ELECTRON EXCHANGE FOR HYDRATED IONS IN THE α-$NiSO_4 \cdot 6H_2O$ LATTICE

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ABSTRACT

Far-infrared and electron paramagnetic resonance spectroscopy on α-$NiSO_4 \cdot 6H_2O$ have confirmed the zero-field splitting predicted by Fisher and Hornung. However, instead of a single sharp pair of levels at 4·74 cm^{-1} we find a band which is 1 cm^{-1} wide and centred near this value. The far-infrared spectrum shows some unresolved structure but it has a sharp edge characteristic of exciton selection rules. Both the molecular field parameter and the far-infrared spectra indicate that the interaction between the $Ni(H_2O)_6^{2+}$ is mainly ferromagnetic exchange.

INTRODUCTION

A very complete low temperature thermodynamic investigation has been made[1] of α-$NiSO_4 \cdot 6H_2O$. This study utilized magnetic fields up to 90 000 gauss which were applied along either the *a*-axis, the *c*-axis, or the *a,b* bisector of a spherical single crystal. Previous work[2] had demonstrated that the $S = 1$ Ni^{2+} ions in this crystal had a non-degenerate ground state and the crystal exhibited paramagnetism at all temperatures.

The thermodynamic results were shown[3] to be very nicely explained by an axial spin Hamiltonian for the Ni^{2+} together with a relatively small molecular field parameter to account for the interactions between the Ni^{2+} in this lattice. The spin Hamiltonian for the Ni^{2+} has a fairly large zero-field splitting parameter ($D = 4.741$ cm^{-1}) and it was completely axial ($E = 0$). The unique axis of this system does closely correspond to one formed by a pair of coordinated water molecules in the $Ni(H_2O)_6^{2+}$ complex, but the crystallographic data[4, 5] do not indicate any measurable difference in the Ni—O distances. The sign of the zero-field parameter D is positive so that the lowest energy level corresponds to the non-degenerate $M_S = 0$ state and the two $M_S = \pm 1$ states are 4.74 cm^{-1} higher in energy. It has been shown[2] that this together with only a small exchange interaction between the Ni^{2+} will not allow any magnetic ordering of the Ni^{2+} in this lattice.

Shortly after the thermodynamic work was completed we set out to see how electron paramagnetic resonance spectroscopy (epr) could be utilized for the Ni^{2+} in α-$NiSO_4 \cdot 6H_2O$. Because of the large zero-field splitting we did not expect a rich epr spectrum, but we were particularly interested in how the fairly weak Ni^{2+}–Ni^{2+} interactions would affect epr. At least two previous workers had attempted to find an epr spectrum in α-$NiSO_4 \cdot 6H_2O$, but to the best of our knowledge we have been the first to correctly assign its spectrum. In addition to epr, we have been fortunate in being able to do far-infrared spectroscopy so that transitions directly involving the zero-field splitting have also been measured.

THE α-$NiSO_4 \cdot 6H_2O$ LATTICE

The Ni^{2+} are arranged[4,5] as a set of equivalent $Ni(H_2O)_6^{2+}$ which are held in four parallel planes by the SO_4^{2-}. The planes are perpendicular to the *c*-axis of a tetragonal lattice. The Ni^{2+} in each plane can be made to correspond to any Ni^{2+} in the other three planes by translation of $C_0/4$, $C_0/2$ or $3C_0/4$ together with rotations of 90°, 180° or 270° around the *c*-axis. As a result, a unit cell contains four Ni^{2+} arranged in each of the four planes and at 0°, 90°, 180° and 270° about the *c*-axis. The crystals do not have a centre of symmetry and have either space group $P4_12_12$ or $P4_32_12$. A drawing of the Ni^{2+} in a three-dimensional model is given in *Figure 1*.

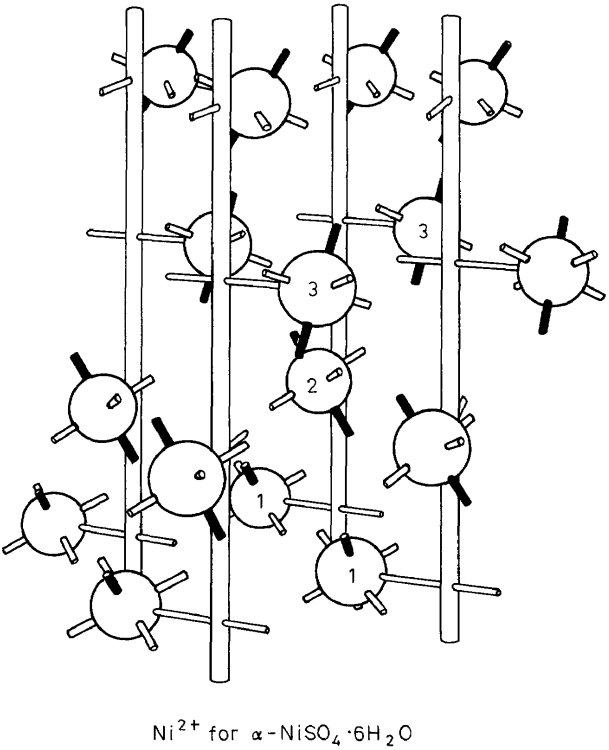

Figure 1. A drawing showing the Ni^{2+} sites in α-$NiSO_4 \cdot 6H_2O$. The *c*-axis is vertical and the *a*- and *b*-axes are perpendicular to the square formed by the four vertical rods. The unique axis of the spin Hamiltonian for each Ni^{2+} is darkened.

The unique axis of the spin Hamiltonian is twisted away from the *c*-axis by the angle ϕ. The twist axis corresponds to one of the two bisectors of the *a*,*b* axis and alternates in the four planes. In *Figure 1* the unique axis is darkened and ϕ is close to 39°. The nearest neighbours of a given Ni^{2+} are in the planes immediately above and below. In *Figure 1* it is shown that the nearest neighbours of an ion in plane 2 are in planes 1 and 3. When a magnetic field is applied along either the *a*-axis or *c*-axis or in the *a*,*b* plane, the Zeeman terms for ions 1 and 3 are identical. Nearest neighbour interactions will be designated as 1–2 interactions.

The ions in each plane are all equivalent. Interactions between these ions are designated as 1–1 interactions. The interactions which account for the molecular field[6] will be approximated as arising from 1–2 exchange, but 1–1 exchange may not be entirely negligible.

The diamagnetic $ZnSeO_4 \cdot 6H_2O$ is isostructural with α-$NiSO_4 \cdot 6H_2O$. We have made epr studies of Ni^{2+}, Cu^{2+} and Co^{2+} in this lattice for reference purposes.

FAR-INFRARED SPECTRUM

The spectrum of a single crystal of α-$NiSO_4 \cdot 6H_2O$ was taken at 4.2 K and 1.3 K from 3 cm^{-1} to 25 cm^{-1}. The instrument was a Fourier transform spectrometer built in the Department of Physics by Professor Paul L. Richards. The spectra were taken by his student, Dr. George Brackett. Data were recorded both with and without magnetic fields up to 50000 gauss applied parallel to the *c*-axis.

The zero-field absorption at 4.2 K is shown in *Figure 2*. On this figure we

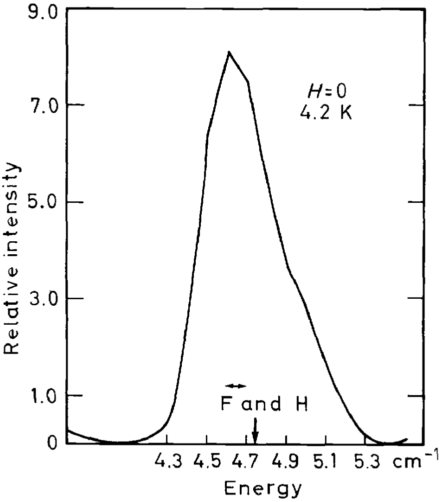

Figure 2. The zero-field far-infrared absorption at 4.2 K. The 4.74 cm^{-1} zero-field splitting value of Fisher and Hornung is indicated by the vertical arrow. The horizontal arrow indicates instrumental resolution.

also indicate both the resolution of the instrument and the position of the D value obtained by Fisher and Hornung.[3]

It is quite clear from this *Figure* that the first excited state of the Ni^{2+}, corresponding to $M_S = \pm 1$, has a band structure extending over 1 cm^{-1} in energy. The D value of Fisher and Hornung must correspond to an average position in this band. The possibility of such a band was recognized by Giauque *et al.*,[1] but it is not possible from thermodynamic measurements to establish more than the average position of the band.

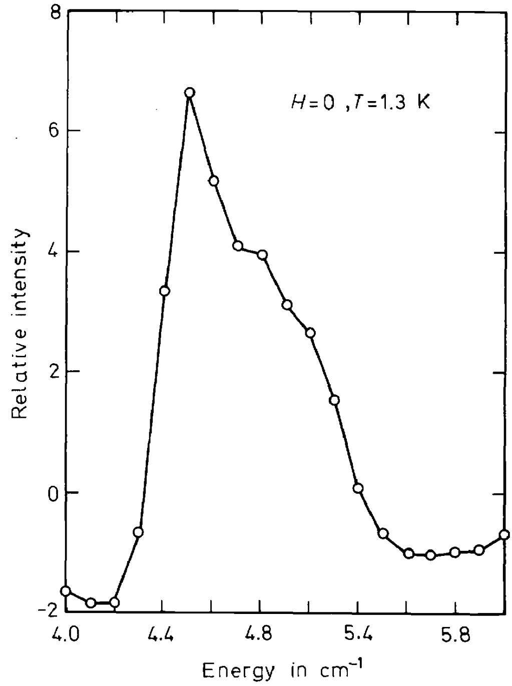

Figure 3. The zero-field far-infrared absorption at 1.3 K.

The spectrum at 1.3 K is shown in *Figure 3*. More structure is revealed at the lower temperature, but no important features are resolved. The width of the band in the spectra seems not to depend upon temperature.

The nature of the band would be expected to depend upon three effects. Exchange between equivalent ions, 1–1 exchange, should contribute an exciton structure. The $k = 0$ exciton selection rule usually leads to a band which is very sharp on one edge. In the case of *Figures 2* and *3* this is clearly the low-frequency edge of the band. When $k = 0$ corresponds to a minimum in energy, the exchange must mainly be ferromagnetic.

In addition to exciton structure the 1–2 exchange should contribute a Davydov splitting. The hints of structure in *Figure 3* could be due to such a splitting. The exciton structure can be complicated by the orbital angular momentum terms in the Ni^{2+}. The D value mainly arises from a spin–orbit mixing of the excited crystal field ${}^3T_{2g}$ states into the ${}^3A_{2g}$ crystal field ground state. The exciton and Davydov splittings which arise from exchange can be expected in bands formed by the excited $^3T_{2g}$. In this way we should also have a small variation of the D value within the band.

EPR FOR Ni^{2+}

With $h\nu \ll D$ we can only expect normal epr transitions from the ground state to the excited state band at very high magnetic fields. However, when the magnetic field is perpendicular to the unique crystal field axis epr transitions are fully allowed between the $M_S = -1$ and the $M_S = 1$ states within the band. This orientation of the magnetic field is obtained for one-half of the Ni^{2+} when it is aligned the *a,b* bisector and for rest of the Ni^{2+} when it is rotated by the angle ϕ away from the *c*-axis in the plane formed by the *c*-axis and the *a,b* bisector.

The epr absorption signal of a single crystal of α-$NiSO_4 \cdot 6H_2O$ is shown in *Figure 4* for the magnetic field along the *a,b* bisector. The very strong high-field absorption can be assigned as due to the $\Delta M_S = 2$ transitions within the band. At 4.2 K the half-width of this high-field absorption is almost doubled and the low field transitions assigned to Ni^{2+} and Co^{2+} cannot be detected. The high-field absorption can still be detected at 77 K.

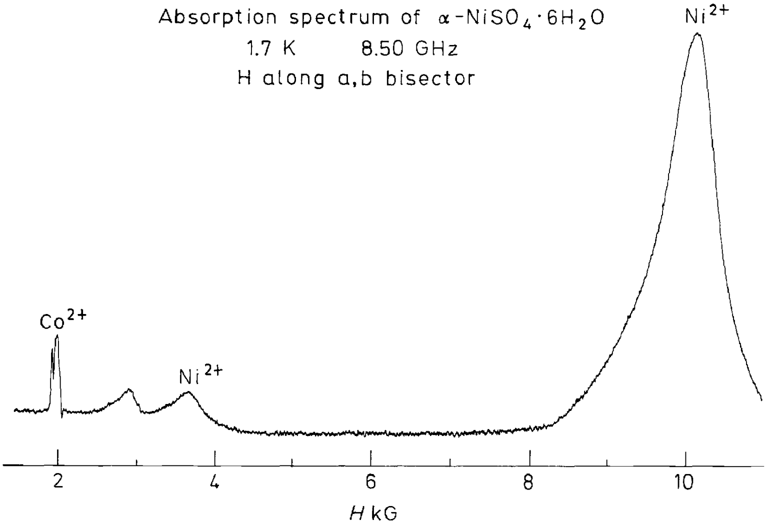

Figure 4. The epr absorption spectrum of a single crystal of α-$NiSO_4 \cdot 6H_2O$ with the field aligned along the bisector of the *a*- and *b*-axes. The second low-field absorption is probably due to an impurity in the epr cavity.

This high-field absorption is predicted within a few hundred gauss by the Ni^{2+} spin Hamiltonian parameters[3] together with the molecular field correction. This molecular field correction is predicted to change by about 500 gauss when the magnetization changes in going from 1.3 K to 4.2 K. The measured position of the high-field absorption does not shift within an experimental error of less than 100 gauss between 1.3 K and 4.2 K. The higher temperature only seems to broaden this absorption and its maximum does not shift.

The half-width of the high-field absorption at 1.2 K is close to 1000 gauss. Its absorption field directly involves the D value and a 1000 gauss half-width can be correlated to a spread in the D value of 1 cm^{-1}. Since this is greater than the apparent half-width of the absorption shown in *Figure 3*, we can conclude that some of the spread in high-field absorption is due to spin relaxation.

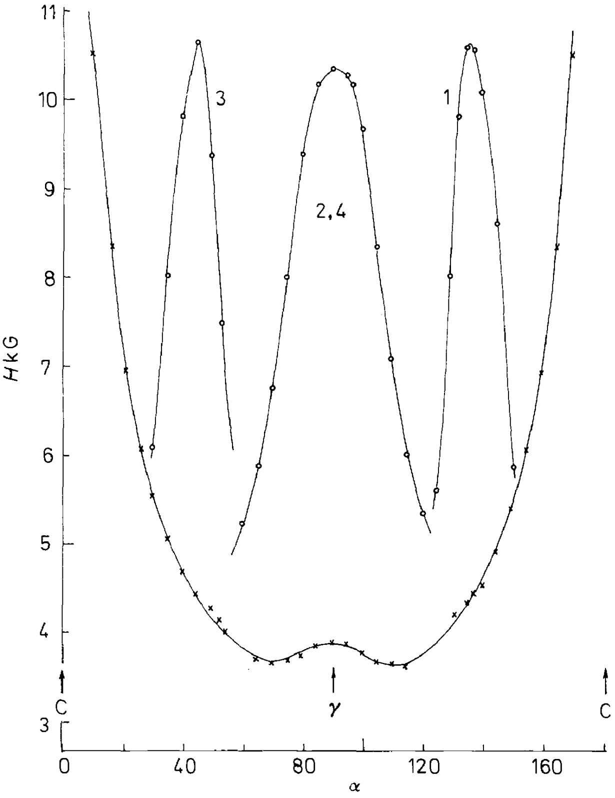

Figure 5. The variation of the Ni^{2+} epr absorptions for a field in the plane formed by the c-axis and the a,b bisector. On the figure the a,b bisector is called the γ-axis.

The position of the high-field absorption for the orientation of the field in the plane formed by the c-axis and the a,b bisector is shown in *Figure 5*. It can be seen that an additional high-field absorption is observed when $\phi = 39.8°$. This is in good agreement with Fisher and Hornung's value for ϕ.

In *Figures 4* and *5* an additional Ni^{2+} absorption is shown. It is much lower in intensity than is the high-field absorption and is usually at a lower field. This absorption can be assigned to a simultaneous pair transition for a 1–2 pair of Ni^{2+}. In *Figure 5* the field is shown as going to a very high value when the field approaches the *c*-axis. This is when the Zeeman splittings of the 1 and 2 ions become identical.

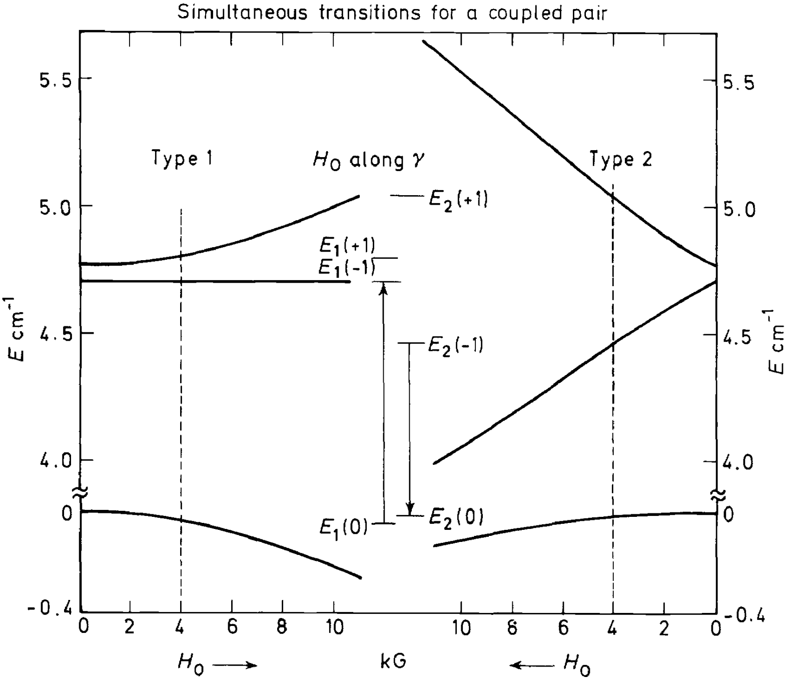

Figure 6. The energetics of a simultaneous 1–2 pair transition. The energy level diagrams correspond to the field along the *a,b* bisector.

In *Figure 6* we show an energy level diagram for both the 1 and 2 ions for a field close to the *a,b* bisector. The energy difference that can be assigned to the low field absorption is indicated on *Figure 6*. It is equivalent to ion 2 dropping from its first excited state to its ground state and the simultaneous absorption of energy by ion 1 from its ground state to its first excited state. Other weak absorptions have been observed and they must also correspond to simultaneous pair transitions. Exchange interactions will allow such simultaneous pair transitions.

The Co^{2+} absorption shown in *Figure 4* is due to the impurity level of Co^{2+} commonly found in Ni^{2+} salts. It is not uncommon for the epr spectrum of Co^{2+} to rapidly broaden with temperature, but the broadening of Co^{2+} found in α-$NiSO_4 \cdot 6H_2O$ may be a special case. We have also observed that when Cu^{2+} is doped into this lattice that it is also broadened when $T \geqslant 2$ K. Since Cu^{2+} can be observed even at 77 K in $ZnSeO_4 \cdot 6H_2O$, there must be enhanced relaxation in the nickel salt.

EXCHANGE INTERACTIONS

The thermodynamic work used the molecular field approximation. In this method the applied magnetic field is corrected by a molecular field H_m. This molecular field is related to the magnetization M of the surrounding ions by

$$H_m = \gamma M.$$

The constant γ for α-$NiSO_4\cdot 6H_2O$ was found by Fisher and Hornung to be 0.272 mole cm^{-3}.

The theory of molecular fields[6] can be used to relate γ to an exchange interaction constant J in the interaction Hamiltonian

$$\mathscr{H}(\mathrm{int}) = -2J\,\overline{S_1\cdot S_2}.$$

The relationship is

$$\gamma = \frac{2Jn}{Ng^2\mu_\beta^2},$$

where n is the number of ions involved in the exchange interaction.

If we assume only 1–2 interactions each ion has four interacting neighbours and Fisher and Hornung's value gives $2J = 0.087\ cm^{-1}$. This value indicates a ferromagnetic exchange, but it is rather smaller than the 1 cm^{-1} width of the band. It is quite possible that some of the interactions are antiferromagnetic and that our simple assumption about 1–2 interactions is incorrect.

When Cu^{2+} is doped into α-$NiSO_4\cdot 6H_2O$ an apparent g value shift upwards of 0.4 to 0.5 is observed. This is again consistent with ferromagnetic exchange and a $2J$ value close to 0.1 cm^{-1}. A much smaller g value shift is observed for Co^{2+} and its exchange interaction with the Ni^{2+} must be much smaller. In order to establish a more quantitative basis for the Ni^{2+}–Ni^{2+} exchange, we are at present studying the epr of Ni^{2+} pairs doped into $ZnSeO_4\cdot 6H_2O$.

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