

Electron-paramagnetic-resonance spectra of ions substituted into transition-metal ion lattices

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Below 2 K it is possible to observe well-resolved electron paramagnetic resonance spectra for Cu^{2+} substituted into $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. Comparison with the g values observed in the diamagnetic isostructural $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ shows a positive g shift of about 0.2 units in the Ni^{2+} lattice due to $\text{Cu}^{2+}\text{-Ni}^{2+}$ exchange interaction. Two equivalent theories for the incorporation of guest-host exchange interaction into the spin Hamiltonian of the guest ion are presented. One of these theories is an extension of the standard perturbation techniques and the other utilizes a molecular-field approach. Both give similar results and indicate a nearest-neighbor ferromagnetic $\text{Cu}^{2+}\text{-Ni}^{2+}$ exchange with $-2J = -0.145 \pm 0.01 \text{ cm}^{-1}$. Experiments are also reported for Co^{2+} , Mn^{2+} , and V^{2+} substituted into either $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$, or $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$. The $\text{Co}^{2+}\text{-Ni}^{2+}$ exchange is only slightly ferromagnetic, but our theories cannot give quantitative agreement with experiment. The $\text{Mn}^{2+}\text{-Ni}^{2+}$ exchange is too small to be measured, but the $\text{V}^{2+}\text{-Ni}^{2+}$ exchange indicates $-2J = +0.06 \pm 0.01 \text{ cm}^{-1}$. All of these exchange interactions are for hydrated ions and take place through hydrogen bonds. The trends that we observe for exchange in the Ni^{2+} lattice are discussed.

I. INTRODUCTION

The observation of the EPR spectra of paramagnetic impurities in paramagnetic host lattices has been hindered by the line broadening associated with the host-impurity interaction. The time dependence of the interaction can be eliminated by confining the host to a single spin state, thus removing fluctuations. The confinement can be accomplished by low temperatures and/or high magnetic fields, a field being necessary for degenerate states. Under these conditions well-resolved spectra of the impurity should be obtainable. Experimentally, only the EPR of impurities doped into hosts with singlet ground states have been observed since less stringent experimental conditions are required to exclusively populate a singlet ground state. Specifically, the previous hosts used were composed of lanthanide ions with ground states derived from a $J=0$ free-ion state which was separated from the next nearest spin-orbit state by energies of the order of a few hundred wave numbers.¹⁻⁶ Thermal restriction of these lanthanides to their ground states was easily accomplished, and well-resolved impurity spectra were recorded with anomalous behavior in some instances.

There are two modes of attack on the problem of incorporating the interaction into the impurity-ion description. If the spin Hamiltonian is known or a reasonable guess can be made, it can be fit to the experimental data. Alternatively, differences in the spectra of the impurity in a paramagnetic lattice and in an isostructural diamagnetic lattice can be singled out as arising from

the interactions. This assumes that the Hamiltonian can be written as a sum of the single-ion Hamiltonian plus interactions; the interactions do not effect the single-ion Hamiltonian. The ideal host material would be one where the host-impurity interaction could be turned on and off by the experimenter. By such a means those features of the spectra due to the host-impurity interactions could be unequivocally isolated. An approximation of this situation can be contrived if the paramagnetic host lattice has an isostructural diamagnetic lattice. Differences between the spectra of the impurity in the paramagnetic lattice (interaction on) and the diamagnetic lattice (interaction off), should be due to the host-impurity interaction and be related to it. Both of these methods will be employed in the analysis of our data.

Transition-metal ions with large zero-field splittings and singlet ground states also meet the requirements for easily observable impurity spectra. One such host is $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$, whose spin triplet is split in its tetragonal crystal field by spin-orbit coupling into a singlet and a doublet with the singlet lying lowest⁷ by 4.74 cm^{-1} . $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ is an isostructural⁸ diamagnetic lattice which can be used as the reference. These two lattices provide a system in which to investigate the magnetic interaction of paramagnetic impurities in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$.

Section II gives a theoretical discussion of the effects of magnetic interactions on the spectra of impurity ions. This is followed in Sec. III with a brief account of the necessary crystallographic data and experimental procedures in Sec. IV. In

Secs. V–VII, a detailed analysis of the g -value shifts of Cu^{2+} in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ is given by a spin-Hamiltonian perturbation method and by an alternative molecular-field method. Lastly, Sec. VIII presents data on Co^{2+} , Mn^{2+} , and V^{2+} doped into the $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ lattice, and Sec. IX discusses the trend in the exchange interactions as the number of d electrons of the impurity is reduced.

II. THEORY

The principal theoretical problem in the interpretation of EPR spectra of ions substituted into paramagnetic hosts is the incorporation of the host-impurity interaction into the impurity-ion description. Since the spin-Hamiltonian formalism has proved to be a convenient and useful method for describing ions in diamagnetic lattices, it would seem desirable to stay within its framework for ions in paramagnetic lattices. The following discussion presents two methods which describe how to incorporate the effects of the host-impurity interactions into the impurity-ion spin-Hamiltonian parameters with emphasis on the g -value shifts. The first approach extends the conventional spin-Hamiltonian perturbation-theory scheme similar to that used by Hutchings *et al.*,³ and the second approach utilizes molecular-field theory.

A. Perturbation method

The physical unit under consideration is defined to be the impurity ion plus a cluster of neighbors. The impurity ion is assumed to interact with each neighbor independently in a pairwise manner. No direct account is taken of possible interaction effects of the neighbors with the other host ions. Since the neighbor-impurity interactions are considered to be independent, the results for a pair can be developed and then summed over an appropriate number of neighbors. The perturbation Hamiltonian is taken to be

$$\mathcal{H} = \mu_B \vec{H} \cdot (\vec{L}_I + 2\vec{S}_I) + \lambda_I \vec{L}_I \cdot \vec{S}_I + \mu_B \vec{H} \cdot (\vec{L}_N + 2\vec{S}_N) + \lambda_N \vec{L}_N \cdot \vec{S}_N + \vec{S}_I \cdot \vec{K}_N \cdot \vec{S}_N. \quad (1)$$

The subscripts I and N refer to the impurity and neighbor, respectively, and the interaction term has been taken as the general bilinear exchange form.

The aim of the spin-Hamiltonian scheme is to evaluate parametrically, or in actuality, if possible, all operators except those of the spin under consideration. For the host-impurity pair, all the orbital operators and the host spin operators need to be evaluated in order to leave a Hamiltonian only in the impurity-spin operator. Using product wave functions of the form $|\psi_I^0 \psi_N^0 \sigma_N^0\rangle$,

where the ψ 's refer to orbital functions and σ to the spin function, and considering only the case of orbitally nondegenerate ions, the first-order spin Hamiltonian for the impurity ion is

$$\mathcal{H}^{(1)} = 2\mu_B \vec{H} \cdot \vec{S}_I + \vec{S}_I \cdot \vec{K}_N \cdot \langle \sigma_N^0 | \vec{S}_N | \sigma_N^0 \rangle. \quad (2)$$

Carrying the development of the spin Hamiltonian to second order requires the consideration of several types of excited-state wave functions. The singly excited forms $|\psi_I^n \psi_N^0 \sigma_N^0\rangle$ and $|\psi_N^0 \psi_I^n \sigma_N^0\rangle$ contribute the normal second-order terms to the g -value and the zero-field splittings of the impurity and host ions, respectively, and add nothing new. The singly excited host spin state, $|\psi_I^0 \psi_N^n \sigma_N^n\rangle$, adds a new term which involves the exchange interaction and is given by

$$\mathcal{H}^{(2)} = \sum_n \frac{|\langle \sigma_N^0 | 2\mu_B \vec{H} \cdot \vec{S}_N + \vec{S}_I \cdot \vec{K}_N \cdot \vec{S}_N | \sigma_N^n \rangle|^2}{E_0 - E_n}. \quad (3)$$

This second-order expression contributes two terms to the impurity-ion spin Hamiltonian, one arising from the cross term of the exchange and host Zeeman energies and one from the square of the exchange energy. All multiple excited states yield no additional terms. The validity of this perturbation approach is specified by Eq. (3), where the condition that the exchange interaction be small compared to the separation of the host ground and excited states is implied.

Retaining only first-order exchange terms and neglecting zero-field terms, the impurity-ion spin Hamiltonian becomes

$$\mathcal{H}_I = \mu_B \vec{H} \cdot \vec{S}_I + \vec{S}_I \cdot \sum_N \vec{K}_N \cdot \langle \sigma_N^0 | \vec{S}_N | \sigma_N^0 \rangle, \quad (4)$$

where the sum is to be taken over an appropriate number of neighbors. To appreciate the effect of the exchange term, knowledge of the host wave function is required. For pure singlet states, the host spin matrix elements are identically zero. However, the presence of a magnetic field generates Van Vleck paramagnetism which arises from the field mixing excited states into the singlet ground state. For low-lying excited states the mixing can be appreciable, thus causing the host spin matrix elements to be significant. Since the mixing is done by the field, the matrix elements acquire a linear field dependence when the wave functions are taken to first order in perturbation theory. Thus, for host ions with a singlet ground state, the first-order exchange term contributes an additional Zeeman term or equivalently a g -value shift. Host ions that possess paramagnetism in addition to the Van Vleck paramagnetism will contribute a zero-field term linear in the impurity spin. This case has not been observed yet and should be a large effect.

The second-order terms also contribute linear field terms as well as higher powers in the field,

$$\mathfrak{H}^{(2)} = \sum_n \sum_N \left\{ \frac{\mu_B \langle \sigma_N^0 | \vec{H} \cdot \vec{g}_N \cdot \vec{S}_N | \sigma_N^n \rangle \langle \sigma_N^n | \vec{S}_I \cdot \vec{K}_N \cdot \vec{S}_N | \sigma_N^0 \rangle}{E_0 - E_n} + \text{c.c.} \right\} + \sum_n \sum_N \frac{\langle \sigma_N^0 | \vec{S}_I \cdot \vec{K}_N \cdot \vec{S}_N | \sigma_N^n \rangle \langle \sigma_N^n | \vec{S}_I \cdot \vec{K}_N \cdot \vec{S}_N | \sigma_N^0 \rangle}{E_0 - E_n}, \quad (5)$$

where c.c. means complex conjugate. These higher-order terms were not found necessary for the interpretation of the experimental data which follows and will not be considered in greater detail.

To summarize, this type of analysis finds the not too surprising fact that the exchange interaction should modify the observed g values and zero-field splittings of the impurity ion. The importance of dipolar interaction will be discussed in Sec. V.

A few practical comments on the use of the equations seems in order. First of all, to evaluate the matrix elements of the host ion, a rather exact knowledge of the host wave function is necessary. There are two sources which may yield this information. Magnetic resonance of the pure host or the host in an isostructural diamagnetic lattice should be able to provide the wave functions. However, in the type of lattice where spectra should be most easily observable, those with singlet ground states, the absorptions will be in the far infrared. Coupling this fact with possible line-broadening problems in the pure host, yields the result that almost no experimental data of the spectroscopic kind are available. Probably a better source of wave-function data is rigorous magnetothermodynamic work where the host energy-level scheme has been determined.⁷ Also, the general bilinear form for the exchange interaction, which may be an asymmetric tensor, can introduce as many as nine additional parameters into the Hamiltonian. This can put a severe burden on the experimental data. However, the Hamiltonian was developed for the orbital singlet-ground-state case where isotropic exchange can be shown to be the dominant term in the exchange interaction.⁹ Therefore, under those conditions where Eq. (4) would be expected to hold, isotropic exchange will be a very good approximation. On the other hand, for ions with appreciable orbital angular momentum, for example Co^{2+} , isotropic exchange as well as Eq. (4) becomes questionable and in all probability cannot give an accurate interpretation of the experimental data.

and various zero-field terms are generated. Explicitly they are given by

B. Molecular-field method

An alternative first-order theory will be presented which combines some ideas of molecular-field theory into the impurity-ion spin Hamiltonian. The starting point will deal more directly with the impurity ion whose Hamiltonian will be assumed to be a sum of the single-ion spin Hamiltonian plus pairwise interactions with its neighbors,

$$\mathfrak{H}_I = \mu_B \vec{H} \cdot \vec{g}_I \cdot \vec{S}_I - 2J \sum_N \vec{S}_N \cdot \vec{S}_I. \quad (6)$$

In Eq. (6), zero-field and hyperfine terms have been neglected, and isotropic exchange has already been assumed.

The problem to be addressed is how to replace the host-ion spin by some known quantities in order to leave a Hamiltonian containing only the impurity spin operators. Moriya and Obata¹⁰ pointed out that the host spin can be divided into two parts, a thermal equilibrium or average value and a time-dependent deviation; mathematically, $\vec{S} = \langle \vec{S} \rangle + \delta S(t)$. The time-dependent part will cause the broadening of the spectra, and the static part will result in an exchange or molecular field at the impurity ion. Molecular-field theory replaces the neighbor spin operators by this average spin. With z equivalent nearest neighbors, Eq. (6) becomes

$$\mathfrak{H}_I = \mu_B \vec{H} \cdot \vec{g}_I \cdot \vec{S}_I - 2zJ \langle \vec{S}_N \rangle \cdot \vec{S}_I. \quad (7)$$

The average spin $\langle \vec{S}_N \rangle$ is in general still a vector quantity since in an anisotropic system spin components will be induced perpendicular as well as parallel to the magnetic field direction. The advantage of this replacement is that the average spin can be related to the macroscopic magnetization \vec{M} or the magnetization per atom \vec{m} by the relation¹¹

$$\langle \vec{S}_N \rangle = - \frac{\vec{M}}{Ng_N \mu_B} = - \frac{\vec{m}}{g_N \mu_B}.$$

Replacement of the average spin by the magnetization implies that all the ions are energetically

equivalent. Though this condition is not in general fulfilled, there are usually symmetry axes where it is. When the energy-level scheme is available, the magnetization per ion may be calculated using the relation¹²

$$\vec{m} = -\left\langle \frac{\delta E_N}{\delta H} \right\rangle.$$

With the above considerations in mind, the exchange interaction becomes

$$\mathcal{H}_{\text{ex}} = -\frac{2zJ}{g_N\mu_B} \left\langle \frac{\delta E_N}{\delta H} \right\rangle S_{zI} = \frac{2zJm_N}{g_N\mu_B} S_{zI},$$

which is applicable when the impurity spin can be considered quantized along the magnetic field direction. Equation (7) now reduces to

$$\mathcal{H}_I = g_I\mu_B H_0 S_{zI} - \frac{2zJ}{g_N\mu_B} \left\langle \frac{\delta E_N}{\delta H} \right\rangle S_{zI}, \quad (8)$$

where for axial symmetry $g_I^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$ in the usual way.

In the true molecular-field approach, the two terms of Eq. (8) would be combined by incorporating the exchange part into an effective field. In the case under consideration, it is also possible to incorporate the exchange part into an effective g value by factoring Eq. (8) in the following way:

$$\mathcal{H}_I = \left[g_I - \frac{2zJ}{g_N\mu_B^2} \left\langle \frac{\delta E_N}{\delta H} \right\rangle \frac{1}{H_0} \right] \mu_B H_0 S_{zI} = g'_I \mu_B H_0 S_{zI}. \quad (9)$$

Here, as in the perturbation method, the exchange interaction results in a g -value shift for host ions with a singlet ground state. In this case, the host-ion energy is principally second-order and thus, quadratic in the field. The derivative of the energy with respect to the field is then nearly linear in the field, and the field term in the denominator will be canceled, resulting in a constant g -value shift.

III. CRYSTAL STRUCTURE OF $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$

X-ray and neutron diffraction studies have determined the complete crystal structure of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\alpha\text{-NiSO}_4 \cdot 6\text{D}_2\text{O}$,¹⁴ respectively. The crystal is tetragonal with space group $P4_12_12$ or $P4_32_12$ depending on the enantiomorphic form. Analysis shows that the unit cell has dimensions $a = 6.790 \pm 0.003 \text{ \AA}$ and $c = 18.305 \pm 0.004 \text{ \AA}$ and contains four $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ complexes.

The spatial symmetry of the ligands around the nickels is not measurably different from octahedral. EPR of the $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ and Ni^{2+} doped into the isomorphous $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ reveal a substantial tetragonal distortion of the Ni^{2+} site.

This distortion has been attributed to increased hydrogen bonding of two of the water molecules, which reduces the crystal field in their directions.¹⁵ The four ions in the unit cell are equivalent except for the orientation of their tetragonal axes. Each of the ion's tetragonal axes is tilted by an angle ϕ from the crystal c axis in a plane defined by the c axis and the ab bisector (hereafter called the γ axis). There are two γc planes, and each contains the axes of two ions with the tilt of ϕ being opposite for these ions. Figure 1 shows four unit cells illustrating the orientation of the ions and Fig. 2 shows the projections of the ion axes on the two γc planes.

Another important feature to be noted is the neighbor arrangement. Referring to Fig. 1, an ion located in site 2 is surrounded by four nearest neighbors at sites 1 and 3 in a tetrahedral fashion and at a distance of 5.72 \AA . There are four more next nearest neighbors located in the plane defined by all ions of type 2. These neighbors are related by a lattice translation along a and are, therefore, located 6.79 \AA away. Further neighbors will not be considered owing to their distance. The nearest-neighbor ions would appear to have an obvious superexchange pathway through the hydrogen bonding of water molecules in the coordination sphere of the two metal ions. Next-

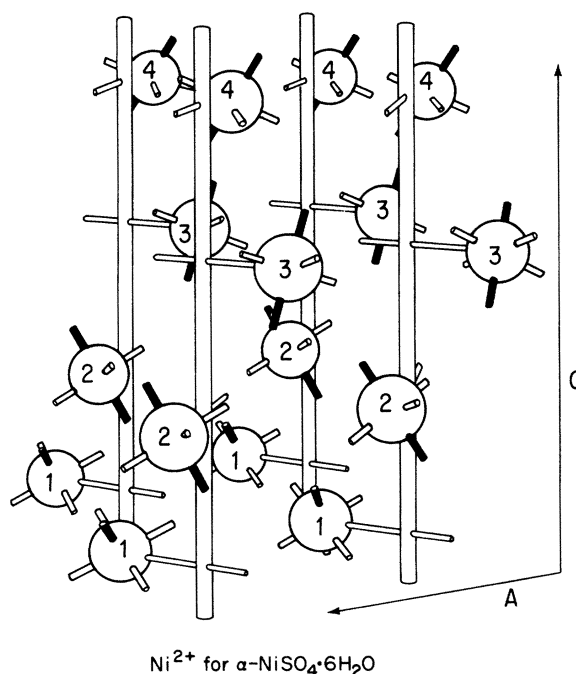


FIG. 1. Positions and orientations of the nickel ions in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ are illustrated. Four unit cells are shown. Each unit cell is shown as composed of four nickel ions attached to the vertical rods. The unique axis of the spin Hamiltonian is darkened.

Ion Coordinates

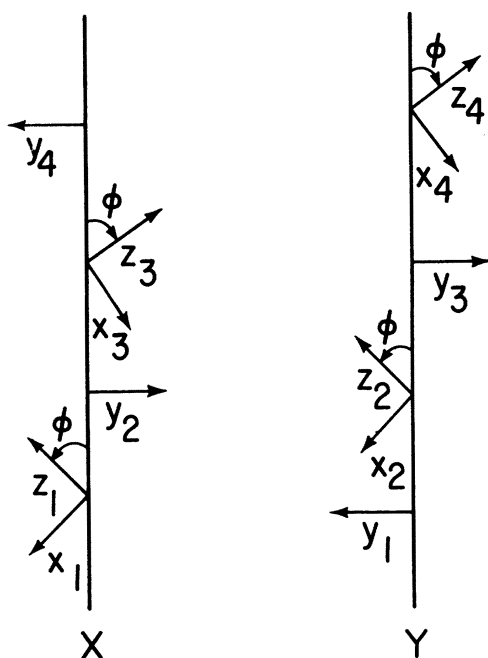


FIG. 2. Projections of the magnetic axes of the ions in the α -NiSO₄·6H₂O lattice on the two γc planes are shown. The angle ϕ is the angle between the ion's unique axis and the crystal c axis.

nearest neighbors have no such obvious pathway and presumably would have to involve an SO₄²⁻ ion between the waters. For this reason, along with the spectral data to be presented, the nearest-neighbor interactions are considered to be dominate.

The diamagnetic reference lattice used was ZnSeO₄·6H₂O. Klein¹⁶ found that it was isomorphous with α -NiSO₄·6H₂O, and EPR spectra of various ions in this lattice by Jindo and Myers¹⁵ has verified this. The lattice ratio is given by Klein to be $\sqrt{2}a:c = 1:1.8949$, which is to be compared with the α -NiSO₄·6H₂O ratio $\sqrt{2}a:c = 1:1.912$, indicating a slight relative expansion in the a direction. X-ray crystallographic data on ZnSeO₄·6H₂O is given by Hajecck and Cepelak.⁸

A more accurate analysis of the data to be presented could have been obtained if a tetragonal form of ZnSO₄·6H₂O was available. However, no such structure has been reported, the monoclinic form being the only hexahydrate.¹⁷

IV. EXPERIMENTAL

Details of the 9-GHz spectrometer and cavities employed can be found elsewhere and was employed except where noted.^{18,19} The cryogenic equipment consisted of a double-Dewar arrange-

ment equipped with a fast pumping system which allowed the temperature of 1.3 K to be reached. The temperature was monitored by the vapor pressure of the helium.

Crystals were grown from saturated aqueous solutions of the host doped with an appropriate amount of impurity ions. The tetragonal form α -NiSO₄·6H₂O is only obtained in the temperature range 30.7–53.8°C, and these crystals were grown in a water bath maintained at approximately 39°C. ZnSeO₄·6H₂O crystals were grown at room temperature. The α -NiSO₄·6H₂O crystals doped with V²⁺ were grown under nitrogen owing to the reactivity of V²⁺ with oxygen, and the V²⁺ doping solution was generated from VOSO₄ by reacting it with Zn in acid solution.

The crystals were mounted on Teflon plugs which filled the cylindrical cavity and were immersed in liquid helium. The well-defined and easily distinguishable crystal faces made crystal-axis identification and mounting straightforward. Angular variation was accomplished by rotation of the magnet in a given plane with the plane being varied by remounting the crystal.

V. EXPERIMENTAL RESULTS Cu²⁺: α -NiSO₄·6H₂O

The general qualitative features of the Cu²⁺ spectra in the paramagnetic host α -NiSO₄·6H₂O are similar to the diamagnetic host ZnSeO₄·6H₂O. The ions exhibit tetragonal symmetry. Four copper spectra are obtained for an arbitrary direction of the magnetic field corresponding to the four ions per unit cell. With the magnetic field along the a and c axes, all spectra coalesce into a single one. Rotation of the field in the ac or ab planes results in two spectra for all directions (ions 1 and 3 being equivalent and 2 and 4 being equivalent). Rotation of the magnetic field in the γc plane results in three spectra which coalesce into two along the γ axis (ions 1 and 3 being equivalent at all angles). Details of the angular dependences can be found in Jindo and Myers.¹⁵ They found a slight doubling of the spectra for arbitrary orientations of the field and attributed this to a tilt of the x axis of the copper ions away from the γc plane. It was discovered that this doubling could be attributed to inaccurate crystal alignment of the order of 1°. For this reason their x -axis tilt is incorrect.

Several deviations from the diamagnetic host-lattice spectra are observed. First, the g values are abnormally large, being 0.2 to 0.6 units higher in the nickel lattice. The value of ϕ is also observed to increase, where ϕ here is defined as the angle between the c axis and the maximum g value found in the γc plane. Two other changes

are a decrease in the hyperfine splittings and an increase in the linewidth. Table I compares the g values and hyperfine values for the external field along the principal magnetic and crystallographic axes.

Jindo¹⁸ attempted to fit the Cu^{2+} spectra to a conventional spin Hamiltonian, but he was unable to obtain a satisfactory fit. Figure 3 shows a comparison of the calculated and observed uncorrected g values. These observations indicate that the copper-nickel interactions must be playing a significant role in the spectra of the Cu^{2+} .

Svare and Seidel²⁰ have pointed out that at low temperatures when it is possible to populate a single state, a paramagnetic sample will show a shape effect similar to that encountered in ferromagnetic resonance. Nearly all the samples used were of prismatic shape, and since it is not practical to calculate the effect for irregular shapes, an unknown error was introduced into the data. The shape effect for $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ would be expected to be small because it is proportional to the magnetization, which is entirely second order at the temperatures of the experiments. The smallness was verified by spectra of Co^{2+} substituted into $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ taken by Batchelder¹⁹ for samples of varying shapes at 1.3 K. Table II gives representative g values of Co^{2+} in samples of different shapes along two crystal axes. The spherical samples should have no shape effect while the plate should show the largest effect. As can be seen the shape effect is not negligible, but it is believed that an upper limit of 0.02 may be set on the prismatic shapes of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. The differences in the uncorrected g values between paramagnetic and diamagnetic hosts cannot be ascribed to the shape effect alone, but it is considered to be the limiting source of error in the g value measurements in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$.

At 1.3 K the Cu^{2+} spectra in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ were, for the most part, well resolved into the

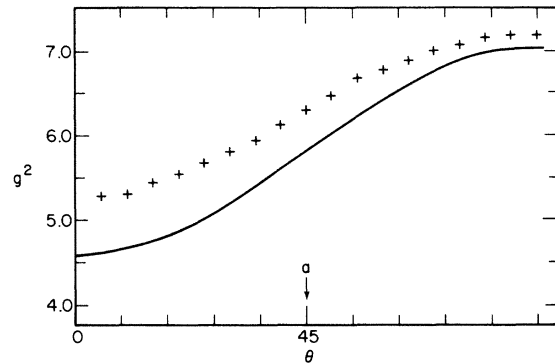


FIG. 3. Experimental angular dependence of g^2 in the ab plane for Cu^{2+} in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ is compared with the dependence calculated from the apparent spin Hamiltonian parameters. Crosses indicate experimental points, and the line is calculated.

characteristic four-line hyperfine pattern with the derivative linewidths of each hyperfine component about 20 G. Natural isotope abundances of Cu^{2+} were used, and the linewidth is the combined width of the two isotopes. A typical absorption spectrum is given in Fig. 4. The linewidth in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ is close to 10 G, and the two isotopes could be resolved in the outer hyperfine lines. The copper lines quickly broaden in the nickel lattice and are nearly undetectable at 2.5 K. This does not occur in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$. This copper broadening corresponds with the populating of the first excited spin state of the nickel ions.

VI. APPLICATION OF THE PERTURBATION METHOD TO Cu^{2+}

Equation (4) of Sec. II reduces to

$$\mathcal{H} = g\mu_B H_0 S_{zI} - 2J\tilde{S}_I \cdot \sum_N \langle \sigma_N^0 | \tilde{S}_N | \sigma_N^0 \rangle, \quad (10)$$

with $g_I^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$ when the impurity ion is axially symmetric and isotropic exchange has been assumed. The summation will be restricted to nearest neighbors only and hyperfine terms are neglected. The following assumptions are made about axes of quantization. The copper spins are taken as quantized along the external field,

TABLE I. Cu^{2+} apparent g and A values in two hosts. a and c refer to the crystal axes and z and x refer to the magnetic axes of the ions (the z axis here is defined as the maximum g in the γc plane).

Axis	$\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$		$\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$	
	g	A (G)	g	A (G)
a	2.68 ± 0.02	59.7 ± 0.6	2.179 ± 0.002	69.9 ± 0.3
c	2.50	91.0	2.279	97.2
γ	2.85	74.6	2.260	90.8
z	2.91	93.8	2.429	115.7
x	2.50	10	2.097	15
	$\phi = 61.8^\circ$		$\phi = 43.3^\circ$	

TABLE II. Co^{2+} : $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$.

Axis	Sample shape	g uncorr.
c	plate	4.282
	sphere	4.301
a	plate	4.744
	sphere	4.688

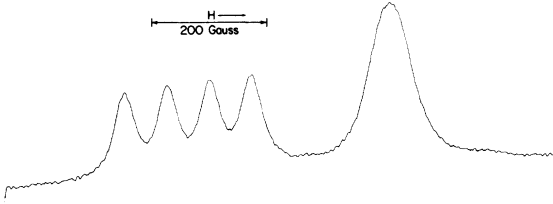


FIG. 4. Typical direct absorption spectra of Cu^{2+} in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ is depicted when the field is along a γ axis, showing two sets of Cu^{2+} spectra. Ions 1 and 3 are equivalent as are 2 and 4 in this direction. The hyperfine pattern is absent in the high-field absorption owing to the small value of A_{\perp} . The tip of the arrow on the right side of the 200-G marker is at 2550 G. $T=1.3$ K and $\nu=9.4533$ GHz.

and the nickel spins are taken as quantized along their crystal-field axes. The nickel coordinate systems used are those given in Fig. 2. These assumptions allow the simplest coordinates for the calculation of the interaction term.

To evaluate the nickel matrix elements in the exchange term, the scalar spin product is written in the coordinate system of the copper ion, and the nickel spin operators are rotated into their crystal-field coordinates, where their wave functions and matrix elements can be determined. The wave functions can then be obtained by diagonalization of the single-ion axial Hamiltonian

$$\mathcal{H}^{(\text{Ni})} = DS_z^2 + g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y),$$

which is in general an imaginary matrix. The nickel spin-Hamiltonian parameters were obtained from Fisher *et al.*,⁷ Jindo,¹⁸ and Myers.²¹ The magnitude of the magnetic field at a nickel ion was taken as $H_{\text{total}} = H_{\text{ext}} + \gamma M$, where H_{ext} is the external field at which a given copper ion resonance took place, γ the molecular-field parameter determined by Fisher *et al.*,⁷ and M the magnetization. The inclusion of the molecular field improved the calculated results and indicates that nickel-nickel interactions have an effect on the impurity ion which can be taken into account in this way.

With H_{ext} along the a , c , and γ axes of the crystal, only components of the exchange in S_{zI} remain. After the nickel matrix elements are computed, the resulting Hamiltonian is of the form

$$\mathcal{H} = g\mu_B H_0 S_{zI} + CJS_{zI}, \quad (11)$$

where C is a combination of matrix elements and angular factors dependent on the field orientation. For arbitrary directions of the field, spin components in S_x and S_y are introduced. That the coefficient C is basically linear in the field H_0 to first order may be seen by inspecting the nickel ground-state wave function. To first order it is

principally $|0\rangle$ with $|\pm 1\rangle$ states mixed in by the off-diagonal Zeeman terms, i.e.,

$$|\sigma_N^0\rangle = |0\rangle + \sum_n \frac{\langle 0 | g_{\perp} \beta (H_x S_x + H_y S_y) | n \rangle}{E_0 - E_n} |n\rangle.$$

An effective spin Hamiltonian can be written from Eq. (11) as

$$\mathcal{H} = [g_{\text{dia}} + CJ/\mu_B H_0] \mu_B H_0 S_{zI} = g' \mu_B H_0 S_{zI}, \quad (12)$$

with the effective g value given explicitly by

$$g_{\text{obs}} = g_{\text{dia}} + CJ/\mu_B H_0 = [g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta] + CJ/\mu_B H_0. \quad (13)$$

Theoretically, the observation of four g values at different orientations where Eq. (13) holds would serve to fix the four unknowns g_{\parallel} , g_{\perp} , J , and ϕ , and the impurity-ion spectra could be solved without recourse to a diamagnetic lattice. Solutions for g_{\parallel} , g_{\perp} , and ϕ should be expected to correspond closely to the diamagnetic values. For the Cu^{2+} in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ four good and simple measurements are available. These are the two g values along the γ axis and one each from the a and c axes. These four measurements turned out to be linearly dependent. Independent determination of the geometrical factor ϕ was not possible though in other cases it may be, e.g., from the hyperfine tensor. The angle ϕ was therefore taken as an adjustable geometrical parameter and varied until g_{\parallel} and g_{\perp} most closely matched the diamagnetic values. The best values are given in Table III. Good agreement is obtained considering the assumptions employed.

Attacking the problem by relating the differences of the g values in the paramagnetic and diamagnetic hosts yields the following equation of the exchange:

$$J = (g_{\text{obs}} - g_{\text{dia}}) \mu_B H_0 / C. \quad (14)$$

Table IV lists the $-2J$ values calculated for different orientations of the magnetic field, providing a further check on the method.

One can see that the differences in the g values of Cu^{2+} doped into the paramagnetic $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$

TABLE III. Comparison of corrected g and ϕ values of Cu^{2+} in $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ with those in diamagnetic $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$.

Lattice (method)	ϕ (deg)	g_{\parallel}	g_{\perp}	$-2J$ (cm^{-1})
$\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$	43.3	2.4295	2.0965	...
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Perturbation)	45	2.40	2.12	-0.146
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (molecular field)	45	2.44	2.05	-0.152

TABLE IV. Cu²⁺-Ni²⁺ isotropic exchange values along crystal axes from perturbation method.

Axis	$-2J$ (cm ⁻¹)
a	-0.139
c	-0.151
$\gamma(\gamma)$	-0.139
$\gamma(\perp)$	-0.156
Ave.	-0.146 ± 0.007

lattice from those in the isostructural ZnSeO₄ · 6H₂O lattice can be satisfactorily explained by the preceding theory. It requires an isotropic ferromagnetic exchange interaction between the Cu²⁺ and Ni²⁺ with $-2J = -0.146 \pm 0.007$ cm⁻¹.

VII. APPLICATION OF THE MOLECULAR-FIELD METHOD

From Eq. (9) in Sec. II the g value in the molecular-field approximation is given by

$$g_{\text{obs}} = [g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta] - \frac{2zJ}{g^{(\text{Ni})} \mu_B^2} \left\langle \frac{\delta E^{(\text{Ni})}}{\delta H} \right\rangle \frac{1}{H_0}, \quad (15)$$

where g_{\parallel} and g_{\perp} are the values which would be obtained in the absence of exchange. The value of $\langle \delta E^{(\text{Ni})} / \delta H \rangle$ was calculated by finding the slope of the energy-vs-field plot of the ground state at the field present at the nickel ions, which was again taken to be $H_{\text{total}} = H_{\text{ext}} + \gamma M$. The use of H_{total} reproduces the measured magnetization found by Fisher *et al.*,⁷ and along the a and c axes $\langle \delta E^{(\text{Ni})} / \delta H \rangle / H_0$ may be replaced by the measured magnetization per atom. Since the ground-state Zeeman energy is principally second order, the derivative is almost linear in the field and over the range of fields used, the g -value correction can be considered constant.

As before only three independent measurements were obtained, and ϕ was again taken as an adjustable parameter. Table III gives the results which most closely match the diamagnetic g values when ϕ is varied. The values of $-2J$ calculated from the paramagnetic-diamagnetic g value differences along the various crystal axes are tabulated in Table V. J is calculated from the formula

$$J = \frac{(g_{\text{obs}} - g_{\text{dia}}) g^{(\text{Ni})} \mu_B^2 H_0}{-8 \langle \delta E^{(\text{Ni})} / \delta H \rangle}. \quad (16)$$

This simple molecular-field approach also gives satisfactory agreement and yields a ferromagnetic copper-nickel isotropic exchange interaction of $-2J = -0.144 \pm 0.008$ cm⁻¹.

TABLE V. Cu²⁺-Ni²⁺ isotropic exchange values along crystal axes from molecular-field method.

Axis	$-2J$ (cm ⁻¹)
a	-0.146
c	-0.138
$\gamma(\gamma)$	-0.157
$\gamma(\perp)$	-0.136
Ave.	-0.144 ± 0.008

VIII. OTHER IMPURITY IONS IN α -NiSO₄ · 6H₂O

A. Co²⁺

The qualitative features of Co²⁺ in α -NiSO₄ · 6H₂O were also found to be similar to the diamagnetic ZnSeO₄ · 6H₂O lattice. However, the data give unreasonable results when the previous theories are applied. Table VI lists the observed g values of cobalt in the two lattices along the principal crystal axes.

The most disturbing observation about the data is the change in sign of the difference $g^{(\text{Ni})} - g^{(\text{Zn})}$, which can only be explained with the present theory if the exchange constant J changes sign. Several reasons can be put forward of why the cobalt should not be satisfactorily explained by the theory. As is well known, the large orbital contribution to the g tensor makes it extremely sensitive to changes in the crystal field. The initial assumption of the theory was that a suitable diamagnetic host was available for comparison, where suitable here means as much like a fictitious diamagnetic α -NiSO₄ · 6H₂O as possible. Ions like Cu²⁺ which do not possess large orbital moment contributions to their g values are relatively insensitive to crystal-field effects, and ZnSeO₄ · 6H₂O provides a suitable comparison lattice. For Co²⁺, ZnSeO₄ · 6H₂O may no longer be a suitable lattice, and exchange effects cannot be unraveled from changes in the crystal field. Support for this can be found in the Tutton salts²² and isostructural lanthanum magnesium nitrate crystals.²³ In these crystals changes of similar ions, e.g., K⁺, Rb⁺, or NH₄⁺, in the Zn Tutton salt, causes changes of 0.2–0.3 of a g -value unit, which is the same order of magnitude as the ob-

TABLE VI. Co²⁺ apparent g values.

Axis	α -NiSO ₄ · 6H ₂ O	ZnSeO ₄ · 6H ₂ O
a	4.69	4.453
c	4.30	4.315
$\gamma(\gamma)$	5.94	5.410
$\gamma(\perp)$	3.12	3.27

served g shifts in the present experiments. The orbital moment should also complicate the exchange interaction. It would be unlikely for isotropic exchange to closely represent the cobalt-nickel interaction.²⁴ As noted in Sec. II the theory was derived for the orbital singlet case, which is not the case for Co^{2+} in an octahedral field. On the basis that the general trend seems to show $g^{(\text{Ni})}$ larger than $g^{(\text{Zn})}$, one would conclude from the molecular-field theory that the cobalt-nickel exchange is probably slightly ferromagnetic.

B. Mn^{2+}

This ion was done in $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$ instead of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. Its crystals can easily be grown at room temperature and Jindo¹⁸ has shown that g -value shifts are very similar in the two nickel lattices. Divalent manganese gave a very complex spectrum in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$. The normal complexity was increased in these lattices by the four ions per unit cell and by "forbidden" transitions which gained appreciable intensity due to the breakdown of selection rules by a large zero-field splitting. When the external field was perpendicular to the crystal-field axes of two of the ions along the γ axis, the full set of five sextets from these ions could be distinguished and g_{\perp} measured for the $\frac{1}{2}$ to $-\frac{1}{2}$ transition. With H_0 parallel the z crystal-field axis, the spectra had the maximum spread, and all but the $\frac{1}{2}$ to $-\frac{1}{2}$ sextet could be completely resolved. From the sextet splittings the zero-field splitting was determined. Table VIII gives g_{\perp} and D in the two lattices.

The largeness of the zero-field splitting made it necessary to use K -band frequencies in order to increase the validity of the second-order Hamiltonian.²⁵ The point to focus on here is that the over-all exchange interaction is very close to zero since the g values are very nearly identical in the two lattices. For this reason a more detailed analysis of the Mn^{2+} was not conducted. There are exchange contributions to the zero-field splitting, but the difference observed in Table VII may be due to crystal-field effects.

C. V^{2+}

V^{2+} is a good choice for study since it has very little orbital angular momentum and represents a case where only t_{2g} electrons are involved in the exchange. However, it is a fairly strong reducing agent and attempts to prepare $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ crystals doped with V^{2+} resulted in reduction of the SeO_4^{2-} to Se. The SO_4^{2-} ion is less susceptible to reduction, and single crystals of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ doped with V^{2+} could be prepared.

TABLE VII. Mn^{2+} apparent g_{\perp} and D values in two hosts.

Parameter	$\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}^a$	$\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}^b$
g_{\perp}	2.02 ± 0.02	1.997 ± 0.003
D (G)	$+624 \pm 10$	$+637 \pm 10$

^a At 1.3 K.

^b At 77 K.

Even though a diamagnetic reference lattice was not available, large deviations of the g value should be discernible since the small orbital contribution to the V^{2+} g value makes them very close to 2.0. A sampling of V^{2+} g values shows that they lie between 1.96 and 2.00 for known octahedral complexes.²⁶

The spectra consisted of the expected three octets per ion. With H_0 along the γ axis, which is perpendicular to the crystal-field axes of two of the ions, the three octets were easily resolved and g_{\perp} was determined from the center octet. The first-order g_{\perp} was 1.836 neglecting the second-order shift which would make it even smaller, and with $g=2.0$ the zero-field splitting was found to be 0.133 cm^{-1} . Thus, the observed g_{\perp} value is considerably outside the range previously observed for V^{2+} . Since the observed g_{\perp} for V^{2+} is smaller than expected for diamagnetic lattices, the implication from Eq. (14) or (16) is that the vanadium-nickel exchange interaction is antiferromagnetic. Estimating g_{dia} as 2.00 one obtains $-2J = 0.06 \text{ cm}^{-1}$ using the molecular-field method.

IX. DISCUSSION

Table VIII summarizes the different types of interacting pairs and the exchange interactions that were obtained. It is believed that the most advantageous superexchange pathway is through a hydrogen bond linking the waters of an ion with its nearest neighbor. Figure 5 illustrates this hydrogen bonding arrangement between the nearest neighbors. All other hydrogen-bonded pathways have at least a sulfate oxygen as an intermediate between two water molecules. Two types of nearest neighbors are possible. The first involves the bonding of an equatorial water of the impurity and an axial water of the nickel. Choosing complex 3 on Fig. 5 as the impurity, the first pathway would be from complex 3 to complex 1. The other pathway involves bonding of an axial water of the impurity with an equatorial water of a nickel. Again, with complex 3 as the impurity, this situation uses complexes 3 and 2. For Cu^{2+} , whose equatorial ($d_{x^2-y^2}$) and axial (d_z^2) orbitals are half-filled and filled, respectively, the exchange between the two types of neighbors may differ

TABLE VIII. Summary of observed exchange interactions.

Pair	Configuration	Interaction	$-2J$ (cm $^{-1}$)
Cu $^{2+}$ -Ni $^{2+}$	$e_g-(e_g)^2$	ferromagnetic	-0.144
Co $^{2+}$ -Ni $^{2+}$	$t_{2g}(e_g)^2-(e_g)^2$	slightly ferromagnetic	...
Mn $^{2+}$ -Ni $^{2+}$	$(t_{2g})^3(e_g)^2-(e_g)^2$...	~ 0
V $^{2+}$ -Ni $^{2+}$	$(t_{2g})^3-(e_g)^2$	antiferromagnetic	+0.06

significantly, and the value of the exchange interaction calculated in the previous sections is really an average of these two exchange interactions. For ions with half-filled configurations ($t_{2g}^3 - V^{2+}$, $t_{2g}^3 e_g^2 - Mn^{2+}$, $e_g^2 - Ni^{2+}$), both types of neighbors should have more nearly identical exchange.

Regardless of this problem, the obvious trend observed in Table VIII is the gradual change in sign of the exchange interaction with impurity configuration on going across the Periodic Table from copper to vanadium. The implication is

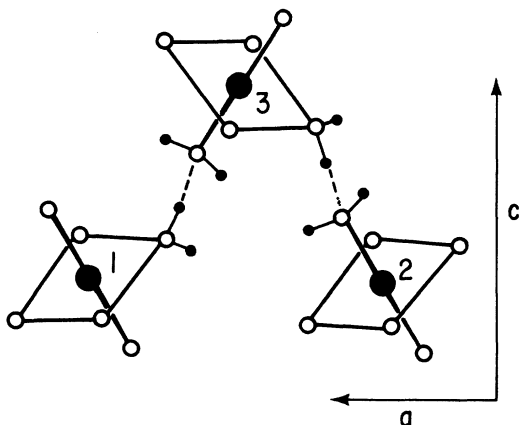


FIG. 5. Three $Ni(H_2O)_6^{2+}$ complexes are illustrated showing the proposed nearest-neighbor superexchange pathway via the hydrogen bonding between complexes. The figure is adapted from Ref. 14.

that $e_g - e_g$ orbital interactions are ferromagnetic and $t_{2g} - e_g$ interactions are antiferromagnetic. This observed trend conforms to the Kanamori-Goodenough rules^{27,28} for ions coupled via a 90° interaction. However, the very complex geometry of the proposed hydrogen-bound superexchange pathway precludes any correlation along these lines.

It is interesting to note that in other hydrogen-bond systems similar results have been obtained. Pair spectra in the hydrogen-bonded double nitrate systems also indicated that $e_g - e_g$ interactions were ferromagnetic and $t_{2g} - e_g$ interactions were antiferromagnetic.^{23,29} Two other reports in hydrated systems yield results conforming to the observed trend, Cu $^{2+}$ pairs in $K_2Zn(SO_4)_2 \cdot 6H_2O$ were ferromagnetic³⁰ ($e_g - e_g$) and Ni $^{2+}$ pairs in $ZnSiF_6 \cdot 6H_2O$ were ferromagnetic ($e_g - e_g$).³¹ In these hydrogen-bonded lattices the magnitude of $2J$ runs from 0.025 to about 0.1 cm $^{-1}$ unless cancellation of the mixed $t_{2g} - e_g$ type occurs.

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