW UP.

CALL NUMIN2 (XL,XM,XM,S,SX)

T3Z=T3

T4ZSP=T4

CALL NUMIN1 (XL,XM,XM,S,SX)

J4ZSP=J4

J5Z=J5

T1Z=T1

T2Z=T2

CALL NUMIN1 (XM,XL,XM,SX,S)

J4Z=J4

T1ZSP=T1

CALL NUMIN2 (XM,XL,XM,SX,S)

T4Z=T4

CALL NUMIN3 (XL,XM,XM,XL,S,R,S,SX,2)

F2A=T3

CALL NUMIN3 (XL,XM,XM,XL,S+SX,R,S,SX,3)

F2Z=T3

CALL NUMIN3 (XL,XL,XM,XM,R,R,S,SX,1)

F1=T3

C THIS SECTION COMBINES THE INTEGRAL INTO THE COMPLETE
C HALIDE-HALIDE INTEGRALS FOR EACH PARTICULAR MO.

GO TO 2000

C AND FINALLY THE SINGLET AND TRIPLET STATES ARE FORMED
C AND THE RESULTS CALCULATED.

98 T0=P(1)-P(2)-P(3)-P(4)+P(5)+P(6)

```

ES0=P(1)-P(2)-P(3)+P(4)-P(5)-P(6)+P(7)+P(8)
T=T0/ZM
ES=ES0/ZN
J=(ES-T)*315885./(2.*DFLOAT(N*N))
90  FORMAT (' Results for the BONDING MO',/)
91  FORMAT (' Results for the ANTIBONDING MO.',/)
92  FORMAT (' Results for the COVALENT MO.',/)
93  FORMAT (' Results for the IONIC MO.',/)
94  FORMAT (' Results for the Single-halide case.',/)
WRITE (6,100) J,ES,T
100  FORMAT (' J(K)=',F12.6,' SINGLET AND TRIPLET=',2F10.6)
WRITE (6,110) ZN,XM
110  FORMAT (' THE ENERGY DENOMINATORS FOR S AND T ARE',2F10.6)
WRITE (6,120) P(1),P(2),P(4)
120  FORMAT (' P1,P2,P4 ARE',3F10.6)
WRITE (6,125) P(5),P(7)
125  FORMAT (' P5 AND P7 ARE',2F10.6,/,/)
IF (SX .EQ. 0.0) GO TO 200
INDEX=INDEX+1
GO TO (2000,3000,4000,200) INDEX
GO TO 200

```

C This subprogram calculates J for the simple linear single-halide case.

```

1000  S2T=S2(S)
      K3T=K3(S)
      J3T=J3(S)
      D2T=D2(S)
      C2T=C2S
      XLT=AL(S)

```

T2T=T2S

T3T=T3S

V=1.0/R+2.0/S+2.0/(S+SX)

K2T=K2(S)

J2T=J2(S)

J4T=J4S

J5T=J5S

T1T=T1S

T4T=T4S

C NEXT THE INTEGRALS ARE COMBINED TO MAKE EACH PERMUTATION
C TERM (WITH THE N-N INTERACION).

P(1)=D1+4.0*D2T-2.0*(K1+2.0*(K2T+K3T))+V

P(2)=C2T+S2T*(2.0*(T1T+XLT-J2T-2.0*(J3T+J4T))-

C S2T*(-D2T+K1+2.0*(K2T+K3T)-V))

P(3)=P(2)

P(4)=C1+S1*(4.0*T2T-(4.0*S1*K3T+2.0*J1+4.0*J5T))

C +S1*S1*V

P(5)=S1*T3T+S2T*(2.0*T4T+S2T*(T2T-J1-2.0*(J5T))

P(5)=P(5)+S1*S2T*(XLT-2.0*(J3T+J4T)-J2T-S2T*2.0*K3T)

P(5)=P(5)+V*S1*S2T*S2T

P(6)=P(5)

P(7)=S2T*S2T*(2.0*C2T+3.0*T3T-S2T*(2.0*(J2T+2.0*(J3T+J4T))

C -V*S2T))

P(8)=P(7)

ZN=1.0-2.0*S2T*S2T*(1.0+S1-S2T*S2T)+S1*S1

ZM=1.0-2.0*S2T*S2T*(1.0-2.0*S1)-S1*S1

WRITE (6,94)

GO TO 98

C This subprogram calculates J for the usual (anti)/bonding MO. That MO
C has the form, $(z(3)+z(4))(z'(3)+z'(4))$

```
2000 Z01=(1.0+GI*Z0)**0.5
      ZK=1.0/(1.414213562373095*Z01)
      S2A=ZK*(S2(S)+GI*S2(S+SX))
      S2B=GI*S2A
      K3T=ZK*ZK*(K3(S)+K3(S+SX)+2.0*GI*J4Z)
      J3T=ZK*(J3(S)+GI*J3(S+SX))
      D2T=ZK*ZK*(D2(S)+D2(S+SX)+2.0*GI*T1ZSP)
      C2T=ZK*ZK*(C2S+C2SX+2.0*GI*T4ZSP)
      XLT=ZK*ZK*ZK*(AL(S)+T1Z+2.0*T4Z+GI*(AL(S+SX)+T2Z+2.0*T3Z))
      T2T=ZK*ZK*(2.0*T2S+GI*2.0*(F1)
      T3T=ZK*(ZK*(2.0*T3S+GI*(F2A+F2Z))
      V=1.0/R+2.0/(S+SX)+2.0/S+1.0/SX
      K2T=(K2(S)+K2(S+SX))
      J2T=ZK*(J2(S)+GI*J2(S+SX))
      J4T=ZK*(J4S+GI*J4SX)
      J5T=J5S
      J4ZSPT=ZK*J4ZSP
      J5ZT=ZK*J5Z
      T1T=ZK*(T1S+GI*T1SX)
      T4T=ZK*(T4S+GI*T4SX)
```

C NEXT THE INTEGRALS ARE COMBINED TO MAKE EACH PERMUTATION
C TERM (WITH THE N-N INTERACION).

```
P(1)=D1+4.0*D2T-2.0*(K1+K2T+2.0*K3T)+V
```

```

P(2)=C2T+S2A*(2.0*T1T+XLT-J2T-J3T-2.0*J4T-(J4ZSPT+GI*J5ZT)
C -S2A*(-D2T+K1+K2T+2.0*K3T-V))
P(3)=P(2)
P(4)=C1+S1*(4.0*T2T-(4.0*S1*K3T+2.0*J1+4.0*J5T))
C +S1*S1*V
P(5)=S1*(T3T+S2A*GI*XLT)+S2A*T4T+S2B*(GI*T4T+S2A*(T2T-J1))
P(5)=P(5)-(S1*S2A*(GI*(J4T+J3T)+J5ZT+GI*J4ZSPT)
C +S1*S2B*(J2T+J4T))
P(5)=P(5)-S1*S2A*S2B*(2.0*K3T-V)-(S2A*S2B*J5T*2.0)
P(6)=P(5)
P(7)=S2A*S2B*3.0*T3T+(S2A*S2A+S2B*S2B)*C2T
P(7)=P(7)-S2A*S2B*(S2A*(GI*(J2T+2.0*J4T+J3T+J4ZSPT)+J5ZT)+
C S2B*(2.0*J4T+J2T+J3T+J4ZSPT+GI*J5ZT))
P(7)=P(7)+S2A*S2A*S2B*S2B*V
P(8)=P(7)
ZM=1.0-S2A*S2A-S2B*S2B-S1*S1+2.0*S1*S2A*S2B
ZN=1.0-S2A*S2A-S2B*S2B+S1*S1-2.0*S1*S2A*S2B+2.0*S2A*S2A*S2B*S2B
IF (INDEX.EQ. 1) GO TO 2001
WRITE (6,90)
GI=-1.0
GO TO 98
2001 WRITE (6,91)
GO TO 98

C This subprogram calculates J for the COVALENT MO which has the
C form,  $z(3)z(4)+z'(3)z'(4)$ .
3000 Z01=(1.0+Z0*Z0)**0.5
ZK=1.0/(1.414213562373095*Z01)
S2A=S2(S)

```

$$S2B=S2(S+SX)$$

$$SA=S2A+S2B*Z0$$

$$SB=S2B+S2A*Z0$$

$$SAB=S2A*S2B$$

$$SA2=S2A*S2A$$

$$SB2=S2B*S2B$$

$$SAAB=SAB*S2A$$

$$SABB=SAB*S2B$$

$$SABZ=2.0*SAB*Z0+SA2+SB2$$

$$SABZ0=2.0*SAB+Z0*(SA2+SB2)$$

$$SA3B=S2A*(SA2+SB2)$$

$$SB3A=S2B*(SA2+SB2)$$

$$K3T=(K3(S)+K3(S+SX)+2.0*Z0*J4Z)$$

$$K3T0=K3(S)*SB2+K3(S+SX)*SA2+2.0*J4Z*SAB$$

$$J3T1=J3(S)*SA+SB*J3(S+SX)$$

$$J3T2=J3(S)*SB+SA*J3(S+SX)$$

$$D2T=D2(S)+D2(S+SX)+2.0*Z0*T1ZSP$$

$$D2T0=D2(S)*SB2+D2(S+SX)*SA2+2.0*SAB*T1ZSP$$

$$C2T=C2S+C2SX+2.0*Z0*T4ZSP$$

$$C2T0=C2S*SB2+C2SX*SA2+2.0*SAB*T4ZSP$$

$$XLT1=S2A*(T1Z+T4Z)+S2B*(T2Z+T3Z)$$

$$XLT2=S2B*(T1Z+T4Z)+S2A*(T2Z+T3Z)$$

$$T2T=2.0*(T2S+Z0*F1)$$

$$T3T=2.0*T3S+Z0*(F2A+F2Z)$$

$$V=1.0/R+2.0/(S+SX)+2.0/S+1.0/SX$$

$$K2T=(K2(S)+K2(S+SX))$$

$$J2T1=J2(S)*SA+J2(S+SX)*SB$$

$$J2T2=J2(S)*SB+J2(S+SX)*SA$$

$$J4T1=J4S*SA+J4SX*SB$$

J4T2=J4S*SB+J4SX*SA

J5T=J5S

T1T=T1S*SA+T1SX*SB

T4T=T4S*SA+T4SX*SB

C NEXT THE INTEGRALS ARE COMBINED TO MAKE EACH PERMUTATION
C TERM (WITH THE N-N INTERACION),

P(1)=D1+4.0*D2T*ZK*XK-2.0*(K1+K2T+2.0*K3T*ZK*ZK)+V

P(2)=ZK*ZK*(C2T+2.0*T1T+XLT1+D2T0-((K1+K2T)*SABZ+2.0*K3T0+J2T1
C +J3T1+J4ZSP*SA+J5Z*SB+J4T1*2.0)+V*(SA2+SB2+2.0*SAB*Z0))

P(3)=J(2)

P(4)=C1+ZK*ZK*S1*4.*T2T-S1*(4.*S1*K3T+2.*J1+4.*J5T)
C +S1*S1*V

P(5)=ZK*ZK*(2.0*(T4T+T2S*SAB)+F1*(SA2+SB2)+S1*(T3T+XLT2)

C -(S1*(2.0*((K3(S)+K3(S+SX))*SAB+J4Z*(SA2+SB2)))

C +J2T2+2.0*J4T2+J3T2+J4ZSP*SB+J5Z*SA)+(J1+2.0*J5T)*SABZ0)

C +V*S1*(2.0*SAB+Z0*(SA2+SB2)))

P(6)=P(5)

P(7)=ZK*ZK*((SA2+SB2)*(F2A+F2Z)+2.0*SA2*(C2S+F2A)

C +2.0*SB2*(C2SX+F2Z)

C +4.0*SAB*(T4ZSP+T3A)-(4.0*(J4A*SA3B+J4B*SB3A)+2.0*(J2(S)*SA3B+

C J2(S+SX)*SB3A)+2.0*(SA3B*(J3(S)+J4ZSP)+SB3A*(J3(S+SX)+J5Z)))

C +V*(SA2*SA2+SB2*SB2+2.0*SA2*SB2))

P(8)=P(7)

ZN=1.0+S1*S1-ZK*ZK*2.0*((1+Z0)*(S2A+S2B)**2.0-(SA2*SB2)**2.0)

ZM=1.0-S1*S1-ZK*ZK*2.0*((1-Z0)*(S2A-S2B)**2.0)

WRITE (6,92)

GO TO 98

C This subprogram calculates the IONIC MO exchange integral. It
 C looks like, $z(3)z'(4)+z'(3)z(4)$.

```

4000 Z01=(1.0+Z0*Z0)**0.5
      ZK=1.0/(1.414213562373095*Z01)
      S2A=S2(S)
      S2B=S2(S+SX)
      SA=S2A+S2B*Z0
      SB=S2B+S2A*Z0
      SAB=S2A*S2B
      SA2=S2A*S2A
      SB2=S2B*S2B
      SAAB=SAB*S2A
      SABB=SAB*S2B
      SABZ=2.0*SAB*Z0+SA2+SB2
      SABZ0=2.0*SAB+Z0*(SA2+SB2)
      K3T=(K3(S)+K3(S+SX)+2.0*Z0*J4Z)
      K3T0=K3(S)*SB2+K3(S+SX)*SA2+2.0*J4Z*SAB
      J3T1=J3(S)*SA+SB*J3(S+SX)
      J3T2=J3(S)*SB+SA*J3(S+SX)
      D2T=D2(S)+D2(S+SX)+2.0*Z0*T1ZSP
      D2T0=D2(S)*SB2+D2(S+SX)*SA2+2.0*SAB*T1ZSP
      C2T=C2S+C2SX+2.0*Z0*T4ZSP
      C2T0=C2S*SB2+C2SX*SA2+2.0*SAB*T4ZSP
      XLT1=S2A*(AL(S)+T4Z)+S2B*(AL(S+SX)+T3Z)
      XLT2=S2B*(AL(S)+T4Z)+S2A*(AL(S+SX)+T3Z)
      T2T=2.0*(T2S+Z0*F1)
      T3T=2.0*T3S+Z0*(F2A+F2Z)
      V=1.0/R+2.0/(S+SX)+2.0/S+1.0/SX

```

$$K2T=(K2(S)+K2(S+SX))$$

$$J2T1=J2(S)*SA+J2(S+SX)*SB$$

$$J2T2=J2(S)*SB+J2(S+SX)*SA$$

$$J4T1=J4S*SA+J4SX*SB$$

$$J4T2=J4S*SB+J4SX*SA$$

$$J5T=J5S$$

$$T1T=T1S*SA+T1SX*SB$$

$$T4T=T4S*SA+T4SX*SB$$

C NEXT THE INTEGRALS ARE COMBINED TO MAKE EACH PERMUTATION
C TERM (WITH THE N-N INTERACION).

$$P(1)=D1+4.0*D2T*ZK*ZK-2.0*(K1+K2T+2.0*K3T*ZK*ZK)+V$$

$$P(2)=ZK*ZK*(C2T+2.0*T1T+XLT1+D2T0-((K1+K2T)*SABZ+2.0*K3T0+J2T1$$

$$C +J3T1+J4ZSP*SA+J5Z*SB+J4T1*2.0)+V*(1+Z0)*(SA2+SB2))$$

$$P(3)=P(2)$$

$$P(4)=C1+ZK*ZK*S1*4.*T2T-S1*(4.*S1*K3T+2.*J1+4.*J5T)$$

$$C +S1*S1*V$$

$$P(5)=ZK*ZK*(2.0*(T4T+T2S*SAB)+F1*(SA2+SB2)+S1*(T3T+XLT2)$$

$$C -(S1*(2.0*((K3(S)+K3(S+SX))*SAB+J4Z*(SA2+SB2))+J2T2+2.0*J4T2$$

$$C +J3T2+J4ZSP*SB+J5Z*SA)+(J1+2.0*J5T)*SABZ0)$$

$$C +V*S1*(1+Z0)*(SA2+SB2))$$

$$P(6)=P(5)$$

$$P(7)=ZK*ZK*(4.0*SAB*T3S+2.0*C2T0$$

$$C +2.0*(2.0*SAB*T3S+SA2*F2Z+SB2*F2A)$$

$$C -2.0*(3.0*(J2(S)*SABB+J2(S+SX)*SAAB)+2.0*(J3(S)+J4ZSP)*SABB$$

$$C +2.0*(J3(S+SX)+J5Z)*SAAB+3.0*(J4S*SABB+J4SX*SAAB))$$

$$C +4.0*V*SA2*SB2)$$

$$P(8)=P(7)$$

$$ZN=1.0+S1*S1-ZK*ZK*2.0*(1+Z0)*(SA2+SB2)*(1+S1)+8.0*ZK*ZK*SA2*SB2$$
$$ZM=1.0-S1*S1-ZK*ZK*2.0*(1+Z0)*(SA2+SB2)*(1-S1)$$

WRITE (6,93)

GO TO 98

200 STOP

END

SUBROUTINE NUMIN1 (XLA,XLB,XLZ,S,SX)

C NUMERICAL PROGRAM TO DO 3 CENTER COULOMB

C INTEGRALS FOR SUPEREXCHANGE CALCULATION.

C THE INTEGRALS ARE J4,J5,T1,T2 AND THEIR VARIANTS.

C THE FORMAT FOR THESE INTEGRALS IS THE FOLLOWING:

C $a=(XLa^{**3}/\pi)^{*}\exp(XLa^{*}Ra)\mu b=(Xlb^{**3})^{**}.5{*}\exp(XLb^{*}S/2{*}SQ)\mu etc.$

C A----- S -----Z--- SX ---B

C AND SQ IS THE DISTANCE FROM THE INT. PT TO B

IMPLICIT DOUBLE PRECISION (A-H,J,O-Z)

DIMENSION DUM1(4),DUM2(4),DUM3(4)

COMMON J4,J5,T1,T2,T3,T4,C2,NA,NB,AMX

C=(AMX-1.)/NA

D=2.0/NB

A=1.+C/2.

A0=S*(XLA+XLZ)/2.

B0=S*(XLA-XLZ)/2.

DO 20 I=1,4

DUM1(I)=0.0

DUM2(I)=0.0

DUM3(I)=0.0

20 CONTINUE

DO 200 I=1,NA

B=(D/2.0)-1.0

DO 100 L=1,NB

AB=A*A+B*B

SQ=(AB+4.*SX*(SX+S)/S/S-2.*A*B*(1.+2.*SX/S))**0.5

E4=A*A-B*B

DUM1(1)=DEXP(-B*B0)

DUM1(1)=E4*DUM1(1)/SQ

```

DUM12=DEXP(-S*(XLA*(A+B)+XLB*SQ)/2.0)
DUM1(2)=DUM12*(A+B)
DUM1(3)=DEXP(-S*XLB*SQ)
DUM1(3)=(1.-DUM1(3)*(1.+S*XLB*SQ/2.))*DUM1(1)
DUMS=DEXP(-S*XLZ*(A-B))
DUM1(4)=DUM12*(A+B)*(1-DUMS*(1.+S*XLZ*(A-B)/2.))
DO 50 K=1,4
DUM2(K)= DUM1(K)*D+DUM2(K)
DUM1(K)=0.0
50 CONTINUE
B=B+D
100 CONTINUE
Y=DEXP(-A*A0)
DUM2(1)= DUM2(1)*Y
DUM2(3)=DUM2(3)*Y
DO 150 K=1,4
DUM3(K)= DUM2(K)*C+DUM3(K)
DUM2(K)=0.0
150 CONTINUE
A=A+C
200 CONTINUE
J4=(S*S*DUM3(1)*((XLA*XLZ)**1.5))/2.
J5=(DUM3(2)*S*S*(XLA*XLB)**1.5)/2.
T1=(S*S*DUM3(3)*((XLA*XLZ)**1.5))/2.
T2=(DUM3(4)*S*S*(XLA*XLB)**1.5)/2.
WRITE (6,1020) J4,J5,T1,T2
1020 FORMAT (4F10.6)
RETURN
END

```

SUBROUTINE NUMIN2 (XLA,XLB,XLZ,R,RO)

C 3CENTER, A PROGRAM TO CALCULATE A 3 CENTER COULOMB

C INTEGRAL FOR MAGNETIC EXCHANGE CALCULATION

C FOR DETAILS SEE L. SNIVELY

C (A)_____ (Z)_____ (B)

C LAMBDA=A,B EXPONENT μ MU=Z EXPONENT

C THETA=ANGLE BETWEEN A-Z AND Z-B AXES

IMPLICIT DOUBLE PRECISION (A-H,J,O-Z)

DIMENSION XI(7),XJ(7),XK(7),XL(7),E(7),P(5),Q(5),P1(5),W(2),XN(2),
CA1(5),A22(5),A3(5),A4(5),D(20),B(20),BP(5),D1(5),D2(5),F(7),G(7)

COMMON J4,J5,T1,T2,T3,T4,C2,NA,NB,AMX

X=(XLA+XLZ)*R/2.0

Y=(XLA-XLZ)*R/2.0

X1=DEXP(-X)

D(1)=1.0

E(1)=1.0/X

B(1)=1.0

B(2)=0.0

D(2)=Y

DO 5 I=2,7

E(I)=E(I-1)/X

5 CONTINUE

DO 10 KI=3,20

B(KI)=B(KI-2)/(KI*(KI-1))

D(KI)=D(KI-1)*Y

10 CONTINUE

IS=1

DO 20 KI=1,7

XDUM=0.0

```

      NJ=21-KI
      DO 15 KJ=1,NJ
      XDUM=XDUM+D(KJ)*B(KJ)
      B(KJ)=B(KJ+1)*DFLOAT(KJ)
15  CONTINUE
      XI(KI)=XDUM*2.0*IS
      IS=-IS
      20 CONTINUE
C  B=INTEGRAL(-1 TO +1) OF (I-1)TH LEGENDRE POLY
C  FOLDED W/ EXP(-Y*BETA)
C  BP=SAME, WITH BETA**2 IN INTEGRAND
      B(1)=XI(1)
      BP(1)=XI(3)
      B(2)=XI(2)
      BP(2)=XI(4)
      B(3)=1.5*XI(3)-0.5*XI(1)
      BP(3)=1.5*XI(5)-0.5*XI(3)
      B(4)=2.5*XI(4)-1.5*XI(2)
      BP(4)=2.5*XI(6)-1.5*XI(4)
      B(5)=35*XI(5)/8-30*XI(3)/8+3*XI(1)/8
      BP(5)=(35*XI(7)-30*XI(5)+3*XI(3))/8
      DA=(AMX-1)/NA
      DB=2.0/NB
      T3=0.0
      T4=0.0
      C2=0.0
C  T3=A(1)*Z(1)*Z(2)*B(2)/R12
C  T4=A(1)*Z(1)*A(2)*B(2)/R12
C  C2=A(1)*Z(1)*A(2)*Z(2)/R12

```

```

A2=1+DA/2
DO 500 I=1,NA
X2=DEXP(-A2*X)
XI(1)=X1*E(1)
  XJ(1)=X2*E(1)
XI(2)=X1*(E(1)+E(2))
  XJ(2)=X2*(A2*E(1)+E(2))
XI(3)=X1*(E(1)+2*E(2)+2*E(3))
  XJ(3)=X2*(E(1)*A2**2.0
C+2*E(2)*A2+2*E(3))
  XI(4)=X1*(E(1)+3*E(2)+6*E(3)+6*E(4))
  XJ(4)=X2*(E(1)*A2**3
C+3*E(2)*A2**2+6*E(3)*A2+6*E(4))
  XI(5)=X1*(E(1)+4*E(2)+12*E(3)+24*E(4)+24*E(5))
  XJ(5)=X2*(
CE(1)*A2**4+4*E(2)*A2**3+12*E(3)*A2**2+24*E(4)*A2
C+24*E(5))
  XI(6)=X1*(E(1)+5*E(2)+20*E(3)+60*E(4)+120*E(5)+120*E(6))
  XJ(6)=X2*(E(1)*A2**5+5*E(2)*A2**4+20*E(3)*A2**3+60*E(4)*A2**2
C+120*E(5)*A2+120*E(6))
  XI(7)=X1*(E(1)+6*E(2)+30*E(3)+120*E(4)+360*E(5)+720*E(6)
C+720*E(7))
  XJ(7)=X2*(E(1)*A2**6+6.0*E(2)*A2**5+30.0*E(3)*A2**4+
C120*E(4)*A2**3+360*E(5)*A2**2+720*E(6)*A2+720*E(7))
  XD=0.5*DLOG((A2+1)/(A2-1))
C NEXT CALCULATE EXP'L INTEGRALS
DO 50 JJ=1,2
W(JJ)=X*(A2-1+2*(JJ-1))
IF (W(JJ).GT.10.0) GO TO 46

```

```

DXN=W(JJ)
  DXNN=W(JJ)
DO 45 KK=2,30
  DXNN=-DXNN*W(JJ)*(KK-1)/(KK**2)
  DXN=DXN+DXNN
45 CONTINUE
  XN(JJ)=-0.577215664-DLOG(W(JJ))+DXN
  GO TO 48
46 NW=DINT(W(JJ))
  DXN=1.0
  DXNN=1.0
DO 47 NN=1,NW
  DXNN=-DXNN*NN/W(JJ)
  DXN=DXN+DXNN
47 CONTINUE
  XN(JJ)=DEXP(-W(JJ))*DXN/W(JJ)
48 CONTINUE
50 CONTINUE
  YI=XN(2)/X1-XN(1)*X1
  YYI=XN(2)/X1+XN(1)*X1
  G(1)=E(1)
DO 60 LL=2,7
  G(LL)=- (LL-1)*G(LL-1)*E(1)
60 CONTINUE
  F(1)=YI
  F(2)=YYI
DO 70 LL=3,7
  F(LL)=F(LL-2)+((-1)**LL)*2*XJ(LL-2)
70 CONTINUE

```

```

XL(1)=F(1)*G(1)
XL(2)=F(2)*G(1)+F(1)*G(2)
XL(3)=F(3)*G(1)+2*F(2)*G(2)+F(1)*G(3)
XL(4)=F(4)*G(1)+3*F(3)*G(2)+3*F(2)*G(3)+F(1)*G(4)
XL(5)=F(5)*G(1)+4*F(4)*G(2)+6*F(3)*G(3)+4*F(2)*G(4)+F(1)*G(5)
XL(6)=F(6)*G(1)+5*F(5)*G(2)+10*F(4)*G(3)+
C10*F(3)*G(4)+5*F(2)*G(5)+F(1)*G(6)
XL(7)=F(7)*G(1)+6*F(6)*G(2)+15*F(5)*G(3)+20*F(4)*G(4)+15*F(3)*G(5)
C+6*F(2)*G(6)+F(1)*G(7)
DO 90 LL=1,7
XK(LL)=XD*XJ(LL)+0.5*XL(LL)*((-1)**(LL-1))
90 CONTINUE
A1(1)=XK(3)
A1(2)=XK(4)-XJ(3)
A1(3)=1.5*XK(5)-0.5*XK(3)-1.5*XJ(4)
A1(4)=2.5*XK(6)-1.5*XK(4)-2.5*XJ(5)+XJ(3)*(2.0/3.0)
A1(5)=(35*XK(7)-30*XK(5)+3*XK(3))/8
C-(35.0/8.0)*XJ(6)+(55.0/24.0)*XJ(4)
A22(1)=XI(3)-XJ(3)
A22(2)=XI(4)-XJ(4)
A22(3)=1.5*(XI(5)-XJ(5))-0.5*(XI(3)-XJ(3))
A22(4)=2.5*(XI(6)-XJ(6))-1.5*(XI(4)-XJ(4))
A22(5)=(35*XI(7)-30*XI(5)+3*XI(3))/8
C-(35*XJ(7)-30*XJ(5)+3*XJ(3))/8
A3(1)=XK(1)
A3(2)=XK(2)-XJ(1)
A3(3)=1.5*XK(3)-0.5*XK(1)-1.5*XJ(2)
A3(4)=2.5*XK(4)-1.5*XK(2)-2.5*XJ(3)+XJ(1)*(2.0/3.0)
A3(5)=(35*XK(5)-30*XK(3)+3*XK(1))/8

```

C=(35.0/8.0)*XJ(4)+(55.0/24.0)*XJ(2)

A4(1)=XI(1)-XJ(1)

A4(2)=XI(2)-XJ(2)

A4(3)=1.5*XI(3)-0.5*XI(1)-1.5*XJ(3)+0.5*XJ(1)

A4(4)=2.5*XI(4)-1.5*XI(2)-2.5*XJ(4)+1.5*XJ(2)

A4(5)=(35*XI(5)-30*XI(3)+3*XI(1))/8

C=(35*XJ(5)-30*XJ(3)+3*XJ(1))/8

P(1)=1.0

P(2)=A2

P(3)=1.5*A2**2-0.5

P(4)=2.5*A2**3-1.5*A2

P(5)=(35*A2**4-30*A2**2+3)/8

Q(1)=0.5*DLOG((A2+1)/(A2-1))

Q(2)=Q(1)*P(2)-1

Q(3)=Q(1)*P(3)-1.5*A2

Q(4)=Q(1)*P(4)-2.5*A2**2+(2.0/3.0)

Q(5)=Q(1)*P(5)-(35.0/8.0)*A2**3+(55.0/24.0)*A2

DO 100 M=1,5

D1(M)=(2*M-1)*B(M)*(A1(M)*P(M)+A22(M)*Q(M))

D2(M)=(2*M-1)*BP(M)*(A3(M)*P(M)+A4(M)*Q(M))

100 CONTINUE

B2=-1.0+DB/2

DUM1=0.0

DUM1A=0.0

DUM1B=0.0

DO 400 J=1,NB

P1(1)=1

P1(2)=B2

P1(3)=1.5*B2**2-0.5

$P1(4) = 2.5 \cdot B2^3 - 1.5 \cdot B2$

$P1(5) = (35 \cdot B2^4 - 30 \cdot B2^2 + 3) / 8$

$SS = A2 \cdot A2 + B2 \cdot B2$

$SQ = (SS + 4 \cdot R0 \cdot (R + R0) / R / R - 2 \cdot A2 \cdot B2 \cdot (1 + 2 \cdot R0 / R))^{0.5}$

$EX = \text{DEXP}(-0.5 \cdot R \cdot (XLZ \cdot (A2 - B2) + XLB \cdot SQ))$

$EXA = \text{DEXP}(-0.5 \cdot R \cdot (XLA \cdot (A2 + B2) + XLB \cdot SQ))$

$EXB = \text{DEXP}(-(X \cdot A2 + Y \cdot B2))$

$DUM2 = 0.0$

$DUM2A = 0.0$

$DUM2B = 0.0$

DO 150 M=1,5

$DUM2 = DUM2 + EX \cdot (D1(M) - D2(M)) \cdot P1(M) \cdot (A2^2 - B2^2)$

$DUM2A = DUM2A + EXA \cdot (D1(M) - D2(M)) \cdot P1(M) \cdot (A2^2 - B2^2)$

$DUM2B = DUM2B + EXB \cdot (D1(M) - D2(M)) \cdot P1(M) \cdot (A2^2 - B2^2)$

150 CONTINUE

$DUM1 = DUM1 + DUM2 \cdot DB$

$DUM1A = DUM1A + DUM2A \cdot DB$

$DUM1B = DUM1B + DUM2B \cdot DB$

$B2 = B2 + DB$

400 CONTINUE

$T3 = DUM1 \cdot DA + T3$

$T4 = DUM1A \cdot DA + T4$

$C2 = DUM1B \cdot DA + C2$

$A2 = A2 + DA$

500 CONTINUE

$T3 = T3 \cdot (R^{0.5}) \cdot ((XLA \cdot XLZ \cdot XLB \cdot XLZ)^{1.5}) / 8.0$

$T4 = T4 \cdot (R^{0.5}) \cdot ((XLA \cdot XLA \cdot XLZ \cdot XLB)^{1.5}) / 8.0$

$C2 = C2 \cdot (R^{0.5}) \cdot ((XLA \cdot XLZ)^{3.0}) / 8.0$

WRITE (6,1060) T3,T4,C2

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1060 FORMAT (3F12.6)

RETURN

END

SUBROUTINE NUMIN3 (XL1,XL2,XL3,XL4,R1,R,S,SX,IAQ)

C 4CENTER, A PROGRAM TO CALCULATE A 4 CENTER COULOMB

C INTEGRAL FOR MAGNETIC EXCHANGE CALCULATION

C FOR DETAILS SEE L. SNIVELY

C (A) _____ (Z) _____ (Z') _____ (B)

C LAMBDA=A,B EXPONENT, MU=Z EXPONENT

C THETA=ANGLE BETWEEN A-Z AND Z-B AXES

IMPLICIT DOUBLE PRECISION (A-H,J,O-Z)

DIMENSION XI(7),XJ(7),XK(7),XL(7),E(7),P(5),Q(5),P1(5),W(2),XN(2),

CA1(5),A22(5),A3(5),A4(5),D(20),B(20),BP(5),D1(5),D2(5),F(7),G(7)

C R1 IS THE DISTANCE BETWEEN THE ENDS OF Ra AND Rb ie. THE INITIAL

C INTEGR. PTS.

COMMON J4,J5,T1,T2,T3,T3,C2,NA,NB,AMX

X=(XL1+XL2)*R1/2.0

Y=(XL1-XL2)*R1/2.0

X1=DEXP(-X)

D(1)=1.0

E(1)=1.0/X

B(1)=1.0

B(2)=0.0

D(2)=Y

DO 5 I=2,7

E(I)=E(I-1)/X

5 CONTINUE

DO 10 KI=3,20

B(KI)=B(KI-2)/(KI*(KI-1))

D(KI)=D(KI-1)*Y

10 CONTINUE

IS=1

```

DO 20 KI=1,7
XDUM=0.0
  NJ=21-KI
DO 15 KJ=1,NJ
XDUM=XDUM+D(KJ)*B(KJ)
B(KJ)=B(KJ+1)*DFLOAT(KJ)
15 CONTINUE
XI(KI)=XDUM*2.0*IS
IS=-IS
20 CONTINUE
C B=INTEGRAL(-1 TO +1) OF (I-1)TH LEGENDRE POLY
C FOLDED W/ EXP(-Y*BETA)
C BP=SAME, WITH BETA**2 IN INTEGRAND
  B(1)=XI(1)
  BP(1)=XI(3)
  B(2)=XI(2)
  BP(2)=XI(4)
  B(3)=1.5*XI(3)-0.5*XI(1)
  BP(3)=1.5*XI(5)-0.5*XI(3)
  B(4)=2.5*XI(4)-1.5*XI(2)
  BP(4)=2.5*XI(6)-1.5*XI(4)
  B(5)=35*XI(5)/8-30*XI(3)/8+3*XI(1)/8
  BP(5)=(35*XI(7)-30*XI(5)+3*XI(3))/8
  DA=(AMX-1)/NA
  DB=2.0/NB
  T3=0.0
  T4=0.0
  C2=0.0
C T3=A(1)*Z(1)*Z(2)*B(2)/R12

```

C T4=A(1)*Z(1)*A(2)*B(2)/R12

C C2=A(1)*Z(1)*A(2)*Z(2)/R12

A2=1+DA/2

DO 500 I=1,NA

X2=DEXP(-A2*X)

XI(1)=X1*E(1)

XJ(1)=X2*E(1)

XI(2)=X1*(E(1)+E(2))

XJ(2)=X2*(A2*E(1)+E(2))

XI(3)=X1*(E(1)+2*E(2)+2*E(3))

XJ(3)=X2*(E(1)*A2**2.0

C+2*E(2)*A2+2*E(3))

XI(4)=X1*(E(1)+3*E(2)+6*E(3)+6*E(4))

XJ(4)=X2*(E(1)*A2**3

C+3*E(2)*A2**2+6*E(3)*A2+6*E(4))

XI(5)=X1*(E(1)+4*E(2)+12*E(3)+24*E(4)+24*E(5))

XJ(5)=X2*(

CE(1)*A2**4+4*E(2)*A2**3+12*E(3)*A2**2+24*E(4)*A2

C+24*E(5))

XI(6)=X1*(E(1)+5*E(2)+20*E(3)+60*E(4)+120*E(5)+120*E(6))

XJ(6)=X2*(E(1)*A2**5+5*E(2)*A2**4+20*E(3)*A2**3+60*E(4)*A2**2

C+120*E(5)*A2+120*E(6))

XI(7)=X1*(E(1)+6*E(2)+30*E(3)+120*E(4)+360*E(5)+720*E(6)

C+720*E(7))

XJ(7)=X2*(E(1)*A2**6+6.0*E(2)*A2**5+30.0*E(3)*A2**4+

C120*E(4)*A2**3+360*E(5)*A2**2+720*E(6)*A2+720*E(7))

XD=0.5*DLOG((A2+1)/(A2-1))

C NEXT CALCULATE EXP'L INTEGRALS

DO 50 JJ=1,2

```

W(JJ)=X*(A2-1+2*(JJ-1))
IF (W(JJ).GT.10.0) GO TO 46
DXN=W(JJ)
  DXNN=W(JJ)
DO 45 KK=2,30
  DXNN=-DXNN*W(JJ)*(KK-1)/(KK**2)
  DXN=DXN+DXNN
45 CONTINUE
  XN(JJ)=-0.577215664-DLOG(W(JJ))+DXN
  GO TO 48
46 NW=DINT(W(JJ))
  DXN=1.0
  DXNN=1.0
DO 47 NN=1,NW
  DXNN=-DXNN*NN/W(JJ)
  DXN=DXN+DXNN
47 CONTINUE
  XN(JJ)=DEXP(-W(JJ))*DXN/W(JJ)
48 CONTINUE
50 CONTINUE
  YI=XN(2)/X1-XN(1)*X1
  YYI=XN(2)/X1+XN(1)*X1
  G(1)=E(1)
DO 60 LL=2,7
  G(LL)=- (LL-1)*G(LL-1)*E(1)
60 CONTINUE
  F(1)=YI
  F(2)=YYI
DO 70 LL=3,7

```

$$F(LL)=F(LL-2)+((-1)^{LL} \cdot 2 \cdot XJ(LL-2))$$

70 CONTINUE

$$XL(1)=F(1) \cdot G(1)$$

$$XL(2)=F(2) \cdot G(1)+F(1) \cdot G(2)$$

$$XL(3)=F(3) \cdot G(1)+2 \cdot F(2) \cdot G(2)+F(1) \cdot G(3)$$

$$XL(4)=F(4) \cdot G(1)+3 \cdot F(3) \cdot G(2)+3 \cdot F(2) \cdot G(3)+F(1) \cdot G(4)$$

$$XL(5)=F(5) \cdot G(1)+4 \cdot F(4) \cdot G(2)+6 \cdot F(3) \cdot G(3)+4 \cdot F(2) \cdot G(4)+F(1) \cdot G(5)$$

$$XL(6)=F(6) \cdot G(1)+5 \cdot F(5) \cdot G(2)+10 \cdot F(4) \cdot G(3)+$$

$$C10 \cdot F(3) \cdot G(4)+5 \cdot F(2) \cdot G(5)+F(1) \cdot G(6)$$

$$XL(7)=F(7) \cdot G(1)+6 \cdot F(6) \cdot G(2)+15 \cdot F(5) \cdot G(3)+20 \cdot F(4) \cdot G(4)+15 \cdot F(3) \cdot G(5)$$

$$C+6 \cdot F(2) \cdot G(6)+F(1) \cdot G(7)$$

$$DO \ 90 \ LL=1,7$$

$$XK(LL)=XD \cdot XJ(LL)+0.5 \cdot XL(LL) \cdot ((-1)^{LL} \cdot (LL-1))$$

90 CONTINUE

$$A1(1)=XK(3)$$

$$A1(2)=XK(4)-XJ(3)$$

$$A1(3)=1.5 \cdot XK(5)-0.5 \cdot XK(3)-1.5 \cdot XJ(4)$$

$$A1(4)=2.5 \cdot XK(6)-1.5 \cdot XK(4)-2.5 \cdot XJ(5)+XJ(3) \cdot (2.0/3.0)$$

$$A1(5)=(35 \cdot XK(7)-30 \cdot XK(5)+3 \cdot XK(3))/8$$

$$C-(35.0/8.0) \cdot XJ(6)+(55.0/24.0) \cdot XJ(4)$$

$$A22(1)=XI(3)-XJ(3)$$

$$A22(2)=XI(4)-XJ(4)$$

$$A22(3)=1.5 \cdot (XI(5)-XJ(5))-0.5 \cdot (XI(3)-XJ(3))$$

$$A22(4)=2.5 \cdot (XI(6)-XJ(6))-1.5 \cdot (XI(4)-XJ(4))$$

$$A22(5)=(35 \cdot XI(7)-30 \cdot XI(5)+3 \cdot XI(3))/8$$

$$C-(35 \cdot XJ(7)-30 \cdot XJ(5)+3 \cdot XJ(3))/8$$

$$A3(1)=XK(1)$$

$$A3(2)=XK(2)-XJ(1)$$

$$A3(3)=1.5 \cdot XK(3)-0.5 \cdot XK(1)-1.5 \cdot XJ(2)$$

```

A3(4)=2.5*XK(4)-1.5*XK(2)-2.5*XJ(3)+XJ(1)*(2.0/3.0)
A3(5)=(35*XK(5)-30*XK(3)+3*XK(1))/8
C=(35.0/8.0)*XJ(4)+(55.0/24.0)*XJ(2)
A4(1)=XI(1)-XJ(1)
A4(2)=XI(2)-XJ(2)
A4(3)=1.5*XI(3)-0.5*XI(1)-1.5*XJ(3)+0.5*XJ(1)
A4(4)=2.5*XI(4)-1.5*XI(2)-2.5*XJ(4)+1.5*XJ(2)
A4(5)=(35*XI(5)-30*XI(3)+3*XI(1))/8
C=(35*XJ(5)-30*XJ(3)+3*XJ(1))/8
P(1)=1.0
P(2)=A2
P(3)=1.5*A2**2-0.5
P(4)=2.5*A2**3-1.5*A2
P(5)=(35*A2**4-30*A2**2+3)/8
Q(1)=0.5*DLOG((A2+1)/(A2-1))
Q(2)=Q(1)*P(2)-1
Q(3)=Q(1)*P(3)-1.5*A2
Q(4)=Q(1)*P(4)-2.5*A2**2+(2.0/3.0)
Q(5)=Q(1)*P(5)-(35.0/8.0)*A2**3+(55.0/24.0)*A2
DO 100 M=1,5
D1(M)=(2*M-1)*B(M)*(A1(M)*P(M)+A22(M)*Q(M))
D2(M)=(2*M-1)*BP(M)*(A3(M)*P(M)+A4(M)*Q(M))
100 CONTINUE
B2=-1.0+DB/2
DUM1=0.0
DO 400 J=1,NB
P1(1)=1
P1(2)=B2
P1(3)=1.5*B2**2-0.5

```

$$P1(4)=2.5*B2^{**3}-1.5*B2$$

$$P1(5)=(35*B2^{**4}-30*B2^{**2}+3)/8$$

$$SS=A2*A2+B2*B2$$

$$QA=S+SX$$

$$AB2=2.0*A2*B2$$

IF (IAQ .EQ. 1) GO TO 120

IF (IAQ .EQ. 2) GO TO 110

$$SQ1=QA/2.*(SS+AB2*(SX-S)/QA-4.*S*SX/QA/QA)^{**0.5}$$

$$SQ2=QA/2.*(SS-AB2*(1.+2.*S/QA)+4.*S*R/QA/QA)^{**0.5}$$

GO TO 140

110 $SQ1=S/2.*(SS-AB2*(1.+2.*SX/S)+4.*SX*QA/S/S)^{**0.5}$

$$SQ2=S/2.*(SS-AB2*(1.+2.*QA/S)+4.*QA*R/S/S)^{**0.5}$$

GO TO 140

120 $SQ1=R/2.*(SS+AB2*SX/R-4.*S*QA/R/R)^{**0.5}$

$$SQ2=R/2.*(SS-AB2*SX/R-4.*S*QA/R/R)^{**0.5}$$

140 $EX=DEXP(-XL3*SQ1-XL4*SQ2)$

$$DUM2=0.0$$

DO 150 M=1,5

$$DUM2=DUM2+EX*(D1(M)-D2(M))*P1(M)*(A2^{**2}-B2^{**2})$$

150 CONTINUE

$$DUM1=DUM1+DUM2*DB$$

$$B2=B2+DB$$

400 CONTINUE

$$T3=DUM1*DA+T3$$

$$A2=A2+DA$$

500 CONTINUE

$$T3=T3*(R1^{**5.})*((XL1*XL2*XL3*XL4)^{**1.5})/8.0$$

WRITE (6,1060) T3

1060 FORMAT (F12.6)

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RETURN

END

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