Exchange through the phonon field between rare-earth Kramers ions under pressure

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An experimental study is reported of the spin-spin interaction in a pair of the rare-earth paramagnetic ions Ce^{3+} in ethyl sulfates under hydrostatic pressures up to 10 kbar. The pair lines cross as the pressure is increased, indicating that the anisotropic part of the interaction is zero at the crossing point. The dependence of the nondipole part of the interaction on the position of the first excited doublet is found and is used to conclude that exchange through the phonon field provides the dominant contribution at normal pressure.

1. INTRODUCTION

Apart from Coulomb exchange and magnetic dipole-dipole interactions between paramagnetic ions with unfrozen orbital angular momentum, there are also weaker interactions such as quadrupole-quadrupole and exchange through the phonon field. There are several theoretical papers predicting the existence of the latter mechanism, which may be appreciable for ions with strong orbit-lattice coupling.[1-3] Calculations of phonon exchange provide only approximate values in specific cases. Experimental detection is also difficult, firstly, because the effect is small in comparison with other mechanisms and, secondly, because of identification difficulties, especially the separation of the quadrupole-quadrupole interaction from phonon exchange.

In his review, Baker[4] lists a number of experimental data on the interaction between ions with orbital angular momentum in insulators. Having analyzed all these results, he suggests that, for some rare-earth ions, exchange through the phonon field may provide an appreciable contribution to the interaction. This refers to non-Kramers ions (for example, Pr^{3+}) as well as Kramers ions (Ce^{3+}, Dy^{3+}) with closely spaced excited states. Since exchange through the phonon field and the quadrupole-quadrupole interaction provide contributions for Kramers ions, but only in the second order of perturbation theory, the strength of the interaction should depend on the energy separation Δ of the excited state. Baker considers[4,5] that both mechanisms should be proportional to Δ^{-1}. In a later theoretical paper,[6] it was shown that phonon exchange in Kramers ions varies as Δ^{-4}. If this difference is real, the contributions due to the two mechanisms can be separated once the dependence of the interaction on the position of the excited state has been determined experimentally. To solve this problem, we used hydrostatic compression of crystals and investigated Ce^{3+} ion pairs in ethyl sulfates.

2. SAMPLES. SPIN-HAMILTONIAN

The trivalent cerium ions Ce^{3+} were introduced as an impurity into two hosts: europium ethyl sulfate (EuETS) and yttrium ethyl sulfate (YETS) in amounts of 1%. This was sufficient to ensure reliable observation of the pair spectrum. The crystal structure of the ethyl sulfate $La(C_2H_5SO_4)_3 \cdot 9H_2O$ has been thoroughly investigated by x-ray methods.[7] The point symmetry of the nearest-neighbor environment, which consists of nine water molecules, is C_{3h}. The disposition of the rare-earth ions and the water molecules in the host is shown schematically in Fig. 1. The nearest interacting cerium ions lie along the threefold axis at a distance of about 7Å (7.0827 in EuETS and 7.057 Å in YETS). The next six rare-earth neighbors lie at a distance of about 8.8Å. These were not investigated. The elastic constants of LaETS are reported in Ref. 8 and will be used below to estimate the dipole-dipole interaction under pressure. We shall assume that the compressibility of different ethyl sulfates is similar to that of LaETS.

The ground state of Ce^{3+} ions with the electronic configuration $4f^1$, ${}^2F_{5/2}$ splits in the crystal field of the ethyl sulfate into three Kramers doublets. In EuETS and YETS, the lowest is the $|\pm 5/2\rangle$ doublet. Figure 2 shows the energy-level scheme of Ce^{3+}. The ESR spectrum of a single ion can be described with the aid of effective spin 1/2 and strongly anisotropic g-factor whose value under normal pressure is as follows: $g_\parallel(\text{EuETS}) = 3.787$, $g_\parallel(\text{YETS}) = 3.810$, and $g_\perp \simeq 0.2$ for both crystals.

The pair spin Hamiltonian has the form:

$$\mathscr{H}=\mathscr{H}_1+\mathscr{H}_2+\mathscr{H}_{12}, \qquad (1)$$

where $\hat{\mathscr{H}}_1 = \hat{\mathscr{H}}_2 = \beta \mathbf{H} \mathbf{g} \hat{\mathbf{S}}$ are the Hamiltonian for the first and second ions and $\hat{\mathscr{H}}_{12} = \hat{\mathbf{S}}_1 K^{12} \hat{\mathbf{S}}_2$ is the interaction Hamiltonian. The interaction tensor K^{12} can be expanded into the isotropic (I) and anisotropic (A^{12}) parts:

$$K_{ij}^{12}=I+A_{ij}^{12}, \qquad \operatorname{Sp} A_{ij}^{12}=0.$$

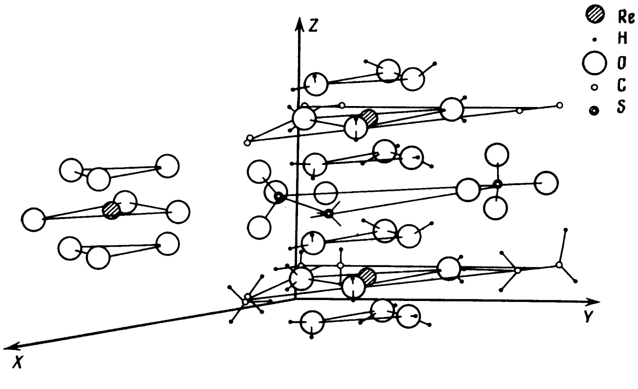

FIG. 1. Fragment of the crystal structure of ethyl sulfate.

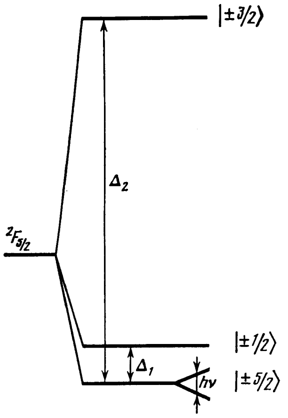

FIG. 2. Energy-level scheme of Ce^{3+} in the crystal field of ethyl sulfate.

Figure 3 shows the energy-level scheme for the pair spectrum and the observed transitions when the external magnetic field lies along the Z (C_3) axis. Since, in the latter case, we are dealing with the interaction between two identical ions, transitions produced by the variable magnetic field are allowed within the triplet, as shown in Fig. 3, and it is possible to determine only the anisotropic part of the interaction. Because of the high degree of anisotropy of the spectrum ($g_\perp \approx 0.2$), the only component of the tensor that can be measured is A_{zz}^{12}. The resonance conditions for the absorption lines in the pair spectrum are as follows:

$$h\nu = g_{\parallel}\beta H_z \pm {}^3/_4 A_{zz}{}^{12}. \qquad (2)$$

3. RESULTS OF THE EXPERIMENT

The pair spectrum was investigated in the temperature range 1.5–4.2 K and for pressures in the range 0 to 10 kbar, using a superheterodyne spectrometer operating at a wavelength of 8 mm (36 GHz) and equipped with a high-pressure attachment.[9] The spectrum of the pair of interacting cerium ions consists of two satellites accompanying the single-ion absorption line. To establish the temperature dependence in the range 1.5–4.2 K, measurements were performed for $P = 0$ and $P \sim 4$ kbar. No detectable changes were observed to within experimental error.

Figure 4 shows the resonance fields corresponding to the pair absorption lines as functions of pressure, relative to the position of the single-ion absorption line (at the origin on the ordinate axis) for the two ethyl sulfates. As the pressure in YETS is increased, only one high-field line is observed; the low-field line is hidden within the single-ion line-width. For EuETS, there is also a number of pressures for which only the high-field line is observed, and for the same reasons. However, the position of the second line and of the center of the spectrum is essential for a correct determination of the pair g-factor and of A_{zz}^{12}.

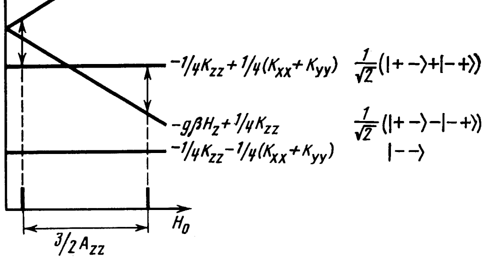

FIG. 3. Energy-level scheme of the pair of ions Ce^{3+}–Ce^{3+} in ethyl sulfate, which corresponds to (1). The indices in the wave function (±) correspond to effective spins (± 1/2) of the first and second ions.

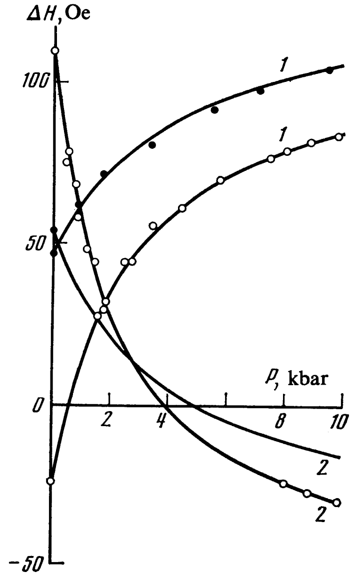

FIG. 4. Pressure dependence of the resonance fields corresponding to the absorption lines of the Ce^{3+}–Ce^{3+} pair spectrum relative to the absorption line of the single atom for YETS (●) and EuETS (○).

The approximation was performed with the aid of the formula

$$\Delta H = A \pm \frac{B}{1+C(D+P)}. \qquad (3)$$

The coefficients were found by a computerized least-squares fit to all the experimental points simultaneously, using the EC-1022 computer. The constants B and C were assumed to be the same for all the curves and the plus and minus signs were used for curves 1 and 2, respectively. The resulting parameter values are listed in the table. Comparison of these coefficients shows that curves 1 for EuETS and YETS are described in an identical manner, i.e., they can be superimposed by shifting curve 1 for YETS downward along the ordinate axis by 18.6 Oe and to the right along the pressure axis by 1.644 kbar. The corresponding coefficients for curve 2 of YETS were obtained by assuming that an analogous situation obtains for these curves as well. The solid lines in Fig. 5 are the corresponding curves based on (3).

The experimental graphs and the fitted curves can be used to construct the dependence of $g_{nn}^{\parallel}$ on hydrostatic pressure. Figure 5 shows the variation in the g-factors, both for pairs and for single Ce^{3+} ions, with pressure for the yttrium and europium ethyl sulfates.

Analysis of the experimental data shows that, firstly, the observed quantities are nonlinear functions of pressure and, secondly, the shift of the $g_{\parallel}^{nn}$ factors for pairs from the

TABLE I.

Host	No. of curve	A, Oe	D, kbar	B, Oe	C, kbar^{-1}
Eu ETS	1	112.05	0	136.0	0.38
	2	−59.25	−0.502		
Y ETS	1	112.05+18.6	1,644		
	2	−59,25+18,6	−0,502+1,644		

single-ion factors $g_\parallel$ toward higher values in both crystals, and, finally, the crossing of the pair lines which occurs for $P \sim 0$ in the case of YETS and 1.85 kbar for EuETS.

4. DISCUSSION

The experimental data can be used together with (2) to obtain A_{zz}^{12} as a function of pressure. Figure 6 shows the anisotropic part of the interaction A_{zz}^{12} as a function of hydrostatic pressure in both crystals. The variation is identical. It is important to note that A_{zz}^{12} changes sign as the pressure increases and this is particularly well defined in EuETS. $A_{zz}^{12} = 0$ at $P = 1.85$ kbar and, at this point, the triplet is not split, and the interaction is represented by the isotropic part alone. This shape of the experimental curve can only be explained by the superposition of several effects contributing to A_{zz}^{12} with different signs. The contribution of the magnetic dipole-dipole interaction can be readily calculated from the formula

$$A_{zz}^{MDD} = -\frac{2}{3}\frac{2(g_\parallel^{nn})^2+(g_\perp^{nn})^2}{R^3}\beta^2, \qquad (4)$$

where β is the Bohr magneton, $g_\parallel^{nn}$, $g_\perp^{nn}$ are the g-factors of the pair spectrum, and R is the separation between the ions. All the quantities in (4) are known. Moreover, the known compressibility of the ethyl sulfates, $\sigma_\parallel = 2.1 \cdot 10^{-6}$ bar^{-1} (4.2 K), enables us to calculate R for different pressures: $R = R_0(1 - \sigma_\parallel P)$ and thus determine A_{ZZ}^{MMD} and its variation with pressure. Of course, it is not quite correct to take R_0 as being equal to the lattice constant C of the ethyl sulfate for the corresponding crystal at atmospheric pressure because the two impurity ions forming the pair modify this distance. The difference must be taken into account in exact calculations, but we are interested not so much in the absolute magnitude as in the functional dependence of the nondipole part of the interaction A_{zz}^{nd}.

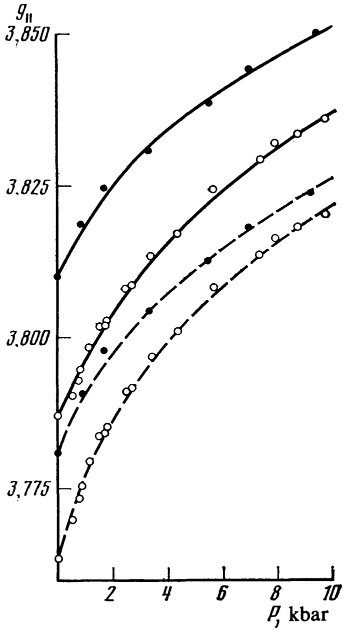

FIG. 5. The g-factors corresponding to the single (solid curve) and pair (broken curve) spectra of Ce^{3+} ions as functions of pressure for EuETS (●) and YETS (O).

The question is: what is the origin of the decrease in the nondipole part of the interaction with pressure? The exchange interaction must be excluded because, as in the case of other rare-earth ion pairs in ethyl sulfates, it is small. For example, it amounts to [10] 2×10^{-4} cm^{-1} for Gd^{3+}, and has been found to increase sharply with pressure (Nd^{3+}). The latter result was established by additional experiments.

The remaining two mechanisms, namely, quadrupole-quadrupole and exchange through the phonon field, can explain the reduction in A_{zz}^{nd} if the energy of the excited state increases with increasing pressure.

Previous studies of the spin-lattice relaxation of the Ce^{3+} ion in the EuETS and YETS lattices under pressure[11] have led to the determination of the energy Δ_1 of the first excited doublet because the temperature dependence of the spin-lattice relaxation is described by the Orbach-Aminov process. The quantity Δ_1 increases with pressure at the same rate for both crystals and is described by the linear relation

$$\Delta_1(P) = \Delta_1(0) + KP,$$

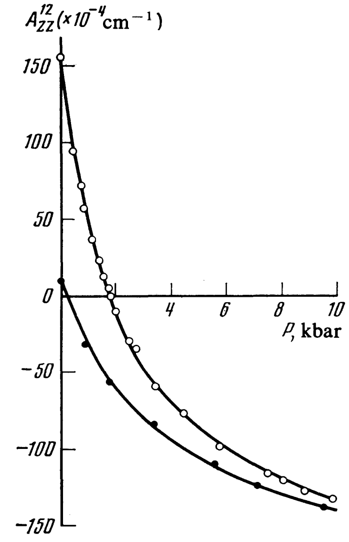

FIG. 6. Anisotropic part of the interaction in Ce^{3+} ion pairs as a function of pressure: O—EuETS, ●—YETS.

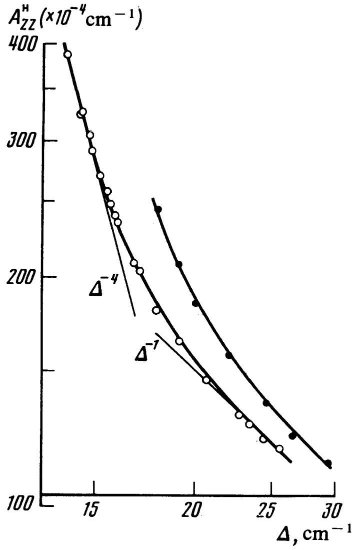

FIG. 7. Nondipole part of the interaction A^{n}_{zz} as a function of Δ_i (logarithmic scale): ○—EuETS, ●—YETS.

where $\Delta_1(0) = 13.8$ cm^{-1} for EuETS and $\Delta_1(0) = 18$ cm^{-1} for YETS, $K = 1 > 2$ cm^{-1}/kbar. By combining all the data, it is possible to construct the dependence of A^{nd}_{zz} on Δ_1. Figure 7 shows the required dependence on the logarithmic scale. The slope of the tangents gives the power of Δ_1. The initial portion of the curve shows quite clearly the Δ_1^{-4} variation but, at higher pressures, the dependence is Δ_1^{-1}. It may therefore be concluded that, for low Δ_1, the dominant nondipole interaction in the Ce^{3+} ion pairs is exchange through the phonon field, and measurements confirm the prediction of McKenzie and Stedman.[6] As Δ_1 increases, the quadrupole-quadrupole interaction becomes the dominant factor. It may be expected that, as the pressure increases still further (and, consequently, so does Δ_1), the rapidly increasing exchange interaction will come into play.

Figure 7 shows the points corresponding to YETS. The range of variation of A^{nd}_{zz} is somewhat smaller in this crystal, but the overall shape of the dependence on Δ_1 is the same.

These experiments have enabled us to understand why the pair spectrum is not observed in LaETS. The distance to the excited state[12] of LaETS is 2 cm^{-1} and the interaction should be much stronger than in EuETS, so that the pair lines may have much smaller splitting. On the other hand, the lines in the pair spectrum may have greater width than in our crystals because of the stronger dependence of this width on Δ_1. It is known that the broadening of the energy interval in LaETS reaches[12] ~ 0.02 cm^{-1}. It is possible that the pair spectrum of LaETS could be observed under pressure by artificially increasing the distance to the excited doublet.

CONCLUSIONS

We have thus established experimentally a situation in which the spin-spin interaction in an ion pair is altered very considerably by transforming the energy spectrum of the impurity ions by hydrostatic pressure. At a pressure of 1.8 kbar, the anisotropic part of the interaction is zero because of the competition between several mechanisms and, as the pressure is increased still further, the interaction increases with the opposite sign.

The nondipole part of the interaction has been determined as a function of the energy of the excited doublet, and this enabled us to confirm the existence of exchange through the phonon field.

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