Spectroscopic investigation of the Schottky anomaly in cerium ethyl sulfate

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The splitting Δ between the lower doublets $|\pm 5/2\rangle$ and $|\pm 1/2\rangle$ of the ground state of the Ce^{3+} ion in cerium ethyl sulfate has been determined for the first time and its temperature dependence has been investigated in the temperature interval 2.5–50 K. An EPR spectrometer operating at a wavelength of 4 mm (frequency of 2.5 cm^{-1}) was used. As the temperature varied from 2.5 to 10 K the splitting Δ varied from 6.7 to 3 cm^{-1}. The experimental results were used to calculate the temperature dependence of the molar heat capacity (investigation of the Schottky anomaly) and magnetic susceptibility of cerium ethyl sulfate. It is shown that there are significant discrepancies between the previously proposed description of these macroscopic properties of this compound and experiment.

INTRODUCTION

The anomaly, found in Ref. 1, in the temperature dependence of the heat capacity of the model crystal cerium ethyl sulfate Ce ETS is explained by the presence of closely spaced spin levels in the energy spectrum of this magnet. Occupation of the excited level as the temperature is raised results in an anomaly, termed the Schottky anomaly. The quantitative calculation of the heat capacity for the case of Ce ETS, however, is not in good agreement with experimental data. Attempts have been made to explain these discrepancies in terms of spin–spin interactions of the cerium ions.[2] These attempts were unsuccessful. In Ref. 3 it is shown that the theoretical results can be made to agree with the experimental results if it is assumed that the splitting Δ between the two lower spin doublets of the ground state of the cerium ion is temperature-dependent.

In Ref. 4 the dielectric susceptibility of Ce ETS was measured and it was shown that the experimental data can likewise be explained by taking into account the temperature dependence of the splitting, but this dependence differed significantly from that found in Ref. 3.

In subsequent work[5] the experimental data on the magnetic susceptibility[6] were analyzed on the basis of the model of Ref. 3. Taking into account the temperature dependence of the splitting obtained from analysis of the heat capacity data did not yield good agreement with experiment in this case either.

Cerium ethyl sulfate has a number of remarkable properties, which distinguish it from other isostructural ethyl sulfates of rare-earth elements. Thus cerium ethyl sulfate is the only crystal that becomes antiferromagnetic at ultralow temperatures.[7] As shown in Refs. 8 and 9, exchange via the phonon field predominates in the spin–spin interactions of Ce ETS, while in other ethyl sulfates the dipole–dipole interaction predominates. Finally, the structure of the energy levels of trivalent cerium ions in the crystal field of ethyl sulfate is extremely sensitive to external deformations of the crystal.[10,11]

It should be noted especially that until recently the lack of spectroscopic equipment that could operate at low temperatures and under conditions of quite strong magnetic fields and microwave radiation with a frequency of several inverse centimeters made it impossible to measure directly the splitting Δ.

In this work we addressed the problem of determining experimentally the splitting Δ between the two bottom doublets of the Stark structure of Ce ETS, studying the temperature dependence of Δ in the temperature interval where the Schottky anomaly is observed, and also explaining, on the basis of the obtained results, the experiments on the heat capacity and dielectric and magnetic susceptibilities.

EXPERIMENTAL TECHNIQUE AND RESULTS

The spectroscopic investigations of Ce ETS were performed using a 4-mm EPR radiospectrometer (the microwave frequency ~ 2.5 cm^{-1}) in the temperature range 2.5–50 K in pulsed (up to 20 T) and static (up to 5 T) magnetic fields.

High quality Ce ETS single crystals were grown from a water solution by the method of lowering the temperature at $t \sim 37\,°C$. The single crystals obtained had a clearly pronounced faceting, which made it possible to prepare well oriented samples.

The sample temperature was measured by means a semiconductor sensor, placed adjacent to the sample in the body of the microwave resonator.[12]

The trivalent cerium ion, which has the electronic configuration $4f^1$ and the ground state $^2F_{5/2}$ in the crystal field of ethyl sulfate with symmetry C_{3h}, has three Kramers doublets $|\pm 1/2\rangle$, $|\pm 3/2\rangle$, and $|\pm 5/2\rangle$, whose relative energy spacing is different in the series of ethyl sulfates. In all crystals, with the exception of La ETS, the lower doublet is $|\pm 5/2\rangle$, on which a weak EPR signal with a g factor close to 4 is observed in a magnetic field. In Refs. 11 and 13 spin-lattice relaxation measurements established the energy separation up to the excited level and its dependence on the pressure in Y ETS and Eu ETS crystals. In Ce ETS crystals a broad EPR signal (~ 1 kOe) is observed on the ground-state doublet $|\pm 5/2\rangle$. As the hydrostatic pressure increases both the shape and width of this signal change very strongly.[9] This fact is related with the strong spin–spin interaction, governed by exchange via the phonon field, and depends, to a large degree, on the position of the excited doublet.

According to estimates made previous studies,[1,3,4] the

energy splitting between the ground-state doublet and the first-excited-state doublet in cerium ethyl sulfate is equal to ~ 5 cm^{-1} (Fig. 1). Experiments in pulsed magnetic fields with $H_0 \| c_3$ and $H_0 \perp c_3$ and a temperature of 4.2 K (Ref. 14) showed that wide intense absorption lines are present. The width of these lines at half-height is equal to tens of kilooersteds. Thus in the perpendicular orientation we have $\delta H \sim 60$ kOe. The energy of the first excited doublet can be calculated from the observed spectrum: 5.76 cm^{-1} with $g_\| = 3.735$ and $g_\perp = 0.2$ for the doublet $| \pm 5/2 \rangle$ and $g_\| = 0.955$ and $g_\perp = 2.17$ for the doublet $| \pm 1/2 \rangle$.[14]

It follows from the experiments performed that for $H_0 \| c_3$ the maximum of the absorption line lies in a field of about 30 kOe, which is easily attainable when working with a superconducting magnetic system. Further experiments were performed in static fields with a parallel orientation of the sample. The high sensitivity of the interdoublet splitting to deformations of the crystal requires that the original single crystal be of high quality and imposes stringent requirements on the sample preparation procedure. Taking these circumstances into account resulted in an appreciable narrowing of the recorded absorption line. In order to study the temperature dependence of the splitting the position of the line in a magnetic field was recorded at different temperatures. Figure 2 shows the experimental tracings of the original absorption. The temperature dependence of the splitting $\Delta(T)$ (Fig. 3) was calculated under the assumption that the g factors are not temperature dependent. In the interval 10–50 K the maximum of the absorption line could not be recorded because of the much greater width of the line and displacement of the line into the region of zero fields. This made it impossible to determine the position of the line and calculate the magnitude of the splitting. It can only be noted that the temperature dependence becomes flatter in this region.
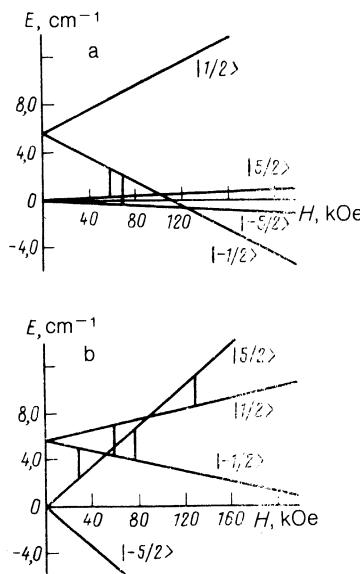
FIG. 2. The form of the spectrum of the Ce^{3+} ion in Ce ETS at different temperatures.

DISCUSSION

We now discuss the obtained results and their consequences on the basis of the model proposed in Ref. 3. The temperature dependence arises owing to the strong coupling between the spin system and the lattice distortions. Thermodynamic analysis showed that in the absence of external pressure the splitting of the levels and the lattice stresses vary smoothly between the high- and low-temperature limits. At a temperature T the splitting $\Delta(T)$ is determined self-consistently by the following equation:

$$\Delta(T) = \Delta_0 (1 + \Gamma \, \text{th} \, [\Delta(T)/2kT]), \tag{1}$$

where Γ is a parameter that determines the spin–lattice coupling and Δ_0 is the high-temperature splitting. At low temperature we have $\Delta(0) = \Delta_0(1 + \Gamma)$. Introducing the parameter $y = \Delta(T)/kT$, we can put the molar heat capacity for a two-level system into the following form:

FIG. 1. Arrangement of the two lower doublets of the ground state of the Ce^{3+} ion in the crystal field of Ce ETS at $T = 4.2$ K. a) The external magnetic field is perpendicular to the c_3 axis of the magnetic center; b) the magnetic field is parallel to the c_3 axis.
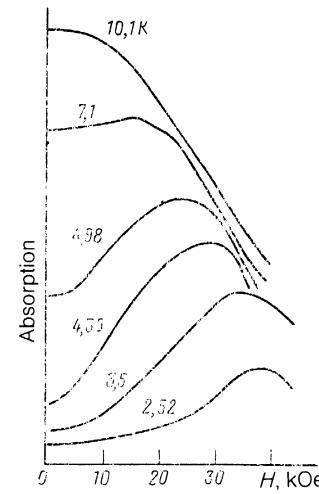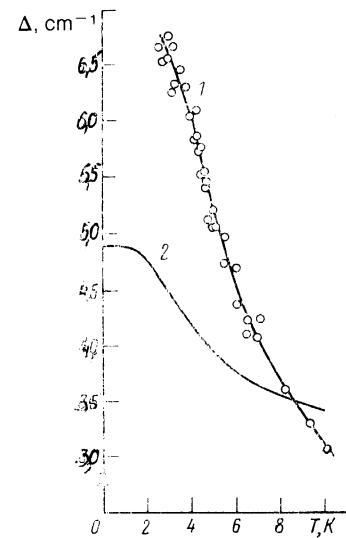
FIG. 3. The temperature dependence of the splitting between the lower doublets of the ground state of the Ce^{3+} ion in Ce ETS. 1) The values of Δ determined experimentally in the present work; 2) the curve constructed from the data of Ref. 5.
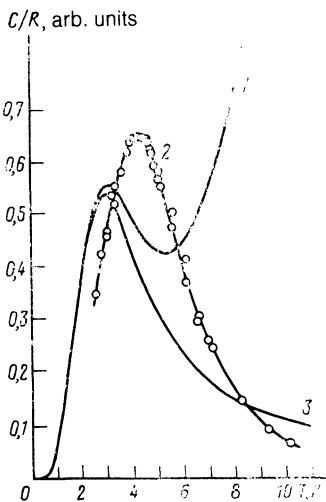
FIG. 4. The temperature dependence of the molar heat capacity of Ce ETS. 1) The curve experimentally obtained in Ref. 1; 2) the curve calculated from the dependence $\Delta(T)$ determined experimentally in the present work; 3) the temperature dependence of the heat capacity of Ce ETS in the absence of spin–lattice coupling (Schottky heat capacity[1]).

$$\frac{C}{R} = \frac{y^2 \operatorname{sech}^2 y}{1 - \dfrac{\Gamma y \operatorname{sech}^2 y}{1 + \Gamma \operatorname{th} y}} \cdot \qquad (2)$$

In the absence of spin–lattice coupling $\Gamma = 0$ holds and the expression (2) assumes the standard form of the Schottky heat capacity. Analyzing with the help of the expressions obtained the experimental data of Ref. 1, presented in Fig. 4, Fletcher and Sheard[3] obtained the following values: $\Delta(0) = 4.9\,\mathrm{cm}^{-1}$, $\Delta_0 = 2.9\,\mathrm{cm}^{-1}$, and $\Gamma = 0.68$, which gave good agreement with experiment.

Figure 3 shows the temperature dependence of the splitting constructed according to these data. In Ref. 8 analysis of the dielectric susceptibility of Ce ETS gave different values for the parameters: $\Delta(0) = 5.8\,\mathrm{cm}^{-1}$, $\Delta_0 = 2.76\,\mathrm{cm}^{-1}$, and $\Gamma = 1.1$. Finally, in Ref. 6 analysis of the magnetic susceptibility reduced Γ to 0.3. Thus we can see that the magnitude of the splitting and its temperature dependence, which were found from the temperature dependence of the different physical quantities—the heat capacity and the dielectric and magnetic susceptibilities—differ from one another and from the change in the splitting determined experimentally in this work. Using Eq. (1) we obtained the parameters $\Delta(0) = 7.0\,\mathrm{cm}^{-1}$, $\Delta_0 = 2.1\,\mathrm{cm}^{-1}$, and $\Gamma = 2.34$, which best describe our experimental data. The curve constructed based on these data is shown in Fig. 3.

The curve of the molar heat capacity, calculated from the formula (2) and the results obtained in this work, is shown in Fig. 4. As one can see, it differs substantially from the results of Ref. 1.

Let us see how the magnetic susceptibility behaves. Since at low temperature only the two lower doublets are occupied, the effect of the doublet $|\pm 3/2\rangle$, lying much higher than the first two doublets ($\sim 80\,\mathrm{cm}^{-1}$), can be neglected. Then the expression for the susceptibility assumes the following form:

$$\chi_\perp = \frac{\mu \beta^2}{4kT} \frac{g_1{}^2 + g_2{}^2 \exp[-\Delta(T)/kT]}{1 + \exp[-\Delta(T)/kT]} . \qquad (3)$$
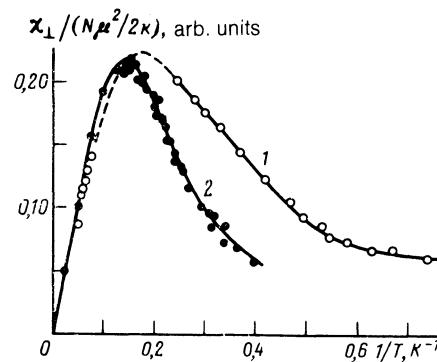

FIG. 5. The temperature dependence of the perpendicular component of the magnetic susceptibility of Ce ETS. 1) The curve calculated from the dependence $\Delta(T)$ determined experimentally in the present work; 2) the curve constructed from the data of Ref. 6.

Here g_1 and g_2 are the g factors of the lower and upper doublets, respectively.

Figure 5 shows the experimental data of Ref. 6 for $\chi_\perp$, and it also shows the curve constructed taking into account the dependence $\Delta(T)$ determined in this work. As we can see, the discrepancy is just as large as for the heat capacity.

In the discussion of the results two questions arise: why are transitions observed between the levels $|+5/2\rangle$ and $|-1/2\rangle$, if the change in the magnetic quantum number is equal to 3, and what causes such a strong disagreement between the characteristics calculated from the experimentally determined dependence $\Delta(T)$ and the measured macroscopic properties of cerium ethyl sulfate?

A partial answer to the first question was given in Ref. 14 in an investigation of the spectrum of the Ce^{3+} ion in La ETS, where the ground state is the doublet $|\pm 1/2\rangle$ and the excited doublet is split from the ground state by $2\,\mathrm{cm}^{-1}$. In Ref. 14 the following transitions were observed: $|-1/2\rangle \leftrightarrow |+5/2\rangle$, $|+1/2\rangle \leftrightarrow |+5/2\rangle$, and $|-5/2\rangle \leftrightarrow |+1/2\rangle$. It was shown that the states of the doublets are not pure states, as should follow from the symmetry of the crystal field of ethyl sulfates, since the strong spin–phonon interaction mixes the wave function of the state $|+5/2\rangle$ with that of the state $|+1/2\rangle$ and the wave function of the state $|-5/2\rangle$ with that of the state $|-1/2\rangle$. As a result, transitions between levels, conventionally denoted in Fig. 1 as $|+5/2\rangle$ and $|-1/2\rangle$, become allowed when the constant magnetic field is perpendicular to the alternating microwave field, and this is actually observed in the experiment.

There are two ways to find an answer to the second question; both can lead to agreement. First, the level width is neglected in the calculations of the heat capacity. It follows from Fig. 2 as well as the measurements in pulsed magnetic fields with $H_0 \| c_3$ that the level width $\sim 2\,\mathrm{cm}^{-1}$. Taking this into account decreases the intensity of the peak on the curve of the temperature dependence of the heat capacity and the broadening of the peak. Second, the spin–spin interaction between the cerium ions is neglected. As shown in Refs. 8 and 9, this interaction is significant and depends very strongly on the relative position of the energy levels in the Stark structure of cerium.

We hope that the foregoing remarks will help to explain these discrepancies.

Thus in this work the energy splitting in the Stark structure of cerium ions in Ce ETS and its temperature dependence were determined by a direct method with the help of electron paramagnetic resonance in strong static and pulsed magnetic fields. The proposition of Ref. 3 was qualitatively confirmed. At the same time it was shown that there is a quantitative disagreement with the previously proposed model and possible ways to improve the model were indicated.

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