

Pressure-induced phase transition in lanthanum ethylsulfate with praseodymium impurity

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(Submitted 23 May 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **32**, No. 2, 111–114 (20 July 1980)

Measurements of the absorption spectra of LaES (lanthanum ethylsulfate) (1% Pr^{3+}) and PrES (praseodymium ethylsulfate) have revealed a phase transition at pressures above 26 kbar and temperatures below 150 K.

PACS numbers: 64.70.Kb, 62.50. + p, 78.20.Hp

Rare-earth ethylsulfates are model materials for many current theoretical and experimental techniques. Electron paramagnetic resonance data on these materials were first used to test the method of equivalent operators, and the theory of complex spectra has been tested most rigorously against the spectra of rare-earth chlorides and ethylsulfates.

The structure of these single crystals has been studied in detail. Nine water molecules on three parallel and triangles surround the rare-earth ion, producing a field with symmetry D_{3h} (see Fig. 1). The minimum distance between praseodymium and oxygen ions is 2.47\AA .

The absorption spectra of rare-earths in ethylsulfates fit the isolated-ion approximation, although EPR methods have revealed a pair interaction between nearest rare-earth ions ($\sim 7\text{\AA}$). When the temperature is lowered to ~ 0.1 K, magnetic ordering occurs (for reference data on the original papers see Refs. 1–3).

The main changes in the spectrum due to the application of pressures up to 25

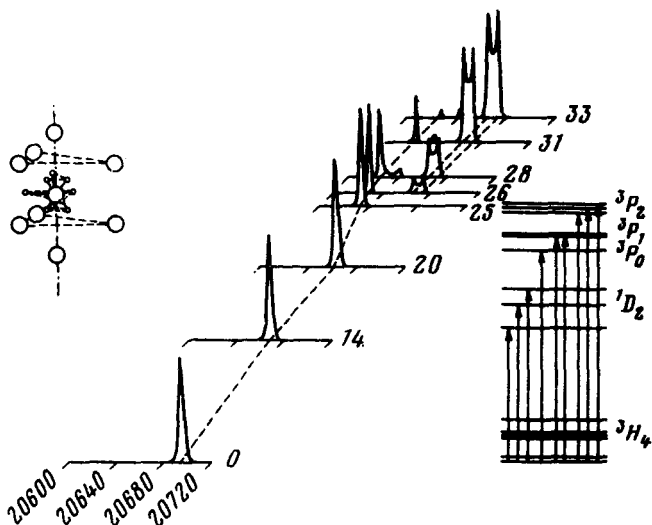


FIG. 1. Absorption spectrum of LaES (1% Pr^{3+}) in the ${}^3H_4 \rightarrow {}^3P_0$ transition region; $P = 0\text{--}33$ kbar, $T = 78$ K. Only lines with σ polarization appear.

kbar (a shift in the long-wavelength region by an average of 50 cm^{-1} without disruption of the overall pattern of the spectrum) are explained by a decrease in the electrostatic interaction between $4f$ electrons and a change in the interaction of the rare-earth ion with the crystal field.³ Thus, the absorption spectra of lanthanum ethylsulfate with a 1% Pr^{3+} impurity obtained at pressures not higher than 25 kbar and temperatures

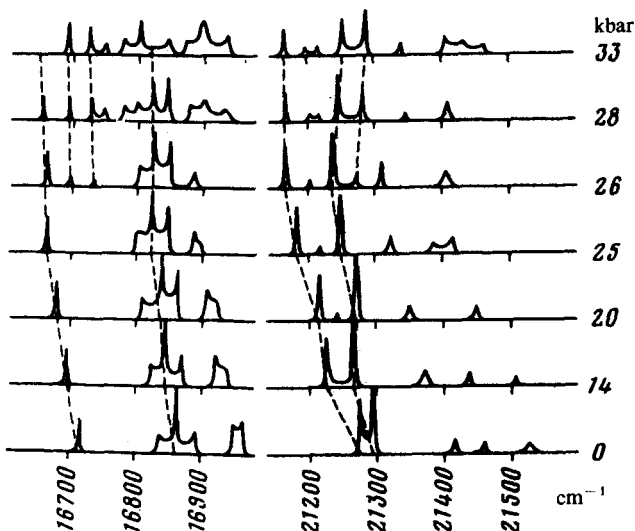


FIG. 2. Absorption spectra of LaES (1% Pr^{3+}) in the ${}^3H_4 \rightarrow {}^1D_2$ and ${}^3H_4 \rightarrow {}^3P_1$ transition regions; $P = 0\text{--}33$ kbar, $T = 78$ K. Only lines of σ polarization appear.

of 78 and 4.2 K can be interpreted without difficulty (see Fig. 1).

The experiments at higher pressures described in this letter gave unexpected results. In the interval from 26 to 32 kbar the spectrum of LaES (1% Pr^{3+}) changes markedly: there is an increase in the number of lines and redistribution of the intensities (see Figs. 1 and 2). The intensity of the lines corresponding to the "low-pressure phase" (below 26 kbar) falls off, while the intensity of the spectrum of the "high-pressure phase" (above 32 kbar) grows. The presence of this intermediate region where the vanishing spectrum of the low-pressure phase is superimposed on the emerging spectrum of the high-pressure phase is evidently due to nonuniform compression of the sample (the nonuniformity is estimated³ to be 3 or 4 kbar).

It is hard to discern the pattern in the changes of the various parts of the spectrum, since the mechanism of the observed phenomenon is not clear. For example, in the simplest part of the spectrum—the region of ${}^3H_4 \rightarrow {}^3P_0$ transitions (see Fig. 1)—instead of the single line observed below 26 kbar (the second π -polarization line is seen only when the axis of the sample is oriented perpendicular to the direction of propagation of the light), at 32 kbar one already sees four lines. The first two of these, which are separated by 16 cm^{-1} , are remnants of the vanishing line of the low-pressure phase, while the second two (separated from each other by 8 cm^{-1}) are newly appearing and are equal in intensity to the former.

The intensity of the first line in the region of ${}^3H_4 \rightarrow {}^1D_2$ transitions, which lags far behind the other lines, falls off. At a pressure of 32 kbar this line is not seen, but instead, as in the ${}^3H_4 \rightarrow {}^3P_0$ region one sees two intense new lines, which are separated from each other by 32 cm^{-1} . The vanishing of the most intense line of the low-pressure phase in this region of the spectrum is not followed by the appearance of a new pair of lines.

In the region of ${}^3H_4 \rightarrow {}^3P_1$ transitions (see Fig. 2) no lines vanish, but a new one appears and the intensities of two of the lines of the low-pressure spectrum fall off. It is

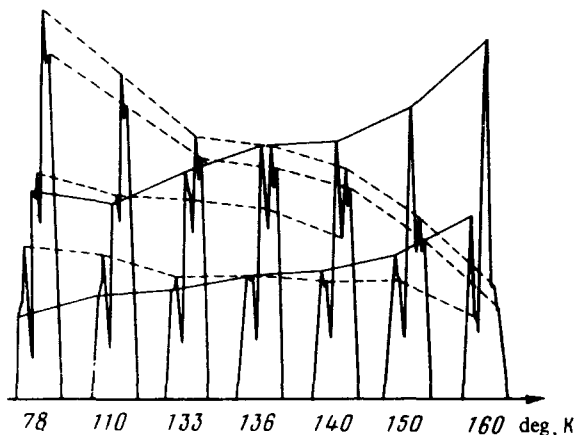


FIG. 3. Changes in absorption spectrum of PrES in the ${}^3H_4 \rightarrow {}^3P_0$ region under heating; $P = 36$ kbar. Lines of σ and π polarization appear.

extremely probable that the changes in this part of the spectrum are more complex and that the redistribution of the intensities is not noticeable because of the small separation between the vanishing and emerging lines. This hypothesis is based on the fact that a similar "hidden" transition was observed in the ${}^3H_4 \rightarrow {}^3P_0$ region in a study of the temperature dependence of the transition for 100% PrES (see Fig. 3). An experiment with 100% PrES was done in order to discover any concentration effects. In this crystal the transition occurs at a higher pressure (36 kbar).

The spectral pattern of the high-pressure phase is destroyed when the sample is heated. In 100% PrES under a pressure of 36 kbar this occurs at ~ 160 K (see Fig. 3), and the first signs of the spectrum of the high-pressure phase appear when the sample is cooled to ~ 145 K.

This experiment on the effect of high pressure was not designed for exact temperature measurements (a copper-iron thermocouple is located in the casing of the high-pressure chamber, separated from the sample by a layer of metal and a layer of sodium chloride, which is used as the pressure medium). Therefore, the fact that the measured temperature dependence was not the same under heating and cooling does not necessarily mean that it was actually different in the two cases.

When the PrES sample was compressed to the maximum pressure possible in our pressure chamber (50 kbar), the spectrum of the high-pressure phase persisted even when the sample was heated to room temperature.

In summary, one can say that the emerging lines of the high-pressure phase appear in the same regions as the previous transitions, but at shorter wavelengths than the vanishing lines. The spacings between pairs of lines appearing in different transition regions are different (2, 16, and 32 cm^{-1}). When the concentration of Pr^{3+} is increased from 1% to 100% the pressure necessary to induce the transition increases, and as the pressure is raised the transition temperature increases.

The spectrum of the high-pressure phase cannot be ascribed to a single isolated ion of trivalent praseodymium.

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