Effect of pressure on the nature of spin-spin interaction in cerium ethyl sulfate

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A change in the nature of the spin-spin interaction in cerium ethyl sulfate was observed. Exchange via the phonon fields dominates in this substance at atmospheric pressure, and magnetic dipole interaction dominates above 5 kbar. The reversal of the sign of the isotropic part of the interaction at 5 kbar indicates that the ordering changes from antiferromagnetic at atmospheric pressure to ferromagnetic above 5 kbar.

The properties of a magnet below the ordering temperature are determined by the nature of the spin-spin interactions. For iron group ions, the main contribution is made by the exchange and magnetic dipole-dipole (MDD) interactions. In rare-earth compounds, other mechanisms can manifest themselves, particularly electric quadrupole-quadrupole interaction and exchange via the phonon field (PFE). Great interest attaches to cases in which interactions of various types are comparable in magnitude and opposite in sign. A small external action can cause then a substantial change in the magnetic properties of the substance.

Among the many rare-earth ethyl sulfates, that of cerium (Ce ETS) is unusual and has anomalous thermal and magnetic properties. Measurements of the heat capacity[1] have revealed an increase of the Schottky peak; the temperature dependences of the magnetic[2,3] and electric[4] suceptibilities in the 2–10 K range are also unusual. Cerium ethyl sulfate becomes an antiferromagnet below 0.008 K, whereas the ethyl sulfates of dysprosium, neodymium and terbium are ferromagnets with Curie temperatures 0.13 K (Ref. 5), 0.07 K (Ref. 6) and 0.24 K (Ref. 7). This is evidence that the nature of the spin-spin interaction between the cerium ions is different from that of the other compounds mentioned, in which magnetic dipole-dipole interaction predominates.

The unusual character of the properties of cerium ethyl sulfates is due to the almost degenerate state of the two Kramers doublets in the ground multiplet of trivalent cerium and to their strong coupling with the lattice vibrations.[8]

The resonant properties of ethyl sulfates with magnetic-dipole interaction are identical: the absorption spectrum is a triplet with a component ratio 1:2:1, as first described in Ref. 9. The spectrum of the cerium ethyl sulfate differs qualitatively from them. It was investigated in Refs. 10 and 11, in which contradictory data were obtained and, naturally, a different explanation was offered for both the nature of the interaction and its resonant manifestations.

We have shown in Ref. 12 that the principal role in the interaction between a pair of cerium ions in Eu ETS and Y ETS matrices is played at atmospheric pressure by the FPE. It is natural to assume that the same mechanism causes the unusual ESR spectrum of Ce ETS.

For Kramers ions, the FPE contribution is of second-order perturbation theory, and should therefore depend strongly on the energy spectrum of the investigated ion. The distance Δ to the first excited level of the Ce^{3+} ion in Eu ETS and Y ETS increases at a rate of 1.2 cm^{-1}/kbar,[13] and this leads to a rapid decrease of the FPE with pressure. If the situation in Ce ETS is similar, an appreciable transformation of the ESR spectrum and of the properties of this material can be expected with increases of pressure.

The Ce ETS crystals were grown from an aqueous solution as the temperature was lowered. The ESR spectrum was investigated at $T = 4.2$–1.5 K at frequencies 9.3 and 36 GHz under hydrostatic pressure up to 14 kbar.

Under the action of the ethyl sulfate crystal field of symmetry C_{3h} and describable by the spin Hamiltonian

$$\hat{\mathscr{H}}_{cr} = B_2{}^0 \hat{O}_2{}^0 + B_4{}^0 \hat{O}_4{}^0 \tag{1}$$

($\hat{O}_m{}^0$ are spin operators, $B_m{}^0$ are coefficients that describe the crystal field) the ground multiplet $J = 5/2$ of the free Ce^{3+} ion (electron configuration $4f^1$) is split into three doublets with wave functions $|\pm 1/2\rangle, |\pm 3/2\rangle, |\pm 5/2\rangle$. The ESR spectrum is observed on the lower doublet $|\pm 5/2\rangle$ and is described by the effective spin Hamiltonian

$$\hat{\mathscr{H}} = g\beta \mathbf{H}\hat{\mathbf{S}}, \tag{2}$$

where g is the spectroscopic splitting factor, β is the Bohr magneton, **H** is the magnetic field, $\hat{\mathbf{S}}$ is the spin operator, and the effective spin is 1/2.

The perturbation (1) leaves the ground state pure, and no ESR spectrum should be manifested in the parallel orientation ($H_0\|z$), since $g_\perp = 2g_0 \langle +5/2|\hat{J}_x| - 5/2\rangle = 0$; in the experiment, however, $g_\perp \sim 0.2$ and the transitions are allowed. A similar picture for cerium impurity ions in Eu ETS and Y ETS was attributed in Ref. 13 to mixing of the states $|\pm 5/2\rangle$ and $|\pm 3/2\rangle$ on account of lattice vibrations. It is possible that the same phenomenon is observed in Ce ETS, but at any rate the dependence of $g_\|$ on the pressure, which can be extrapolated by the expression

$$g_\| = 3.84 - 1/(9.2 + 1.58P),$$

is of similar form for these substances.

Since $g_\perp$ is small, we investigated the influence of hydrostatic compression on the ESR spectrum of Ce ETS only in the case $H_0\|z$. The results are shown in Fig. 1. We note the following important features of the behavior of the compressed-crystal spectrum.

1. At low pressures the line shape is close to rectangular. With decrease of temperature, the intensity of the weak-field part of the spectrum decreases, an effect much more pronounced at 36 GHz. The line-shape distortion is due to the lower populations of the higher energy levels, and makes it possible to determine the sign of the interaction.

2. With increase of pressure, the line becomes narrower
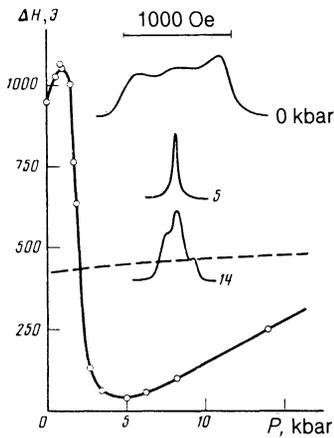
FIG. 1. Plot of ESR spectrum of Ce ETS (center) at pressures 0, 5, and 14 kbar; $T = 2$ K. Solid curve—absorption-spectrum width, measured between maximum slope points, vs pressure. Dashed line—calculated dependence of spectrum width on pressure in the presence of only magnetic dipole-dipole interaction (width of individual component 50 Oe).

but remains rectangular up to 5 kbar, where it turns into a single line of width (50 ± 10) Oe.

3. At high pressures the spectrum is a triplet similar to that investigated in Ref. 6, with a component intensity ratio 1:2:1 (at $T = 4.2$ K). The intensity of the higher-field part of the spectrum decreases with decreasing temperature.

The aggregate of the data obtained leads to the following qualitative picture. At atmospheric pressure the energy interval Δ equals 4.7 cm^{-1} (Ref. 2 and 15) several times smaller than in Eu ETS and Y ETS. The contribution of the PFE to the investigated compound is therefore large, as manifested by the large spread of the absorption spectrum. The value of Δ increases with pressure, and this decreases the PFE contribution. At 5 kbar this contribution becomes equal to that of the other mechanisms that contribute to the interaction with opposite sign, and the MDD interaction begins to prevail with further compression. The character of the interaction at normal pressure is antiferromagnetic, as is attested by the decrease of the intensity of the low-field part of the spectrum,[11] and leads to antiferromagnetic ordering of the cerium ethylsulfate at $T = 0.08$ K (Ref. 2). At high pressures ($P > 5$ kbar) the character of the interaction becomes ferromagnetic, as is evidenced by the decrease of the intensity of the high-field part of the spectrum. This gives grounds for assuming that the antiferromagnetic-ordering temperature will decrease will increasing pressure, and the ordering will become ferromagnetic above 5 kbar.

The Hamiltonian $\mathscr{H}$ of the interacting Ce^{3+} ion can be written in the form

$$\hat{\mathscr{H}} = \sum_{i}^{N} \hat{\mathscr{H}}_{i} + \sum_{i > j}^{N} \hat{S}^{i} K^{ij} \hat{S}^{j}, \tag{3}$$

where $\hat{\mathscr{H}}_{i}$ is the Hamiltonian (2) of a single ion, K^{ij} is the tensor of the interaction of the ith and jth ions and can be resolved into isotropic J^{ij} and anisotropic A^{ij} parts:

$$\hat{S}^{i} K^{ij} \hat{S}^{j} = J^{ij} \hat{S}^{i} \hat{S}^{j} + \hat{S}^{i} A^{ij} \hat{S}^{j}, \quad \mathrm{Sp}\, A^{ij} = 0,$$

$$A_{\|}^{ij} = {}^{2}/_{3} (K_{\|}^{ij} - K_{\perp}^{ij}), \quad J^{ij} = {}^{1}/_{3} (K_{\|}^{ij} + 2K_{\perp}^{ij}). \tag{4}$$

In the general case it is impossible to diagonalize (3).

Using, however, the properties of the ethyl sulfate structure, whose cell is shown in greatest details in Ref. 12 in accordance with the data of Ref. 14, this expression can be greatly simplified. We first discard the interaction with the second "neighbors," the direction of the interaction with which makes an angle 66.5° with the c axis. It can be shown that, at least for the MDD interaction, this can be done with sufficient justification. Next, the second "neighbor" along the string is located at a distance twice that of the nearest, we therefore neglect the interaction with these ions. We find ultimately that the interacting ions in the ethyl sulfate are arranged in the forms of chains in which only the nearest neighbors interact.

Baker[15] restricted the chain to three ions, and this enabled him to explain illustratively but incorrectly the triplet structure of the ESR spectrum of Nd ETS. In this case the Hamiltonian (3) can be diagonalized analytically and it follows from the calculation results that the spectrum consists of seven lines. In the particular case of Nd ETS, for which $|K_{\|}^{1,2}| \gg |K_{\perp}^{1,2}|$, some of the lines overlap and the spectrum should consists of five components with an intensity ratio 1:4:2:4:1.

At $K_{\perp}^{1,2} = 0$ expression (3) becomes so simple that it is possible to calculate the spectrum of a rather large chain; this was done with a computer for various $3 \leqslant N \leqslant 20$. It turned out that the length of the chain, while not affecting the positions of the spectrum components, exerts a substantial influence on the intensity ratio, which depends on N as

$$1 : 4/(N-2) : 2 : 4/(N-2) : 1$$

($N \geqslant 3$), and at a suffecent chain length a triplet structure should be observed with an intensity ratio 1:2:1. The foregoing conclusions allow us to calculate the ESR spectrum of Ce ETS in the case of pure MDD interaction, using the known equations:

$$K_{\|}^{M} = -2g_{\|}^{2} \beta^{2} R^{-3}, \quad K_{\perp}^{M} = g_{\perp}^{2} \beta^{2} R^{-3}. \tag{5}$$

Since $|K_{\|}^{M}| \gg |K_{\perp}^{M}|$, the distance between the outermost components of the spectrum is equal to $2K_{\|}^{M}$. It can be seen from Fig. 1 that at high pressures the experimental curve tends to this value.

For added analysis, a computer was used to calculate the spectrum of a chain of five ions at different values of $\gamma = K_{\perp}^{1,2} / K_{\|}^{1,2}$ (Fig. 2). Its analysis reveals certain regularities: 1) the shape of the spectrum is determined by the value of γ; 2) at $\gamma \approx -0.25$ the spectrum has a nearly rectangular shape; 3) at $A_{\|}^{1,2} = 0$ the spectrum consists of a single line. This phenomenone, well known as exchange narrowing, is manifested in this case by the fact that the ESR of ions coupled only by an isotropic interaction is indistinguishable from the spectrum of non-interacting ions.

Assuming that the result describes qualitatively correctly the spectrum of an infinite chain, we use it to estimate the size of the interaction in Ce ETS, recognizing that as $N \to \infty$ account must be taken of the intensity ratio given above.

At a pressure 5 kbar, the ESR spectrum of Ce ETS is a single line. This can occur if the interaction mechanisms cancel out or the interaction is isotropic, as follows from item 3. In the pressure range 0–5 kbar the absorption-spectrum line should be nearly rectangular. It follows from Item
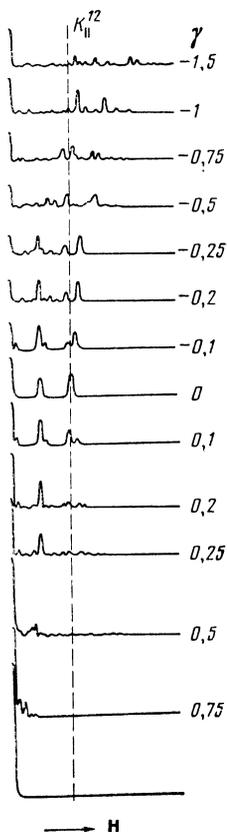
FIG. 2. Calculated spectrum of linear chain of five interacting ions at different values of $\gamma = K_\perp^{1,2}/K_\parallel^{1,2}$ (upper-field part). Lower curve—$\gamma = 1$.

2 that the relation $K_\parallel^{1,2} \approx -4K_\perp^{1,2}$ remains in force here. Using (4) we get $J^{1,2} \approx \frac{1}{5} A_\parallel^{1,2}$. Since $A_\parallel^{1,2} \approx 0$ at $P = 5$ kbar, we have also $J^{1,2} \approx 0$, i.e., the Ce^{3+} ions hardly interact.

Let us estimate the spin-spin interaction at atmospheric pressure. It follows from Fig. 2 that at $K_\parallel^{1,2} = -4K_\perp^{1,2}$ the distance between the outer components of the spectrum is $\sim 2,1K_\parallel^{1,2}$. The distance between the peaks in the ESR spectrum of Ce ETS is ~ 800 Oe and $g_\parallel = 3.735$, whence

$K_\parallel^{1,2} \approx 6,4 \cdot 10^{-2}$ cm^{-1}, $\qquad K_\perp^{1,2} \approx -1,7 \cdot 10^{-2}$ cm^{-1}, $A_\parallel^{1,2} \approx 5,4 \cdot 10^{-2}$ cm^{-1}, $J^{1,2} \approx 1 \cdot 10^{-2}$ cm^{-1}. At atmospheric pressure the non-dipole part of the interaction is thus $K_\parallel^n \approx 0,1$ cm^{-1}, close to the value obtained in Ref. 8.

Notice must be taken also of two singularities in the experimental spectrum: a) the widths of the spectrum components in the range 0–5 kbar decrease with increase of pressure and subsequently decrease, but much more slowly; b) anomalies exist in the behavior of the spectrum width in the 0–1.5 kbar range. The first singularity can be attributed to the interaction with the far neighbors, but no reasonable explanation has been found for the second singularity.

Thus, an investigation of the baric dependence of the width and shape of the absorption line in Ce ETS has explained the unusual shape of the ESR line and provided an estimate of the magnitude and sign of the non-dipole contribution to the spin-spin interaction. Compression of the crystal leads to a change of the nature of the spin-spin interaction, and this in turn should cause a change in the character of the ordering at infralow temperatures and a transition from the antiferromagnetic phase to the magnetic one.

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