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ELECTRON EXCHANGE FOR HYDRATED IONS IN THE α-$NiSO_4 \cdot 6H_2O$ LATTICE-- ELECTRON PARAMAGNETIC RESONANCE STUDY OF TRANSITION-METAL IONS IN $ZNSeO_4 \cdot 6H_2O$

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Abstract

The magnetothermodynamic measurements of Giauque et al. showed that the Ni^{2+} in α-$NiSO_4 \cdot 6H_2O$ could be fit very well by an axial spin Hamiltonian. We have studied the EPR of Ni^{2+}, Co^{2+} and Cu^{2+} in both this lattice and in the isostructural lattices of $NiSeO_4 \cdot 6H_2O$ and $ZnSeO_4 \cdot 6H_2O$. In both of the nickel lattices exchange effects are very important, but the diamagnetic zinc lattice can be used as a reference, and this paper reports the EPR of these ions in $ZnSeO_4 \cdot 6H_2O$.

The axial spin Hamiltonian is a result of the hydrogen bonding of the $M(H_2O)_6^{2+}$ complex. Two axial H_2O groups have three hydrogen bonds vs. only two for the other four waters. This results in a tetragonal crystal field with decreased negative charge along the four-fold axis, and we find that the spin Hamiltonian axis is very nearly along the axis formed by the unique waters.

For $Ni(H_2O)_6^{2+}$ we obtain $g_{\parallel} = 2.219$, $g_{\perp} = 2.238$ with $D = +4.20\ cm^{-1}$. For $Co(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$ we obtain $g_{\parallel} = 5.975$, $g_{\perp} = 3.45$, $A_{\parallel} = 77.0$ G, $A_{\perp} = 20$ G and $g_{\parallel} = 2.4295$, $g_{\perp} = 2.0965$, $A_{\parallel} = 115.6$ G, $A_{\perp} = 9.5$ G, respectively. Some variations in the orientation of the principal axes were also determined for the three ions. A short discussion is also given for the effects of electron exchange on these ions in α-$NiSO_4 \cdot 6H_2O$.

I. Introduction

As part of an investigation of the magnetic properties of α-$NiSO_4 \cdot 6H_2O$ and $NiSeO_4 \cdot 6H_2O$, we have determined the spin Hamiltonian parameters for Co^{2+}, Ni^{2+} and Cu^{2+} in $ZnSeO_4 \cdot 6H_2O$. This diamagnetic lattice is isostructural with the two nickel hydrates, and the structure of α-$NiSO_4 \cdot 6H_2O$ has been determined by both x-ray[1] and neutron diffraction.[2]

In α-$NiSO_4 \cdot 6H_2O$ the Ni^{2+} is present as a $Ni(H_2O)_6^{2+}$ complex which is hydrogen bonded to both the SO_4^{2-} and the waters of other $Ni(H_2O)_6^{2+}$. There is only one kind of $Ni(H_2O)_6^{2+}$ but the unit cell contains four Ni^{2+} ions in a tetragonal structure. All four ions are equivalent when a magnetic field is along the a, b or c axes.

The magnetothermodynamic properties of α-$NiSO_4 \cdot 6H_2O$ have been extensively investigated.[3] The spin Hamiltonian formalism was found[4] to fit the $Ni(H_2O)_6^{2+}$ very well, but it was necessary to use a molecular field correction as a means of accounting for the interactions between nickel ions. A preliminary electron paramagnetic resonance (EPR) study[5] of α-$NiSO_4 \cdot 6H_2O$ showed that spectra could be observed both for the Ni^{2+} and for impurity amounts of Co^{2+} and Cu^{2+}. There was good agreement between the EPR and magnetothermodynamic parameters for Ni^{2+}, but the Cu^{2+} spectrum seemed to indicate serious exchange interaction with the surrounding Ni^{2+}. Similar effects were observed for $NiSeO_4 \cdot 6H_2O$. It was decided that before further work could be done on these exchange interactions, we needed to know the spin Hamiltonian parameters in the absence of these interactions. Since the reports of a tetragonal form

of $ZnSO_4 \cdot 6H_2O$ seem to be in error,[6] we decided to make an EPR investigation of Co^{2+}, Ni^{2+} and Cu^{2+} in the easily prepared tetragonal $ZnSeO_4 \cdot 6H_2O$.

II. Experimental Methods

A. Crystal Preparation

The selenates of the divalent metallic elements are easily synthesized by reacting metal carbonates with a small excess of selenic acid.[7] The reaction proceeds with vigorous effervescence and generation of heat. Large single crystals of $ZnSeO_4 \cdot 6H_2O$ are readily grown by slow evaporation of the resulting solution. Tetragonal $ZnSeO_4 \cdot 6H_2O$ is the stable form[7] from -7° to 35°C, but it was stored in a refrigerator at 5°C since single crystals dehydrate if left in dry air at room temperature.

Identification of the crystal axes was usually unambiguous from the well developed tetragonal shapes. However, when the identification seemed uncertain a cross-polaroid optical technique was employed. Zinc selenate crystallizes in two forms: tetragonal prismatic at room temperature and tetragonal bipyramidal at 5°C. Both of these two forms contain six water molecules per zinc atom, and have the same crystal structure.

EPR samples were prepared by growing a single crystal from a mixed solution of zinc selenate and the paramagnetic ion selenate. Only a small amount of paramagnetic ion was used and the resulting single crystals were determined to be about 1% paramagnetic ion.

B. Crystal Structure

The crystal structure of $ZnSeO_4 \cdot 6H_2O$ has not been examined in detail. But it is isomorphous with the tetragonal α-$NiSO_4 \cdot 6H_2O$ and its lattice dimension is $a_o:c_o = 1:1.8949$.[7] Here we will discuss the crystal structure of α-$NiSO_4 \cdot 6H_2O$, for a complete structure has been established for it.[1,2]

The crystal is tetragonal with a space group of either $P4_12_12$ or $P4_32_12$ depending upon its enantiomorphic form. There are four molecules in a unit cell whose dimensions are $a_o = b_o = 6.790 \pm 0.003$ Å and $c_o = 18.305 \pm 0.004$ Å. The $Ni(H_2O)_6^{2+}$ and SO_4^{2-} groups form a layer lying in the (001) plane at positions of 0, 1/4, 1/2 and 3/4 in units of c_o. Figure 1 shows a projection of one-half of a unit cell on the (001) plane along the c axis. The two layers at $z = 0$ and $z = c_o/4$ are depicted here with the relative positions of Ni, S and O atoms. The numbers within circles represent the coordinates in units of c_o along the c axis as determined by Beevers and Lipson. The numbers in parentheses indicate the five nonequivalent oxygen atoms as denoted by O'Connor and Dale.

In each layer the $Ni(H_2O)_6^{2+}$ is located between two SO_4^{2-} units; one sulfate having the horizontal plane oxygen, O(5), closer to Ni^{2+} and the other having the vertical plane oxygen, O(4), closer to Ni^{2+}. For a given layer there is a two-fold symmetry about the ab bisector which we will hereafter call the γ axis. Adjacent layers are generated by the three successive operations of a four-fold rotation about the c axis, a translation of $c_o/4$ along the c axis and a translation of $a_o/\sqrt{2}$ units along the γ axis. The sense of the four-fold rotation may be right- or

left-handed, corresponding to the two enantiomorphic forms of α-$NiSO_4 \cdot 6H_2O$. Each layer is linked to another by the hydrogen bonds between O(1') and O(3) and between O(3') and O(4). O'Connor and Dale concluded that the Ni-O bond distances do not show significant deviation from their mean value, 2.06±0.02 Å. One should be careful not to place any significance upon the reported variation in the three Ni-O bond distances. All the bond angles of O-Ni-O within a $Ni(D_2O)_6^{2+}$ group are close to 90°, forming nearly a perfect octahedron. The crystallographic distances alone do not indicate any distortion of the octahedron at the Ni^{2+} site.

The major difference among the six water molecules about Ni^{2+} is that O(1) and O(2) have two hydrogen bonds, while O(3) has three. The O(3) acts as a proton acceptor and its negative charge should be diminished by the additional hydrogen bonding. Purely electrostatic arguments predict that the oxygen atoms of type 1 and 2 are more strongly bonded to Ni^{2+} than that of type 3. One would assume that the Ni-O(3) axis is the z axis of the crystalline electric field affecting the central metal ion. We will find that the EPR results support this assumption.

The magnetic axes at the Ni^{2+} sites are shown in Fig. 2. There is exact two-fold symmetry for each of the Ni^{2+} along a γ axis. In Fig. 2 these are denoted as the x magnetic axes. The z axes differ from c by rotation by ϕ about the x axis. The y axes must lie in a γc plane. In α-$NiSO_4 \cdot 6H_2O$ Fisher and Hornung[4] found that $\phi = 39°$. The crystallographic value, based upon the assumption that z is equivalent to the Ni-O(3) axis,[2] is $\phi = 42°$. Within the accuracy of both methods we can conclude that z is the same as the Ni-O(3) axis. Fisher and Hornung

also found for Ni^{2+} that x and y are magnetically equivalent although there is no crystallographic requirement for such an assumption. This is consistent with the similar hydrogen bonding of O(1) and O(2).

For Co^{2+}, Ni^{2+} and Cu^{2+} substituted in $ZnSeO_4 \cdot 6H_2O$ the x, y and z axes need not correspond exactly to those of the Zn^{2+} sites. The angle ϕ may be altered and x need not be along a γ axis. One might expect a small rotation of the $M(H_2O)_6^{2+}$ complex as the hydrogen bonding adjusts to the size of the hydrated ion in the $Zn(H_2O)_6^{2+}$ site.

C. EPR Techniques

The single crystals were mounted in Teflon filled cavities resonant near 9 GHz. The cavity was usually immersed in liquid helium, and with a fast pumping system spectra could be taken from 4.2° to 1.3°K. Without liquid helium, spectra could also be taken near 77°K. Details of the EPR spectrometer and cavities can be found elsewhere.[5,8]

With a properly oriented crystal and a rotating magnet, spectra could be taken in the ab, ac or γc planes. The angle α in the ac or γc planes corresponds to the angle between H and the c axis. In the ab plane α is measured with respect to the x axis of ion 4, and $\alpha = 45°$ should correspond to the a or b axes. It is clear from Fig. 2 that ϕ is best determined by measuring spectra in the γc plane, but spectra in the ab and ac planes also depend upon ϕ.

The Ni^{2+} spectra were fit with the usual S = 1 spin Hamiltonian, while the Co^{2+} and Cu^{2+} were fit with S = 1/2 together with hyperfine terms.[9] In all cases, an axial spin Hamiltonian was found to be quite

satisfactory to explain the observed spectra. From the work[4,5] on α-$NiSO_4 \cdot 6H_2O$ and $NiSeO_4 \cdot 6H_2O$, we expected that the paramagnetic ions would have spin Hamiltonian parameters for Ni^{2+} with $D \sim 5\ cm^{-1}$ and for Co^{2+} and Cu^{2+} with $g_{\parallel} > g_{\perp}$. These results are consistent with a decreased crystal field along the z axis due to the nature of the hydrogen bonding.

The spin Hamiltonian of Cu^{2+} and Co^{2+} in D_{4h} symmetry is

$$H_{spin} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (1)$$

At X-band the quantization axis is taken along the direction of the magnetic field, for the Zeeman term is much greater than hfs. A coordinate transformation to a new set of axes will diagonalize the Zeeman term to a form $g\beta H S_z'$, where

$$g^2 = (g_{\parallel}^2 - g_{\perp}^2)n^2 + g_{\perp}^2 \quad (2)$$

where n is the direction cosine of the z axis with respect to the magnetic field. A plot of g^2 vs. n^2 will result in a straight line with a slope of $(g_{\parallel}^2 - g_{\perp}^2)$ and an intercept of $g_{\perp}^2$. This turns out to be a good method to check the value of ϕ and to extrapolate $g_{\parallel}$ and $g_{\perp}$. It should be noted that the data from only one plane will not unambiguously determine the g and hfs constants with axial symmetry.

If the hf tensor has the same principal axes as the g tensor, a similar transformation of the nuclear spin components will diagonalize the hf tensor to the form $AS_z'I_z'$. The hyperfine constant A, measured in units of energy, is given by

$$g^2A^2 = (g_{\parallel}{}^2A_{\parallel}{}^2 - g_{\perp}{}^2A_{\perp}{}^2)n^2 + g_{\perp}{}^2A_{\perp}{}^2 \tag{3a}$$

or in units of gauss,

$$g^4A^2 = (g_{\parallel}{}^4A_{\parallel}{}^2 - g_{\perp}{}^2A_{\perp}{}^2)n^2 + g_{\perp}{}^2A_{\perp}{}^2 \tag{3b}$$

In the first order approximation the measured separation of the central two hfs lines can be substituted for A in Eq. 3b. A plot of g^4A^2 vs. n^2 will again yield a straight line, provided that the principal axes of the g and hfs tensors coincide.

The transitions we observe in the EPR of Cu^{2+} are of the type $\Delta M = \pm 1$ and $\Delta m_I = 0$. Then, the spin Hamiltonian (1) gives

$$H = H_o - Am_I - \left(\frac{A_{\perp}{}^2g_{\perp}{}^2}{4H_og^2}\right)\left(\frac{A_{\parallel}{}^2g_{\parallel}{}^2 + A^2g^2}{A^2g^2}\right)\left[I(I+1) - m_I{}^2\right]$$
$$- \frac{1}{2H_o}\left(\frac{A_{\parallel}{}^2g_{\parallel}{}^2 - A_{\perp}{}^2g_{\perp}{}^2}{Ag^2}\right)^2\left(\frac{g_{\parallel}g_{\perp}}{g}\right)^4\left[n^2(1-n^2)m_I{}^2\right] \tag{4}$$

where $A_{\parallel}$, $A_{\perp}$ and A are all in gauss and $H_o = h\nu/g\beta$. The deviation of H_o from the actual magnetic field is small enough to be ignored. In Eq. 4 the second term is responsible for 2I+1 equally spaced lines that are centered at H_o. The third and the fourth terms shift each line to lower field, disturb the equal spacings of the lines and give a progressive linear change in the spacing. When the magnetic field is either parallel or perpendicular to the z axis, the fourth term is zero and the third term makes the spacing successively smaller toward the high-field end. If $A_{\parallel} \gg A_{\perp}$, the second order effect becomes very important near the perpendicular direction.[10]

III. Experimental Results

A. Ni^{2+} in $ZnSeO_4 \cdot 6H_2O$

The EPR signal of Ni^{2+} in our crystals of $ZnSeO_4 \cdot 6H_2O$ was strong enough for derivative detection with a 825 Hz field modulation at 77°K. The EPR spectra at 4.2° and 1.3°K showed that the intensities of Ni^{2+} appreciably decreased while that of diphenylpicrylhydrazyl (DPPH) and a Co^{2+} impurity increased as the temperature was lowered. Thus, the sign of D is positive as expected. The thermodynamic work[3] on α-$NiSO_4 \cdot 6H_2O$ has clearly established its D value as being positive. Contrary to many Ni^{2+} crystals that are known to change the magnitudes of g and D with temperature, Ni^{2+} in $ZnSeO_4 \cdot 6H_2O$ shows practically no temperature dependence between 1.3° and 77°K.

When H was rotated in the γc plane, four lines of large anisotropy were observed. All four lines merged at the c axis ($\alpha = 0$), and at the γ axis ($\alpha = 90°$) ions 1 and 3, and ions 2 and 4 became equivalent. Ion 3 reached a maximum field near $\alpha = 55°$. This should be the angle between the c axis and the y axis of ion 3 and ϕ must be about 35°. Because of a slight misorientation of the crystal we did not fully analyze over γc plane data. In addition, our magnet could not quite produce sufficient field to obtain resonance when H was along the x or y axes.

In the ac plane two pairs of doublets were seen at all orientations except when H was along the c axis. Ions 1 and 4 and ions 2 and 3 moved together. One pair reached a maximum field at an angle of 63° from the c axis, and from this fact we can determine that $\phi = 35.7°$. In order to explain the doublet structures, we assume that the x axes of the four

ions are all tilted away from the γ axes in the γc plane by an angle β. Introduction of the new angle β breaks the equivalence of ions 1 and 4 and ions 2 and 3 in the ac plane, and of ions 2 and 4 in the γc plane. The theoretical field positions of the four Ni^{2+} lines were calculated by an exact diagonalization procedure and the parameters $g_{\parallel}$, $g_{\perp}$, D, ϕ and β were adjusted to give the best fit. An example of such a fit is shown in Fig. 3.

Spectra were also taken with H in the ab plane. If the only deviation of the x axes from the γ directions was a tilt in the γc plane, the ab plane spectra would be little affected by this deviation. The ab plane spectra was affected, and it consisted of two sets of doublets. The doublet separation reached a maximum near $\alpha = 20°$. When H was close to the a or b axes the two sets superimposed, but the doublet structure remained. This effect suggests that ions 1 and 3 and ions 2 and 4 become equivalent with H near the γ axis, but that ions 1 and 4 and ions 2 and 3 are equivalent with H near the a or b axes.

The most logical explanation for the doublet structure in both the ac and ab plane spectra is that the x axis is tilted away from the γ direction in a way that it is no longer in the γc or ab planes. The site occupied by the $Ni(H_2O)_6^{2+}$ has two-fold symmetry in the γ direction, but since this ion does not exactly fit this site it is possible to have a tilting of the x axis away from the γ axis. This tilt has equal probability of being in one of two directions and as a result it appears as if the equivalence of the paired ions is broken. Since both forms of tilt are possible, some ions of type 1 will have one direction

of tilt and an equal number will have the opposite tilt. The ions in the unit cell have a helical nature and it seems probable that the tilt could be characterized as mainly along the pitch of the helix or mainly transverse to it. We did not establish the absolute configuration of any of our crystals and we could not establish the helical sense of the tilt.

For the ab plane spectra we introduced another tilt angle β' for the deviation of x away from γ in the ab plane. A fit which is reasonable is shown in Fig. 4. The best parameters to fit all of our data for Ni^{2+} are given in Table I. These parameters are rather similar, but not equal, to those reported by Fisher and Hornung[4] for Ni^{2+} in α-$NiSO_4 \cdot 6H_2O$. The major difference is the smaller D value, where $D = 4.74\ cm^{-1}$ was found to fit the thermodynamic data for α-$NiSO_4 \cdot 6H_2O$. The significance of our results will be discussed later.

B. Cu^{2+} in $ZnSeO_4 \cdot 6H_2O$

A rectangular plate (6.5x6.5x2 mm^3) was cleaved from a large crystal of Cu^{2+}: $ZnSeO_4 \cdot 6H_2O$ grown at 5°C in a refrigerator. The sample was mounted horizontally, or in the ab plane, in an X-band cylindrical cavity and cooled to liquid nitrogen temperature in the double Dewar.

Two sets of four lines, characteristic of Cu^{2+} hfs, were seen at all angles except at one orientation where the two sets became equivalent. The lines were strong, narrow (peak-to-peak width of a derivative spectrum ranging from 8.4 G to 12 G) and easily detectable at this temperature with the 825 Hz field modulation. The effect of the two copper isotopes

Table I

The Spin Hamiltonian Parameters for Ni^{2+} in $ZnSeO_4 \cdot 6H_2O$

$g_{\parallel}$	$= 2.219 \pm 0.003$
$g_{\perp}$	$= 2.238 \pm 0.003$
D	$= +4.20 \pm 0.04\ cm^{-1}$
E	$= 0$
ϕ	$= 35.5° \pm 0.1°$
tilt angle[a]	$= 2.5° \pm 0.5°$

[a] The tilt of the x axis away from the γ direction. The tilt is approximately equal in the γc and ab planes.

were clearly seen in the splittings of outer lines. The ratio of the two hfs constants was 1:1.07, in close agreement with the ratio of their nuclear magnetic moments, 2.22:2.38 = 1:1.07.

Near the ab bisector, or the γ axis, one set was at the lowest field, and the other was at the highest field. The low field hf lines were clearly separated, the center of which gave g = 2.259 and A = 90.9 G. The high field lines were partially overlapping and made accurate determination of g and A difficult. A rotation of 45° made the two sets completely merge to give four lines evenly spaced with g = 2.278 and A = 96.5 G.

A powdered sample of Cu^{2+}: $ZnSeO_4 \cdot 6H_2O$ was examined over the temperature range of 20° to -160°C at X-band with 100 kHz modulation. The spectra consisted of two groups: four evenly spaced, half-derivative parallel lines in the low field and extensively overlapped perpendicular lines in the high field. At -160°C the powder spectrum resulted in

$$g_{\parallel} = 2.4291, \quad g_{\perp} = 2.098$$
$$A_{\parallel} = 115.9 \text{ G}, \quad A_{\perp} < 21 \text{ G}$$

Next a single crystal was mounted vertically with the field in the γc plane. The two sets, 2 and 4, moved closely together as the magnetic field was rotated. All four sets merged perfectly at the c axis. As the magnetic field direction was moved away from the c axis, ion 1 went toward the lower field or higher g value, and ion 3 shifted to the higher field. At α = 43.3° ion 1 reached the lowest field with g = 2.4293 and A = 115.7 G. Rotating the magnet to α = -42.9° (the sign of the angle

is only relative), we saw another minimum with the same g and A values. Thus, the angle ϕ, between the c and the z axes, must be close to 43°. Along the γ axis ions 1 and 3 merged in the low field, while ions 2 and 4 overlapped in the high field. Judging from the fact that we detected no splitting in the ab plane nor at the c axis, we assume that the x axis of each electron spin can only be tilted from the γ axis by a small angle β in the γc plane.

The angular dependence of g and A in the γc plane were fit by computer methods and they are shown in Figs. 5 and 6. The dotted curves were drawn by a computer using the parameters given.

The ab plane spectra were predicted very well by these same parameters and no splittings were observed. The ac plane had splitting as predicted by a small tilt of the x axis in the γc plane, but the observed splittings were not quite as large as expected with β = 4.1°. The average g values of the split pairs was fit very well as shown in Fig. 7, and our final parameters for Cu^{2+} are given in Table II.

C. Co^{2+} in $ZnSeO_4 \cdot 6H_2O$

Because the microwave quanta used for our EPR is much smaller than crystal field splittings, we can consider only the transition between the lowest Kramers doublet ($\tilde{J}_z = \pm 1/2$). The spin Hamiltonian for this ground doublet is identical with Eq. 1. Cobalt has one stable isotope Co^{59} with 100% natural abudnacne, I = 7/2. The analysis of the g and hf constants used for Cu^{2+} can be applied to the ground state doublet of Co^{2+} as well. The second order effect of the hf interaction in Eq. 4 can become very

Table II

Spin Hamiltonian Parameters for Cu^{2+} and Co^{2+} in $ZnSeO_4 \cdot 6H_2O$

Parameter	Cu^{2+}	Co^{2+}
$g_{\parallel}$	2.4295 ± 0.0005	5.957 ± 0.010
$g_{\perp}$	2.0965 ± 0.0005	3.45 ± 0.10
$A_{\parallel}$	(-)115.6 ± 0.3 G	77.0 ± 0.5 G
$A_{\perp}$	(+) 9.5 ± 1.0 G	20 ± 4 G
ϕ	43.3 ± 0.1°	58.5 ± 0.5°
tilt angle[a]	3 ± 1°	4.5 ± 1°

[a] The tilt of the x axis away from the γ direction in the γc plane.

large for Co^{2+}. In fact, this second order line shift is so large near the perpendicular direction that the hf lines of large m_I components cross over in some hydrated Co^{2+} ions.[11] This makes the accurate determination of $g_\perp$ and $A_\perp$ rather difficult.

A colorless rectangular plate was readily cleaved from a large single crystal of Co^{2+}: $ZnSeO_4 \cdot 6H_2O$ grown in a refrigerator. The Co^{2+} concentration was about 4% in the mother liquor but no chemical analysis of Co^{2+} contained in the single crystal was made.

We observed no EPR of Co^{2+} in this host lattice at 77°K or above. All the experiments were carried out at 1.7°K. The lines were strong at this temperature and slightly broader (width 9 ~ 10 G) than the Cu^{2+} lines.

The ab plane spectra showed only two groups of eight hf lines that merged near the a axis at g = 4.453 and A = 81.6 G. In the first order the hf splitting constant was taken directly from the separation of the central hf lines ($m_I = \pm 1/2$). The validity of this method will be discussed. The hf spacings were found to decrease progressively toward the high field. Near the γ axis one set reached the maximum g of 5.424 with A = 78.3 G, and the other set of partially overlapping eight lines reached the minimum g of about 3.26 with A ~ 15 G. Unlike the spectra of other orientations the perpendicular lines showed progressively smaller hf spacings toward lower field. The lowest three hf components were superimposed on top of one another.

When the crystal was mounted vertical so that H was rotated in the γc plane, four sets of eight lines were detected. The general behavior of these four sets resembled closely that of Cu^{2+}. The splittings of

ions 2 and 4 were real in Co^{2+}. The four sets merged perfectly at the c axis at g = 4.315 and A = 79.2 G. The lowest field in the γc plane occurred at $\alpha = 58°$ from the c axis. The results are shown in Figs. 8 and 9. As before, the experimental points are drawn in as open circles. We assume that the x axes of the Co^{2+} ions are tilted from the γ axes toward the c axis. This assumption is made on the following considerations. First, there were only two types of Co^{2+} ions detected in the ab plane. Secondly, the four ions became identical at the c axis, while ions 2 and 4 and ions 1 and 3 became equivalent at the γ axis. These observations require both the x and z axes of the four ions to lie in the γc planes, as in Cu^{2+} in $ZnSeO_4 \cdot 6H_2O$.

The plots[8] of g^2 vs. n^2 and of g^4A^2 vs. n^2 showed nearly straight lines with $g_{\parallel} = 5.976$, $g_{\perp} = 3.454$, $A_{\parallel} = 76.6$ G, $A_{\perp} = 24.4$ G, $\phi = 58°$ and $\beta = 2.5°$. We varied the above parameters until we obtained the best fit to the experimental points and the values given for Co^{2+} in Table II. The agreement is not very good. The large uncertainties involved in the perpendicular components of the g and the hfs constants are due to the difficulty in determining the center position of the eight lines, which are shifted as much as thirty gauss by the second order effect. This point will be discussed in the next section.

In the analysis of the experimental data we have consistently made two assumptions. The first assumption was that the g value could be calculated from the average position of the two central hf lines. The second one was that the hf splitting was taken as the spacing of these two center lines. Here we examine the validity of these two assumptions.

In Table III we compare the observed line positions and spacings with those calculated from Eq. 4. For H along the c axis we find that the agreement is better than 0.1% for the parameters that are consistent with the values given in Table II. The agreement was much worse for the perpendicular direction, and we had to use parameters that have considerable departure from those of Table II.

A point to note is the difference between H_o and H_{center}. The field H_o is the theoretical line center that determined the g value ($H_o = h\nu/g\beta$), while H_{center} is the average field position of the two central hf lines. The experimental g values in this work were calculated from H_{center}, which was always smaller than H_o. The difference between these two quantities is about 3 G for H parallel to c and over 30 G for the perpendicular spectrum. These shifts make the observed g values larger by 0.2% (or $\Delta g = +0.008$) for H parallel to c and by 1.5% (or $\Delta g = +0.05$) for H parallel to x. The error involved in the observed g factor becomes appreciable near the perpendicular direction, and yet the deviation of the $g_\perp$ value in Table II from the observed $g_\perp$ is much greater than the uncertainty involved in the assumption that $H_o = H_{center}$. In fact, the second order hf correction changes the g factors in the wrong direction. We have encountered this problem in other Co^{2+} systems,[8] and we do not know the reason for this large discrepancy.

In Eq. 4 one finds that the first, third and fourth terms make the same contribution to the line position of $+m_I$ as to that of $-m_I$. The separation of the $\pm m_I$ lines is equal to $2Am_I$, and

$$A = [H(m_I) - H(-m_I)]/(2m_I). \qquad (5)$$

Since the two central lines of Co^{2+} (and of Cu^{2+}) always correspond to $m_I = \pm 1/2$ lines, $A = H(1/2) - H(-1/2)$. Thus, we can safely take the separation of the two center lines as the true hf splitting. In Table III we see that experimental observation substantiates the above statement fairly well.

In conclusion, we can say that the first assumption of $H_o = H_{center}$ may contain a considerable error near the perpendicular direction which we do not fully understand, but that the second assumption seems valid for all directions.

IV. Discussion

A. $Ni(H_2O)_6^{2+}$

The parameters obtained for $Ni(H_2O)_6^{2+}$ in $ZnSeO_4 \cdot 6H_2O$ can be compared to the magnetothermodynamic values[4] in α-$NiSO_4 \cdot 6H_2O$ where $g_{\parallel} = 2.216$, $g_{\perp} = 2.250$, $\phi = 39.0°$ and $D = 4.741\ cm^{-1}$. The g values are remarkably close and the angle ϕ must be affected by the fact that the two hydrates have different lattice parameters. The same argument could also be applied to the difference in D values, but we have evidence that this is not the case.

We have done EPR work[5,8] on both α-$NiSO_4 \cdot 6H_2O$ and on $NiSeO_4 \cdot 6H_2O$ and far-infrared work[5] on α-$NiSO_4 \cdot 6H_2O$. These data suggest that the thermodynamic value for D includes some contributions from Ni^{2+}-Ni^{2+} exchange interaction. These contributions are ~0.1 to ~0.5 cm^{-1} in value and they can account for the apparent low D value for the isolated ion. If one is to use the molecular field approximation[4] to make a full account

Table III

Hyperfine field positions of Co^{2+} in $ZnSeO_4 \cdot 6H_2O$ [a]
(in units of gauss)

	H parallel to c				H parallel to γ			
	Observed		Calculated[b]		Observed		Calculated[c]	
Lines	H	ΔH	H	ΔH	H	ΔH	H	ΔH
1	1342.1		1340.9				2124.5	
		86.5		87.7				7.8
2	1428.6		1428.6				2132.3	
		85.0		85.0				10.6
3	1513.6		1513.7				2142.9	
		82.2		82.4				13.4
4	1595.8		1596.0		2158		2156.3	
		79.2		79.7		14		16.2
5	1675.0		1675.7		2172		2172.5	
		76.9		77.1		19		19.0
6	1751.9		1752.8		2191		2191.5	
		75.6		74.4		22		21.8
7	1827.5		1827.2		2213		2213.3	
		73.2		71.7		25		24.6
8	1900.4		1898.9		2238		2237.9	
H_o			1638.7				2196.8	
H_{center}	1635.4		1635.9		2165		2164.4	

[a] Measured at 9.8615 GHz

[b] Calculated with $g_{\parallel} = 5.96$, $g_{\perp} = 3.45$, $A_{\parallel} = 77.5$ G, $A_{\perp} = 24$ G, $\phi = 58°$, and $\beta = 5°$.

[c] Calculated with $g_{\parallel} = 5.99$, $g_{\perp} = 3.21$, $A_{\parallel} = 77$ G, $A_{\perp} = 16$ G, $\phi = 58.8°$, and $\beta = 2.5°$.

of Ni^{2+}-Ni^{2+} exchange interactions, it is necessary to alter the isolated ion D value to include the exchange contributions which are not field dependent. One of the reasons for this study was to determine the D value for the isolated ion without exchange.

The sign of the D value for the distorted $Ni(H_2O)_6^{2+}$ is of special interest. A survey[8] of the D values for Ni^{2+} has shown that only in a tetragonally distorted ion can crystal field theory account for the sign of D. For trigonal distortion one must take into account other considerations such as anisotropy in spin-orbit coupling and configurational interaction with excited electronic states.

Fisher and Hornung[4] found that crystal field theory (CFT) would fit their $Ni(H_2O)_6^{2+}$ results very well. This agrees with our conclusions about Ni^{2+}, and one can use the well known CFT equations with our Ni^{2+} results. These give

$$\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3 = 2.232$$

$$\langle g \rangle - g_e = 0.229$$

$$g_{\parallel} - g_{\perp} = -0.019$$

and CFT predicts that[12]

$$\lambda = \frac{-\Delta(\langle g \rangle - g_e)}{8} \sim -245 \text{ cm}^{-1} \qquad (6)$$

$$D = \frac{-\lambda(g_{\parallel} - g_{\perp})}{2} \sim +2.3 \text{ cm}^{-1} \qquad (7)$$

$$\Delta_o - \Delta_1 = \frac{D}{4}\left(\frac{\Delta}{\lambda}\right)^2 \sim 1200 \text{ cm}^{-1} \qquad (8)$$

where Δ is the geometric mean of Δ_o and Δ_1 and should be equal[12] to about 8500 cm^{-1}. This spin-orbit coupling constant[12] of the free Ni^{2+} ion, -324 cm^{-1}, is about 20% too large to account for the g shift. This discrepancy is often ascribed to bonding effects, but the free ion spin-orbit coupling constant is

roughly 50% too small to explain the observed D value. This type of discrepancy is not uncommon and is found in many crystals cited in Reference 12. McGarvey[13] attributes this discrepancy to the neglect of the charge transfer states. The contribution of the charge transfer state, excited $^1T_{2g}$ state for example, is of the same sign as that of the lower lying $^3T_{2g}$ and $^3T_{1g}$ and will increase the magnitude of the calculated D, but for g the effect is opposite to that of lower energy states so as to bring the calculated g closer to the free spin value. The tetragonal distortion is calculated to be about 1200 cm^{-1}, with the orbital doublet lying lower than the singlet. This result supports our assumption that the tetragonal distortion at the Ni^{2+} site corresponds to an elongation.

B. $Cu(H_2O)_6^{2+}$

The cupric ion has been most extensively studied by EPR. It has nine 3d electrons, one of which is unpaired. In a free ion the unpaired d electron possesses two units of orbital angular momentum, constituting a ^2D term. For hexahydrates the highest symmetry that Cu^{2+} can have is octahedral, in which the five-fold degeneracy is split into a lower doublet and an excited triplet. The Jahn-Teller theorem, however, requires that the local symmetry of Cu^{2+} must be distorted in such a way that the orbital degeneracy is removed. Because this distortion involves changes in sigma bonding, Cu^{2+} is known to prefer large distortions. In $ZnSeO_4 \cdot 6H_2O$ we assume this distortion to be tetragonal D_{4h}.

Let us see if the hydrogen-bond arrangement can precict the crystal field symmetry of Cu^{2+} substituted in the Ni^{2+} site of α-$NiSO_4 \cdot 6H_2O$. In

Cu^{2+} the ground state is a hole in either x^2-y^2 or z^2. Since the x^2-y^2 orbital has no electron distribution along the z axis, it is relatively unaffected by the more positive charge on O(3) caused by the additional hydrogen bond. The z^2 orbital, on the other hand, has its greatest electron density along the z axis. Hence, the electron in the z^2 orbital is stabilized, while the hole in the x^2-y^2 orbital is stabilized. Therefore, the ground state of Cu^{2+} in D_{4h} is expected to be x^2-y^2.

Whether the tetragonal distortion is an elongation or a compression becomes apparent in the g values of the Cu^{2+} ions. In almost all Cu^{2+} complexes, which have been studied by EPR, the tetragonal distortion is an elongation of an octahedron along the z axis relative to the xy plane. The only exception known is K_2CuF_2, where a compressed octahedron was found.

An elongation of an octahedron along the x axis stabilizes electrons in a_{1g} (z^2) orbital state but holes in b_{1g} (x^2-y^2) state. Cu^{2+} is conveniently treated as one unpaired hole. The g values of Cu^{2+} in the ground state of (x^2-y^2) and (z^2) are[14]

$$\begin{array}{ccc} & \text{ground state} & \\ & x^2-y^2 & z^2 \\ g_{\parallel} & g_e(1-4\lambda/\Delta_o) & g_e \\ g_{\perp} & g_e(1-\lambda/\Delta_1) & g_e(1-3\lambda/\Delta_2) \end{array} \quad (9)$$

Noting the negative value of λ for Cu^{2+}, we see

$$g_{\parallel} > g_{\perp} \text{ in } x^2\text{-}y^2 \quad \text{and} \quad g_{\parallel} < g_{\perp} \text{ in } z^2.$$

An observation of $g_{\parallel} > g_{\perp}$ clearly indicates that the tetragonal distortion is an elongation rather than a compression along the z axis.

In Table II we list the results for Cu^{2+} in $ZnSeO_4 \cdot 6H_2O$. We feel that the assignments of the g values are quite certain but that of $A_{\perp}$ may contain a large uncertainty. The Cu^{2+} spectra can be explained by an axial spin Hamiltonian, if the magnetic x axis is tilted by a few degrees from the γ axis toward the c axis. The fact that the Cu^{2+} spectrum remained axial over the temperature range of 77° to 300°K suggests that the distortion of an octahedron is tetragonal rather than trigonal. Judging from the g values, we conclude that the ground state of Cu^{2+} is (x^2-y^2). This result is consistent with the nature of the hydrogen bondings in the host crystal and with the interpretation of the Ni^{2+} spectra in $ZnSeO_4 \cdot 6H_2O$.

From Eq. 9 the CFT predicts

$$\left.\begin{aligned} g_{\parallel} - g_e &= -8\lambda/\Delta_o = 0.4272 \\ g_{\perp} - g_e &= -2\lambda/\Delta_1 = 0.0942 \end{aligned}\right\} \quad (10)$$

The ratio of $\Delta_1/\Delta_o = 1.1$ also supports the elongated octahedron model. Bleaney, Bowers and Pryce[15] have calculated the effects of order $(\lambda/\Delta)^2$ on the spin Hamiltonian parameters. The theoretical g values given for the ground state (x^2-y^2) are

$$\left.\begin{aligned} g_{\parallel} &= g_e(1+4w-3u^2/2-2uw) \\ g_{\perp} &= g_e(1+u-2w^2) \end{aligned}\right\} \quad (11)$$

Here we distinguish 2.0023 for g_e from 2.000 and define the quantities u and w as

$$u = \lambda/\Delta_1$$
$$w = \lambda/\Delta_o$$

The use of successive approximations in Eq. 11 yield the values of u and w.

	Eq. 10	Eq. 11
u	0.0471	0.0533
w	0.0534	0.0559

The optical spectra of $Cu(H_2O)_6^{2+}$ have been observed in solution and the cubic field splitting is found[16] to be $\Delta = 12600\ cm^{-1}$. If we assume that the average of Δ_o and Δ_1 is close to this value, we obtain the spin-orbit coupling constant,

$$\lambda = -\ 12600 \times (0.0546) = -690\ cm^{-1}$$

which is 83% of that of the free Cu^{2+} ion. This kind of a reduction is commonly ascribed to bonding effects.

The hfs constants can be treated in a similar fashion. Bleaney et al.[15] give the following equations.

$$\begin{aligned} A_{\parallel}/P &= -\kappa(1-u^2) - 4/7 + 6u/7 + 8w - 3u^2/7 - 40uw/7 \\ A_{\perp}/P &= -\kappa(1-u^2/2 - 2w^2) + 2/7 + 11u/7 + 9u^2/14 - 4w^2/7 \end{aligned} \qquad (12)$$

where $$P = g_e g_n \beta\beta_n \langle r^{-3} \rangle \qquad (13)$$

P will be calculated below. The constant κ is an empirical parameter, often called the core polarization parameter, which represents a measure

of the admixture of excited configurations with unpaired s electrons. There are two stable isotopes of copper, both with $I = 3/2$. Cu^{63} (69.1% abundance) has a nuclear magnetic moment, μ_n, of +2.226, while Cu^{65} (30.9% abundance) has $\mu_n = +2.385$, in units of the nuclear magneton. We will take the weighted average of the two isotopes as $\mu_n = 2.275$ n.m. 1 n.m. = 5.050×10^{-24} erg. gauss^{-1}. Then

$$g_e g_n \beta\beta_n = g_e \beta \mu_n / I = 1.422 \times 10^{-43} \text{erg}^2.\text{gauss}^{-2}$$

Changing erg into cm^{-1}, we obtain

$$g_e g_n \beta\beta_n = 7.160 \times 10^{-27} \text{cm}^{-1}.\text{cm}^3$$

The quantity $< r^{-3} >$ is listed in Table 7.6 of reference 9 and for a free Cu^{2+} ion is equal to 8.252 in atomic units. Therefore, for the free Cu^{2+} ion

$$P_o = 0.399 \text{ cm}^{-1}$$

in close agreement with the 0.036 cm^{-1} value of Abragam and Pryce, who used $< r^{-3} > = 7.25$ a.u. for the Cu^{2+} ion.

Substitution of u and w into Eq.12 results in

$$\begin{aligned} 1.003\, A_{\parallel}/P &= -\kappa - 0.0971 \\ 1.008\, A_{\perp}/P &= -\kappa + 0.372 \end{aligned} \qquad (14)$$

A general equation of the form

$$A_i'/P = -\kappa + f_i \qquad (15)$$

shows that a plot of A_i' vs. f_i will result in a straight line of slope P and of intercept κ with the abscissa. The sign of the hf constants is experimentally indeterminant, but Eq.14 and the plot of Eq.15 usually determine the sign. For example, in Cu^{2+}:$ZnSeO_4 \cdot 6H_2O$, $|A_{\parallel}| > |A_{\perp}|$, hence $\kappa > 0$ and $A_{\parallel} < 0$. We plot in Fig. 10 the results of Cu^{2+} in $ZnSeO_4 \cdot 6H_2O$ and also in LMN and in $Zn(BrO_3)_2 \cdot 6H_2O$. The last two systems possess trigonal symmetry.[8]

Table IV lists the parameters calculated for the three systems. The three straight lines of nearly equal slopes in Fig. 10 demonstrate the correct signs of the hf constants and the soundness of the prediction of the CFT. The calculated value of P for Cu^{2+}:$ZnSeO_4 \cdot 6H_2O$ is 82.7% of the free ion value. The amount of reduction is quite similar to the reduction in the spin-orbit coupling. This indicates that both reductions are due to bonding effects. The degree of covalency in the three systems is expected to be similar, since all three are coordinated with six water molecules in nearly octahedral symmetry. This expectation is supported by the similar values of λ/λ_{free} in the three systems. However, the smaller values of P/P_o in Cu^{2+}:LMN and in Cu^{2+}:$Zn(BrO_3)_2 \cdot 6H_2O$ are surprising. We should probably not take too literally the parameters of Table IV as a measure of the degree of covalency in the Cu^{2+} hydrated salts.

We may say, from Eq.13, that in a solid $\langle r^{-3} \rangle$ is reduced to 6.49 a.u. Then χ is calculated to be

$$\chi = -3\kappa\langle r^{-3}\rangle/2 = -3.14 \text{ a.u.}$$

Table IV Analysis of hf constants of Cu^{2+}.

	$ZnSeO_4 \cdot 6H_2O$	LMN[a]		$Zn(BrO_3)_2 \cdot 6H_2O$ [a]	
	77°K	1.7°K	77°K	1.7°K	77°K
u	0.0533	0.0561	0.0593	0.0521	0.0575
w	0.0559	0.0605		0.0582	
$A_{\parallel}$[b]	-131.5	-111.5	-26.7	-112.0	-25.9
$A_{\perp}$[b]	+ 8.3	+ 16.8		+ 18.7	
$f_{\parallel}$	- 0.097	- 0.060	0.232	- 0.080	0.225
$f_{\perp}$	0.372	0.377		0.370	
κ	0.339	0.316		0.305	
p[b]	330	298		291	
p/p_o	82.7%	74.7%		72.9%	
λ[c]	-690	-730		-700	
λ/λ_{free}	83%	88%		84%	
$\langle r^{-3} \rangle$[d]	6.82	6.16		6.02	
χ[d]	- 3.47	- 2.92		- 2.75	
He/S[e]	289	244		229	

a. Calculated for the isotropic spectra of the dynamic Jahn-Teller interaction. (see reference 8). LMN is $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$.

b. In units of 10^{-4} cm^{-1}.

c. In units of cm^{-1}.

d. In atomic units (a.u.)

e. In units of kG.

The value of χ has been found to be nearly constant at about -3 a.u. for the ions of the iron-group. It depends on the nature of the ligand, and decreases a little with increasing covalency.

The hf field due to the core polarization alone can be computed from

$$H_e = -\beta\chi S = -83.4\ \chi\ S\ \text{kG}$$

when χ is in atomic units (Reference 9, Eq. 7.68). The fact that χ remains constant for all the $3d^n$ ions predicts the nearly identical core polarization field of 250 kG per unit of electron spin, which is in very good agreement with experimental results (see Table 7.21 of Reference 9 and the references given there).

The $Cu(H_2O)_6^{2+}$ seems to have fit in the sites as well as $Ni(H_2O)_6^{2+}$. The two ϕ values are fairly close in value and for Cu^{2+} the tilting is limited to the γc plane. The sizes of the hydrated complexes are not too well known,[17] but $Cu(H_2O)_6^{2+}$ appears to be closer in size to $Zn(H_2O)_6^{2+}$ than is $Ni(H_2O)_6^{2+}$. This is consistent with a decreased tilt for Cu^{2+}.

C. $Co(H_2O)_6^{2+}$

Abragam and Pryce[18] discussed the theory of $3d^7$ with a small axial distortion of an octahedral field. They chose the wavefunctions of the ground state doublet ($\tilde{J}_z = \pm 1/2$) as the linear combinations of $|\tilde{\ell}_z, S_z\rangle$.

$$|1/2\rangle = a|-1,3/2\rangle + b|0,1/2\rangle + c|1,-1/2\rangle$$
$$|-1/2\rangle = a|1,-3/2\rangle + b|0,-1/2\rangle + c|-1,1/2\rangle$$

with $a^2 + b^2 + c^2 = 1$.

They expressed the g factor and the axial splitting in a parametric form of x:

$$g_{\parallel} = 2 + 4(2-\alpha)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right]\cdot\left[P + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]^{-1}$$

$$g_{\perp} = 4\left[P - \frac{2-\alpha}{(x+2)} + \frac{12}{x(x+2)}\right]\cdot\left[P + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]^{-1} \tag{16}$$

$$\Delta = \lambda\frac{\alpha'^2}{\alpha}\left[\frac{3}{x} + \frac{4}{x+2}\right] - \alpha\lambda(x+3)/2 \tag{17}$$

with $P = (\alpha'/\alpha)^2$, $a:b:c = \frac{\sqrt{6}}{x} : -\frac{\alpha}{\alpha'} : \frac{\sqrt{8}}{x+2}$, and $\lambda = -180\ cm^{-1}$ for the free Co^{2+} ion. It is noted that the signs of α and α' here are opposite to those given in Abragam and Pryce. They also assumed $g_e = 2.00$. The x is a positive number and equals 2 in a cubic symmetry. The parameter α is expected to lie between -1 and -3/2.

An introduction of a non-zero Δ will add one more parameter to be determined. Without an accurate knowledge of Δ, we will not be able to determine all the three unknown parameters, (α, p, x), from the two experimentally known values ($g_{\parallel}$, $g_{\perp}$). If we assume p = 1, or $\alpha = \alpha'$, we can eliminate x in Eq.16 and determine α. More conveniently a graph of $g_{\parallel}$ vs. $g_{\perp}$ can be plotted as a function of α and x.

A number of Co^{2+} salts that have been investigated in the past show g values lying between curves A and B. The data of Co^{2+} in $ZnSeO_4 \cdot 6H_2O$ were plotted in reference 8 and we found that α must be close to -1.5. We conclude that

$$\alpha = -1.4 \sim -1.5, \quad P = 0.7 \sim 1.0, \quad x = 1.21 \sim 1.25$$

$$\Delta = 280 \sim 440\ cm^{-1}$$

These values are comparable to those found for Co^{2+} in Tutton salts and in zinc fluorosilicate discussed in Abragam and Pryce. The positive Δ means that the orbital doublet is higher than the singlet in accord with a tetragonal elongation of an octahedron.

The value for ϕ for Co^{2+} is quite different from that found for Cu^{2+} and Ni^{2+}. It does not seem probable that the $Co(H_2O)_6^{2+}$ complex could rotate about x by as much as 20° and still only have a small tilt angle. The size of the $Co(H_2O)_6^{2+}$ is also not expected to be greatly different from $Cu(H_2O)_6^{2+}$. A similar large value for ϕ has been found,[5,8] for Co^{2+} in α-$NiSO_4 \cdot 6H_2O$. It seems possible that for Co^{2+}, the z axis of the spin Hamiltonian deviates from the Co-O(3) axis. The great sensitivity of the g values for Co^{2+} to bonding effects could make such a deviation reasonable.

D. Exchange Effects in α-$NiSO_4 \cdot 6H_2O$ and $NiSeO_4 \cdot 6H_2O$

Our interest in Ni^{2+}, Cu^{2+} and Co^{2+} in $ZnSeO_4 \cdot 6H_2O$ is based upon our attempts to explain the observed[5,8] properties of these ions in α-$NiSO_4 \cdot 6H_2O$ and in $NiSeO_4 \cdot 6H_2O$. As mentioned earlier, the D value for the Ni^{2+} in $ZnSeO_4 \cdot 6H_2O$ can be compared with the observed far-infrared[5] zero-field splittings and with the assigned[4] thermodynamic D value of α-$NiSO_4 \cdot 6H_2O$. The far-infrared spectrum should correspond to the edge of the band ($k = 0$), while the thermodynamic D value should correspond to an average position in the band. The observed order of these energy values is D(thermo) > I.R. > D($ZnSeO_4 \cdot 6H_2O$).

The difference between the thermodynamic D value and the center of the assigned infrared absorption is only about 0.2 cm^{-1}, and it can be readily explained by exchange interaction between the equivalent $Ni(H_2O)_6^{2+}$ in the α-$NiSO_4 \cdot 6H_2O$. With D(thermo) > I.R. the coupling must be ferromagnetic, and we can conclude that the equivalent $Ni(H_2O)_6^{2+}$ interact in α-$NiSO_4 \cdot 6H_2O$ in a manner rather similar to that Dixon and Culvahouse[19] found for $Ni(H_2O)_6^{2+}$ pairs doped into double-nitrate crystals. The infrared spectrum also contains a noticeable structure which must be due to exchange between non-equivalent $Ni(H_2O)_6^{2+}$. At one time it was thought that part of this structure was due to a finite E value for the isolated ion, but it now seems clear that one must also consider a bi-quadratic exchange term of the type $J'(S_1 \cdot S_2)^2$. If this is true, then this term is much more important for α-$NiSO_4 \cdot 6H_2O$ than for double-nitrates.[19]

The difference between the thermodynamic D value and the isolated Ion D value measured in $ZnSeO_4 \cdot 6H_2O$ is 0.5 cm^{-1}. This value is too large to be explained by a band only 0.2 to 0.4 cm^{-1} wide. It is possible that the isolated ion D value in the selenate lattice is smaller than in the sulfate lattice, but we have some evidence that the opposite is true. There are second-order effects of exchange on the zero-field splittings, but these should be 0.1 cm^{-1} or less. Further work will have to be done before we can explain this apparent shift in the zero-field splittings by exchange.

For Cu^{2+} and Co^{2+} in α-$NiSO_4 \cdot 6H_2O$ we observe some interesting effects due to exchange. The EPR spectrum of each of these ions can be roughly fit using an ordinary spin Hamiltonian, but for Cu^{2+} their g values

are 0.2 to 0.4 of a unit too large in α-$NiSO_4 \cdot 6H_2O$ compared to the normal values in $ZnSeO_4 \cdot 6H_2O$. A 10-20% g value shift has many of the characteristics of the molecular field correction[4] used in the thermodynamic work. This molecular field correction is not satisfactory for the Cu^{2+} EPR, for we find that the g value shifts do not follow the temperature dependence of the bulk magnetization required by the molecular field model.

The major effect of raising the temperature near 1.5°K on Cu^{2+} in α-$NiSO_4 \cdot 6H_2O$ is to broaden its EPR line width. In fact, above about 2.2°K the Cu^{2+} spectrum is too broad to be readily observed. Similar effects were observed for Cu^{2+} doped into mixed crystals of $NiSeO_4 \cdot 6H_2O$ and $ZnSeO_4 \cdot 6H_2O$. At high temperature, only those Cu^{2+} are observed which are surrounded by Zn^{2+} and not by Ni^{2+}.

Limited EPR experiments have been done on Mn^{2+} doped into α-$NiSO_4 \cdot 6H_2O$. We are unable to fit this spectrum with an ordinary spin Hamiltonian even if we assume a large zero-field splitting. It is quite apparent that exchange effects can be readily observed for ions doped into the α-$NiSO_4 \cdot 6H_2O$ lattice. For ions with $S > \frac{1}{2}$ these effects can lead to quite complicated spin properties. By a combination of EPR and zero-field spectroscopic studies we hope to explain, on a quantitative basis, the full effects of exchange interaction.

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Figure Captions

Fig. 1. A projection of one-half of a unit cell of α-$NiSO_4 \cdot 6H_2O$ on the (001) plane. Two layers of $Ni(H_2O)_6^{2+}$ and SO_4^{2-} groups are depicted here with their relative positions along the c axis.

Fig. 2. A projection of the magnetic axes of the four Ni^{2+} ions in a unit cell on the γc planes. A and B refer to the respective corners of the diagram in Fig. 1.

Fig. 3. The observed points in the ac plane for Ni^{2+} are fit by a computer simulated spectrum with $g_{\parallel} = 2.216$, $g_{\perp} = 2.235$, $D = 4.16\ cm^{-1}$, $E = 0$, $\phi = 35.4°$, $\beta = 1.5°$.

Fig. 4. The observed points in the ab plane for Ni^{2+} are fit by a computer simulated dotted spectrum with $g_{\perp} = 2.222$, $g_{\parallel} = 2.241$, $D = 4.22\ cm^{-1}$, $E = 0$, $\phi = 35.5°$, $\beta' = 2.0°$.

Fig. 5. The observed g values in the γc plane for Cu^{2+} are fit by a computer simulated dotted spectrum with $g_{\parallel} = 2.4295$, $g_{\perp} = 2.0965$, $\phi = 43.2°$, $A_{\parallel} = 115.6$ G, $A_{\perp} = 9.5$ G, $\beta = 4.1°$.

Fig. 6. The observed A values in the γc plane for Cu^{2+} are fit by a computer simulated dotted spectrum with the parameters used in Fig. 5.

Fig. 7. A computer drawn simulation for the ac plane spectrum with the same parameters as used in Figs. 5 and 6. The points show the average position of the observed split pairs.

Fig. 8. The observed g values in the γc plane for Co^{2+} are fit by a computer simulated dotted spectrum with the parameters given in Table II.

Fig. 9. The observed A values in the γc plane for Co^{2+} are fit by a computer simulated dotted spectrum with the parameters given in Table II.

Fig. 10. Plots of Equation 15 for three Cu^{2+} systems. The LMN and $Zn(BrO_3)_2 \cdot 6H_2O$ results come from reference 8.

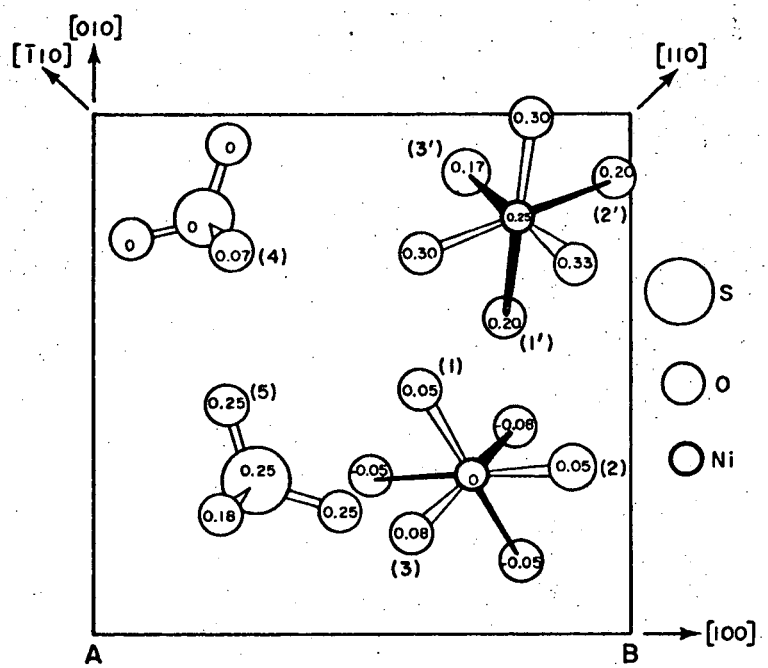
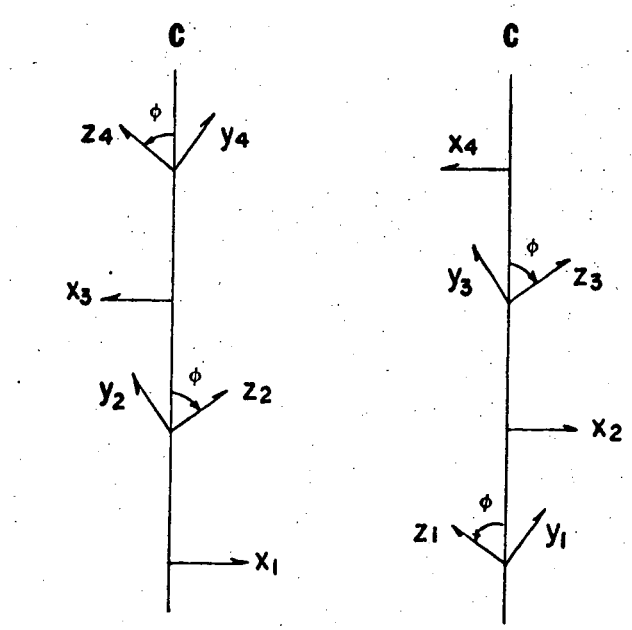


Fig. 1

Fig 1
Jindo + Myers
Electron Exchange...



XBL 7012-7309

Fig. 2

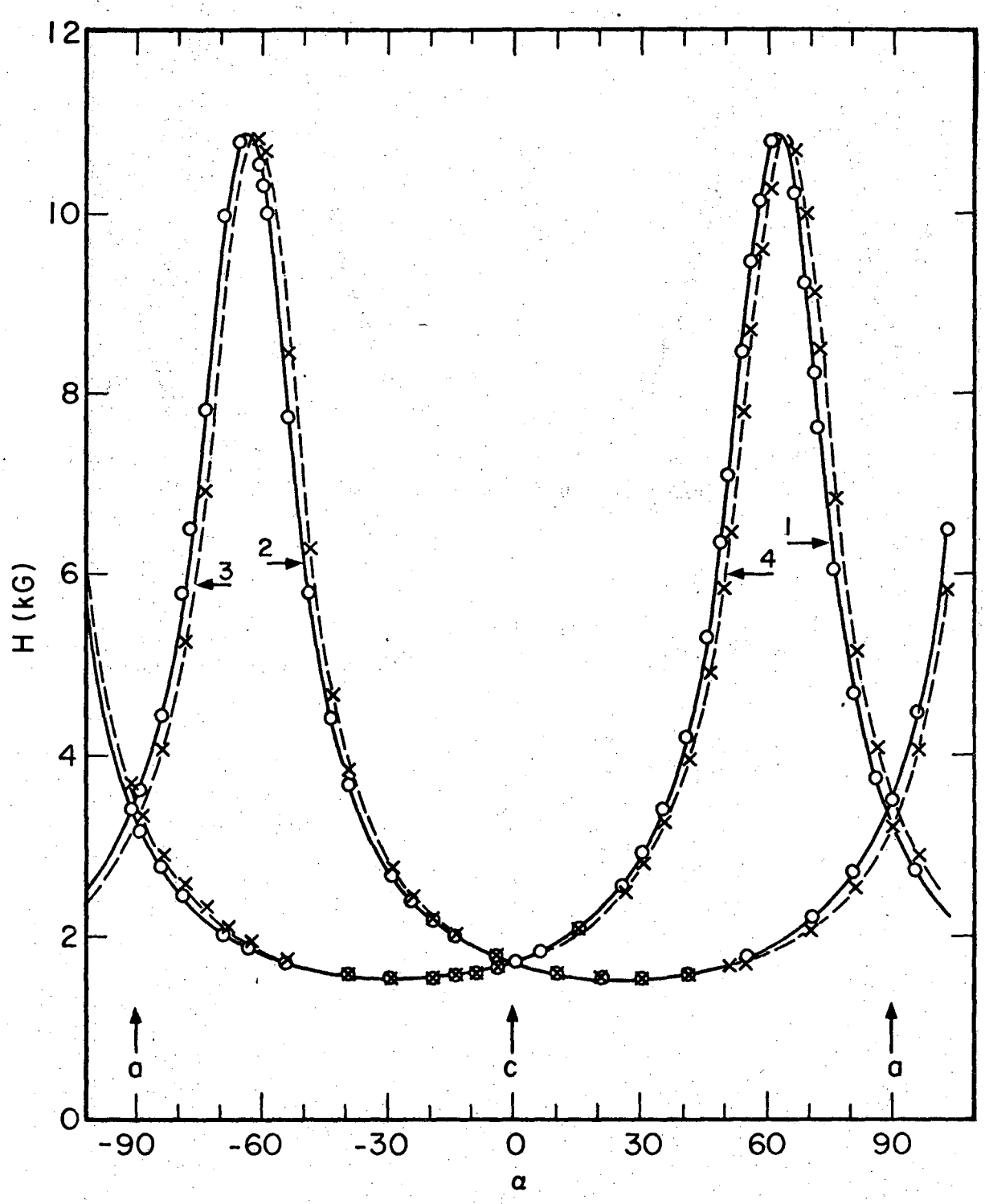


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Fig. 3

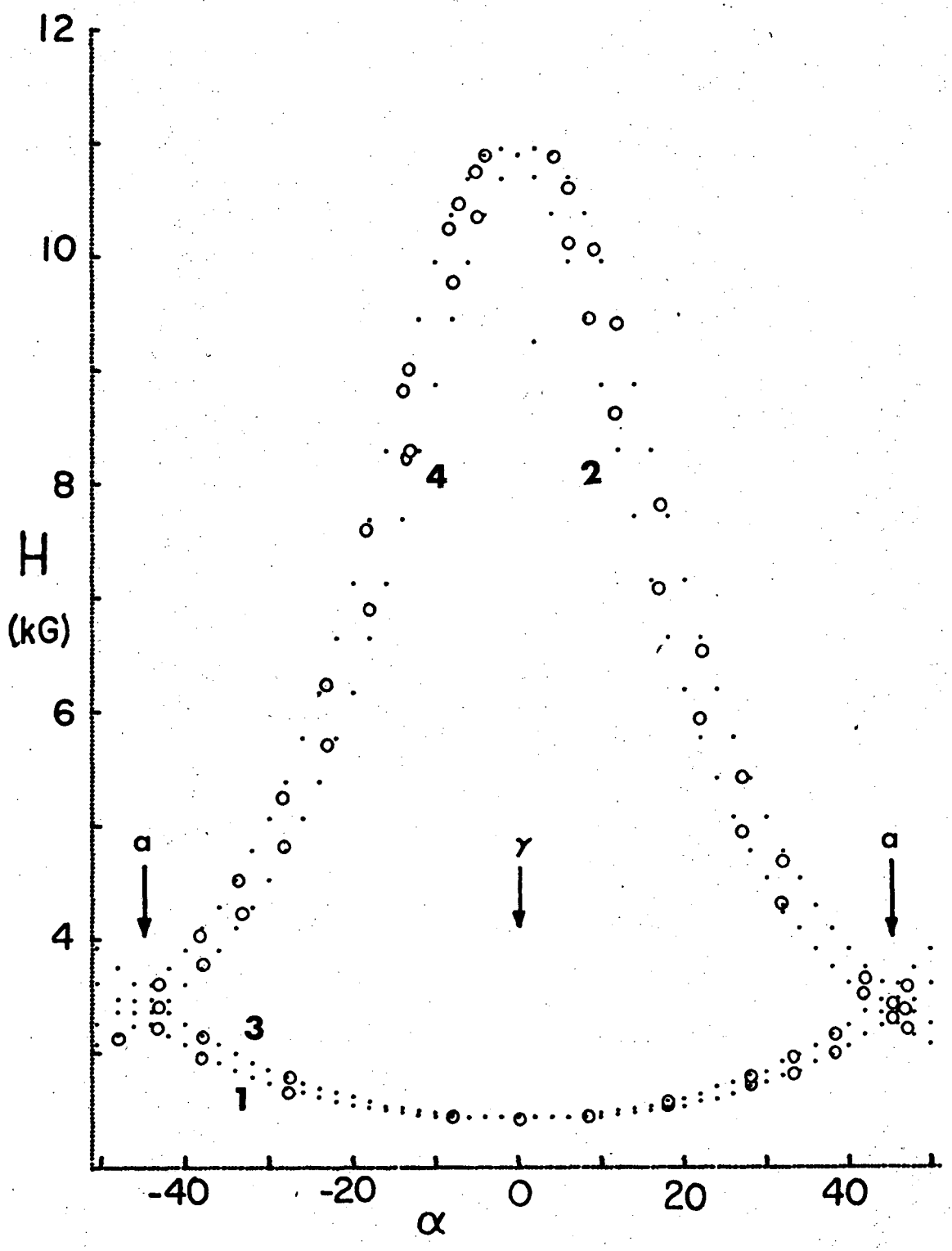

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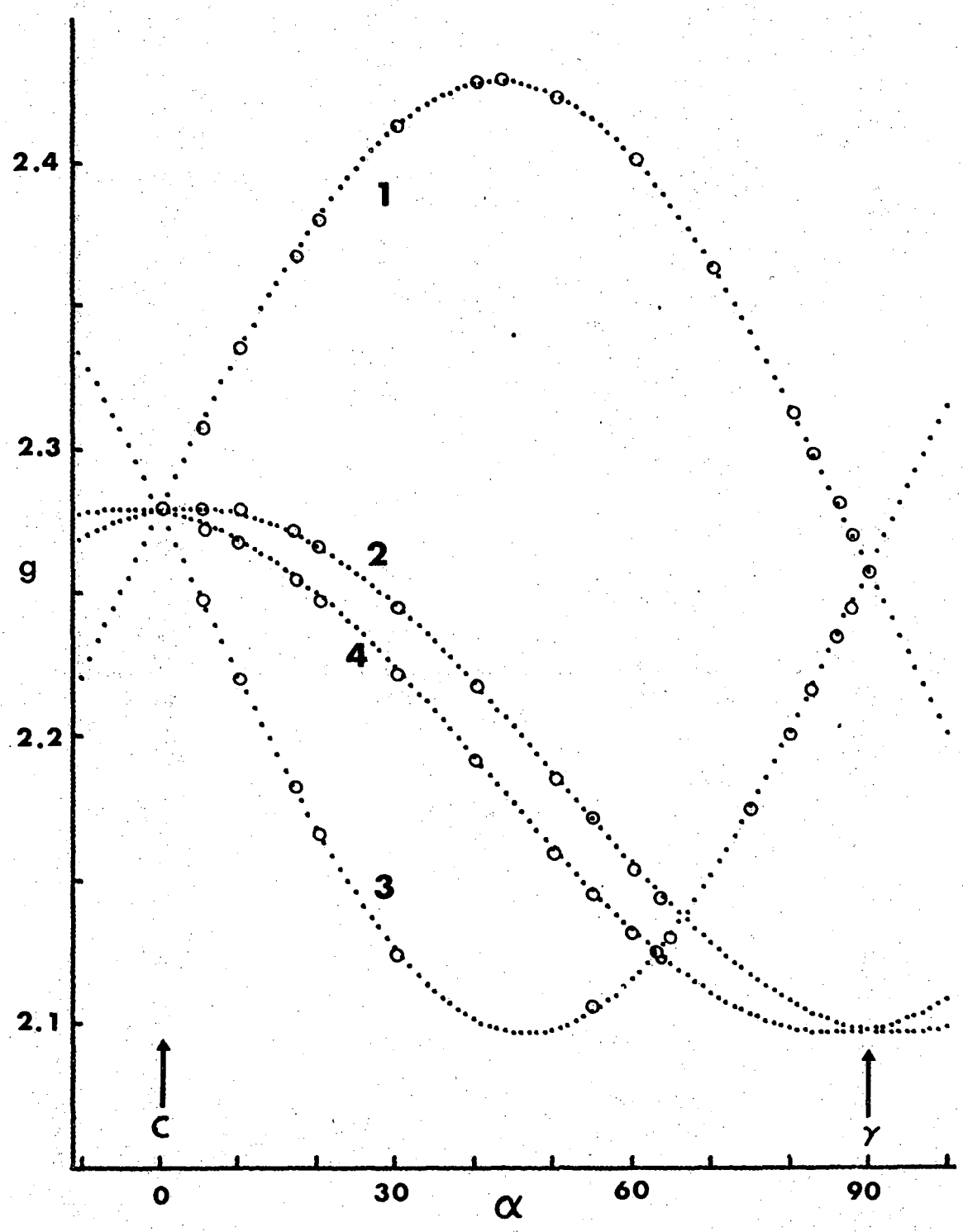
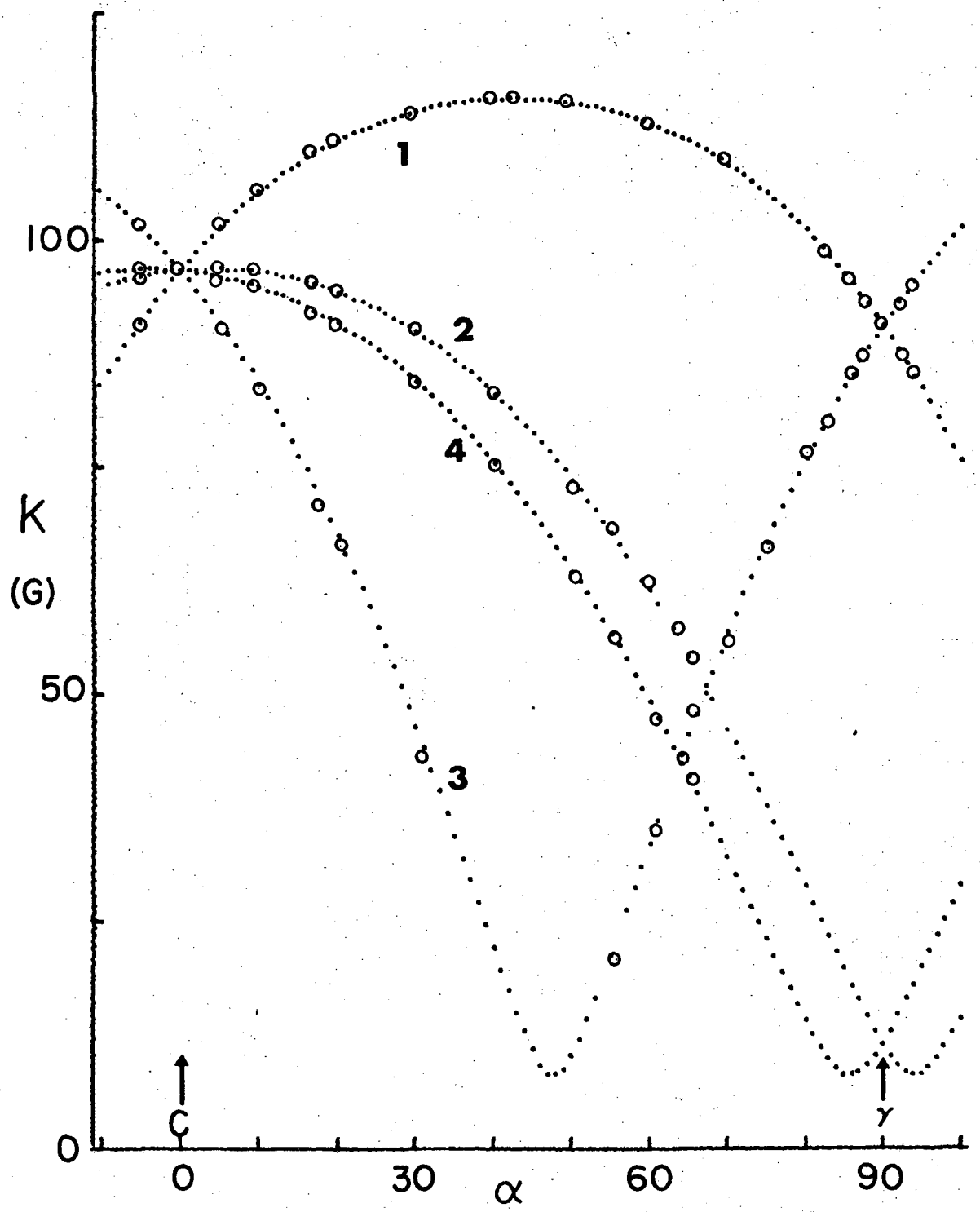
Fig. 4



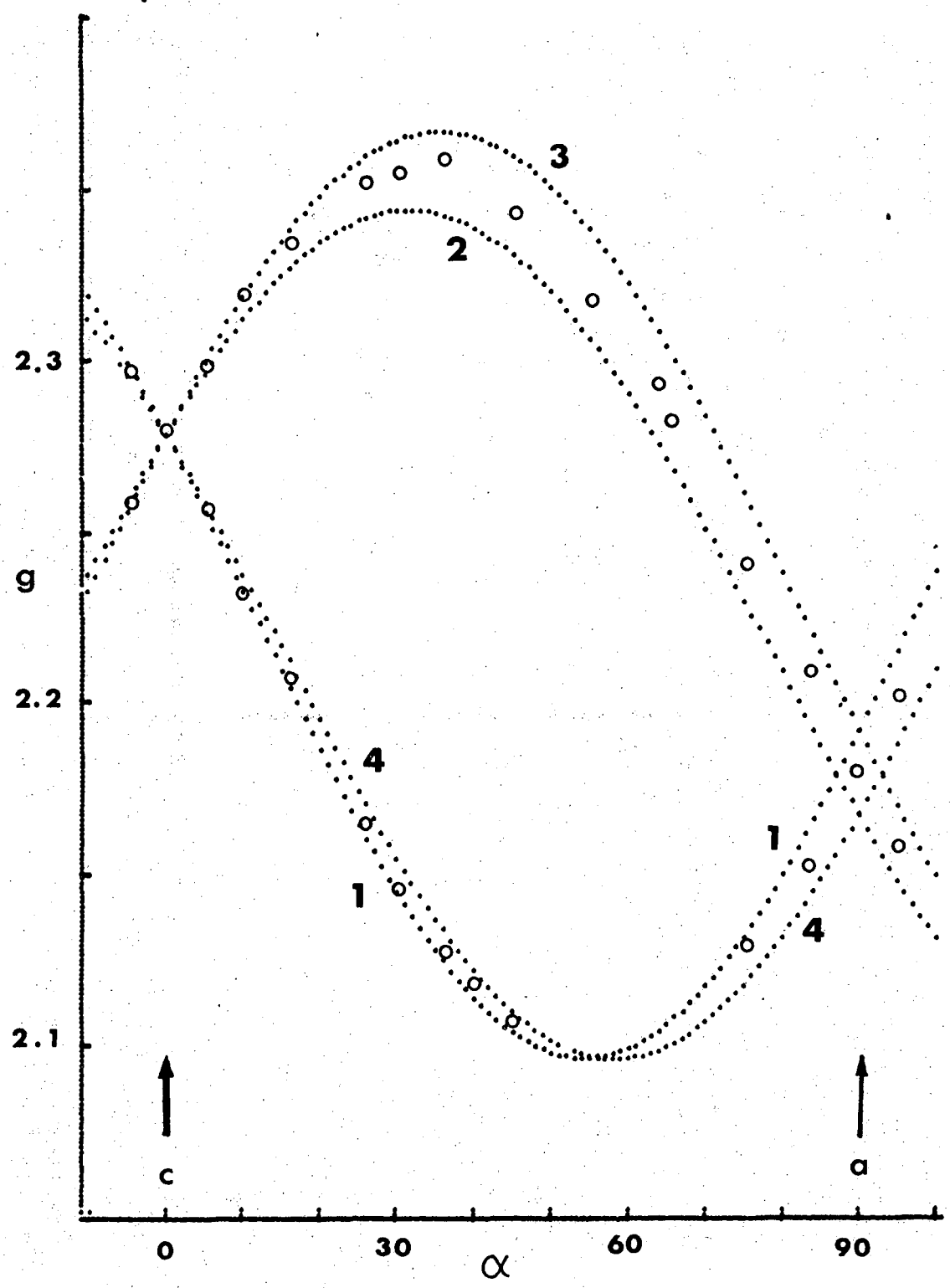
XBL 7012-7306

Fig. 5



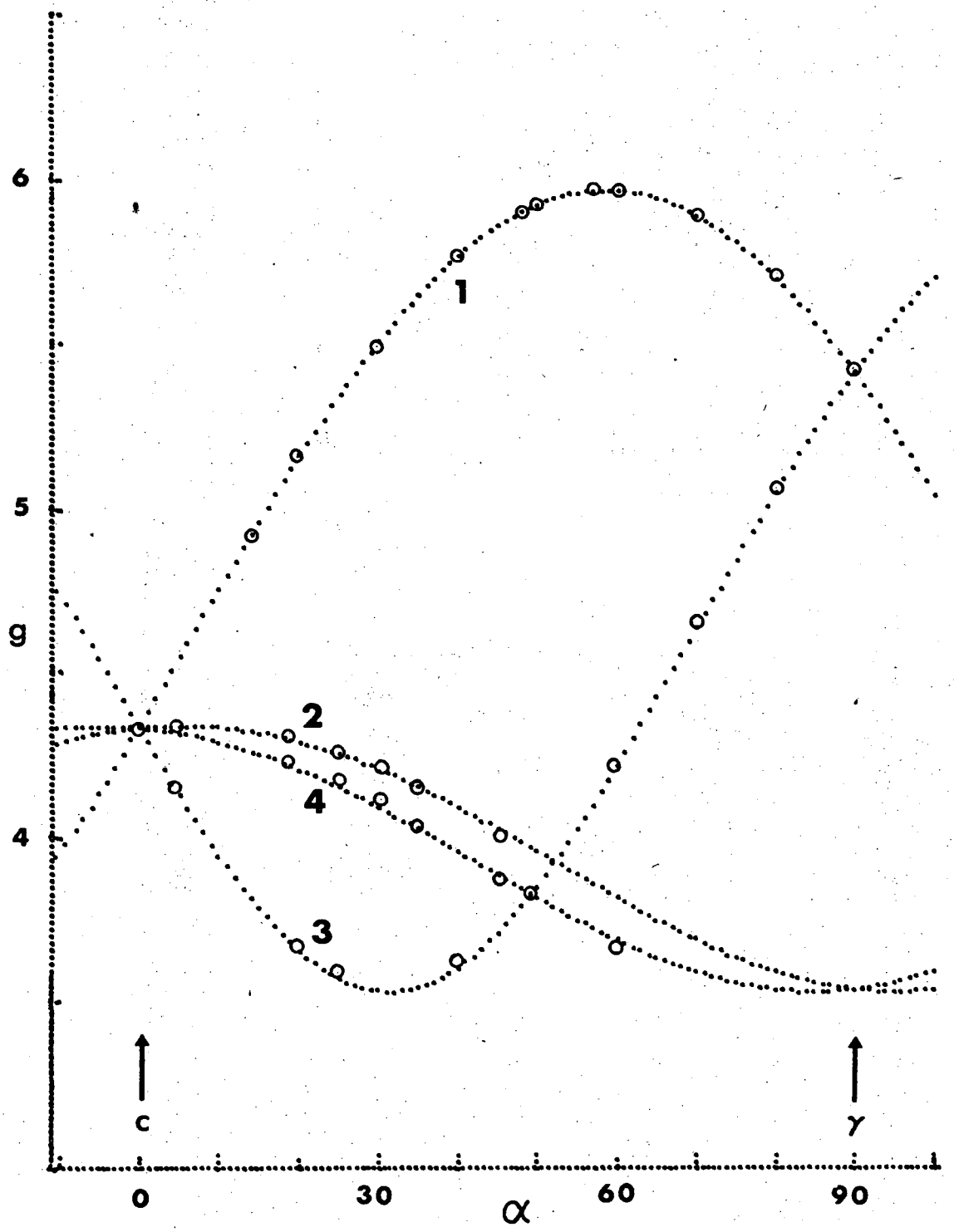
XBL 7012-7293

Fig. 6



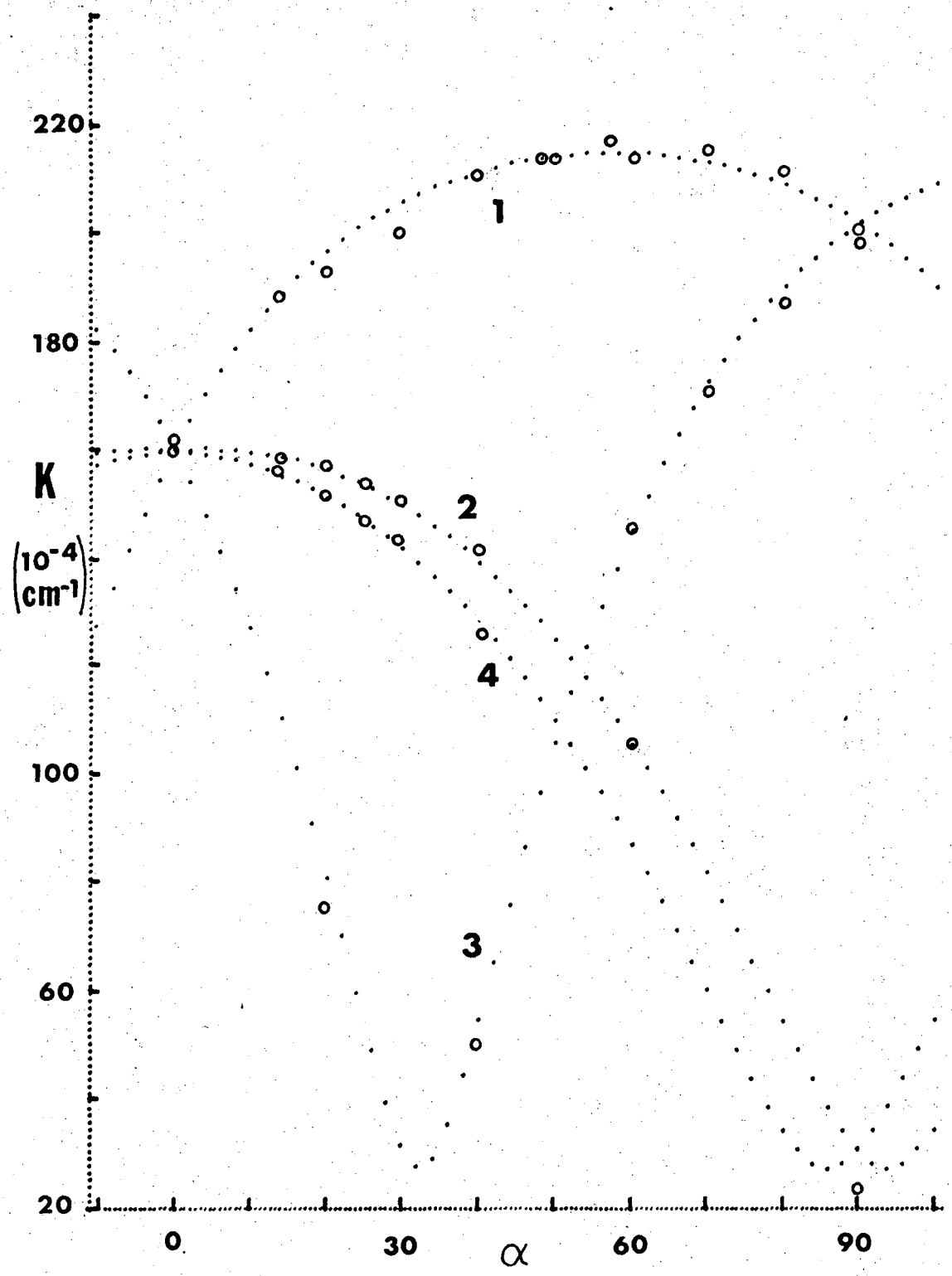
XBL 7012-7307

Fig. 7



XBL 7012-7290

Fig. 8



XBL 7012-7408

Fig. 9

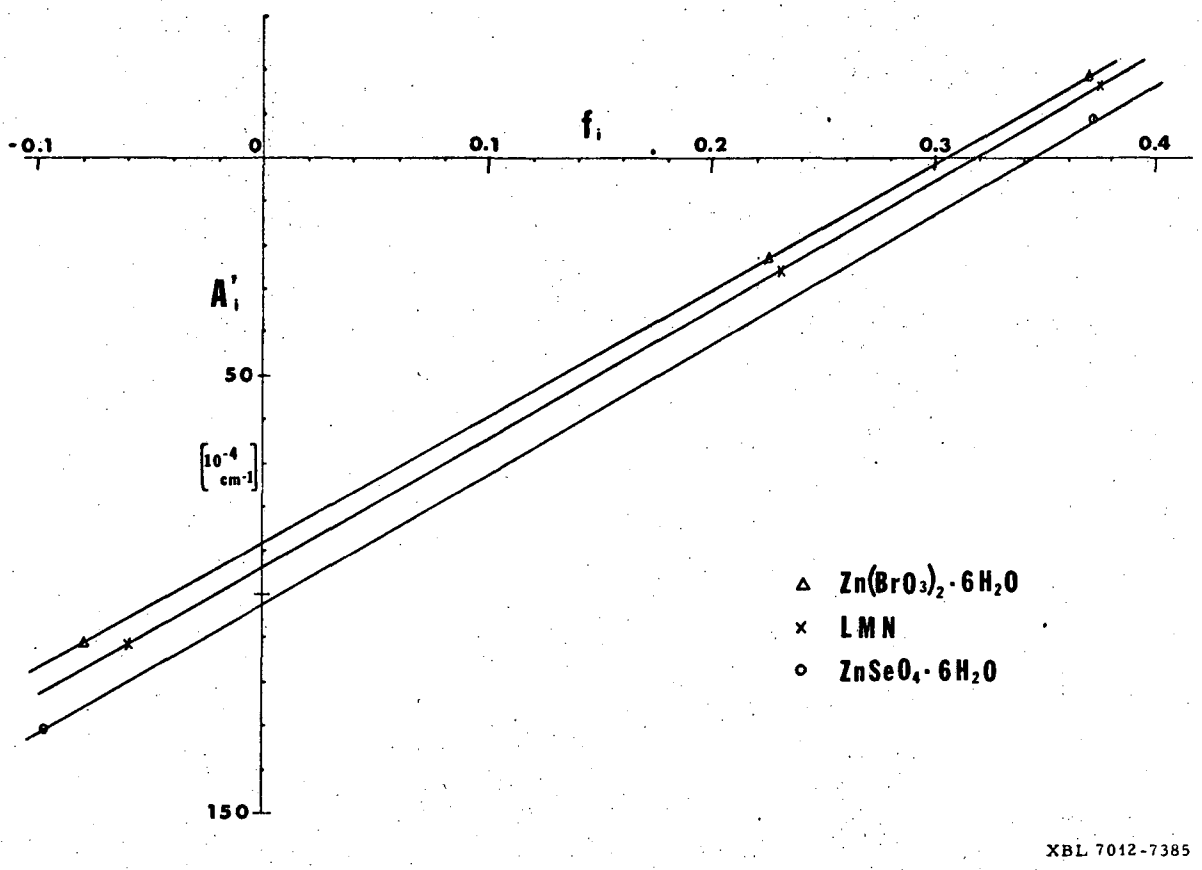

-0.1
0
0.1
f_i
0.2
0.3
0.4
A'_i
50
$[10^{-4}\ cm^{-1}]$
150
$Zn(BrO_3)_2 \cdot 6H_2O$
LMN
$ZnSeO_4 \cdot 6H_2O$
XBL 7012-7385

Fig. 10

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