MAGNETIC FIELD EFFECTS ON THE FLUORESCENCE OF Cr^{3+} IN $GdAlO_3$

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The fluorescence spectrum of Cr^{3+} in $GdAlO_3$ has been examined at 4.2 K as a function of magnetic field up to 60 kG. The resulting splitting of the $^2E \rightarrow {}^4A_2$ emission lines are explained in terms of a modified molecular field approximation, which incorporates the effect of the spin fluctuations. The exchange constant in the relaxed excited state is found to be 1.2 cm⁻¹, which differs from that reported from absorption data. It is suggested that the difference may be related to the Frank–Condon effect.

1. INTRODUCTION

Cr^{3+} IN SMALL QUANTITIES ($\sim 1\%$ or less) enters the $GdAlO_3$ perovskite lattice substituting Al^{3+}.

The fluorescence spectra of Cr^{3+} was studied by Blazey and Burns [1] and Murphy and Ohlmann [2] who found it to consist of a broad emission band around 730 nm, with four resolved peaks. The splitting $\epsilon(T)$ was studied as a function of temperature in the range between 1.6 and 77 K in the absence of external magnetic fields. Both, the splitting and the line-widths were interpreted in terms of the Cr^{3+}–Gd^{3+} and Gd^{3+}–Gd^{3+} exchange interactions which account for the difference between these spectra and those found in non magnetic hosts which normally give rise to very narrow emission lines [3].

$GdAlO_3$ is an antiferromagnetic insulator, its phase diagram was studied in detail by Blazey and Rohrer [4]. The phase diagram shows a Néel temperature $T_N = 3.89$ K and that the antiferromagnetic (AF) to spin flop (SF) and (SF) to saturated paramagnetic (SP) transitions happen at fields below 42 kG. These low values of the transition fields makes this system particularly suitable for the study of the Cr^{3+} fluorescence under externally applied magnetic fields.

The constant splitting (~ 20 cm⁻¹) observed above T_N was explained by the effect of the randomly fluctuating exchange field of the 8 nearest Gd^{3+} ions acting upon the $^4A_2$ Cr^{3+} ground state [1, 2].

The authors in [1] and [2] observed a decrease in $\epsilon(T)$ below T_N which they related to the onset of anti-ferromagnetic ordering of the $GdAlO_3$ lattice. The random field approach was latter extended to include the effect of Cr^{3+} on the magnetic ordering of the neighbour Gd^{3+} ions and shown to account for the behaviour of $\epsilon(T)$ below T_N, within the investigated temperature range down to 1.6 K [5].

In the present paper we study the fluorescence spectra of Cr^{3+} under magnetic fields up to 60 kG and extend the model of [5] to explain the effect of the applied field H on the splitting $\epsilon(T, H)$ of the ground state multiplet.

2. EXPERIMENTAL

A $GdAlO_3$ single crystal having a nominal Cr^{3+} concentration of 1%, was placed directly in the He⁴ bath inside a $N_d T_i$ superconducting split pair magnet from Intermagnetics General. The crystal was oriented with the [100] direction along the magnetic field H. The fluorescence was excited using a Hanovia 500 W high pressure Hg arc lamp and measured along H by a 0.5 in. Jarrell–Ash scanning monochromator followed by an EMI 9558B photomultiplier. The excitation light was
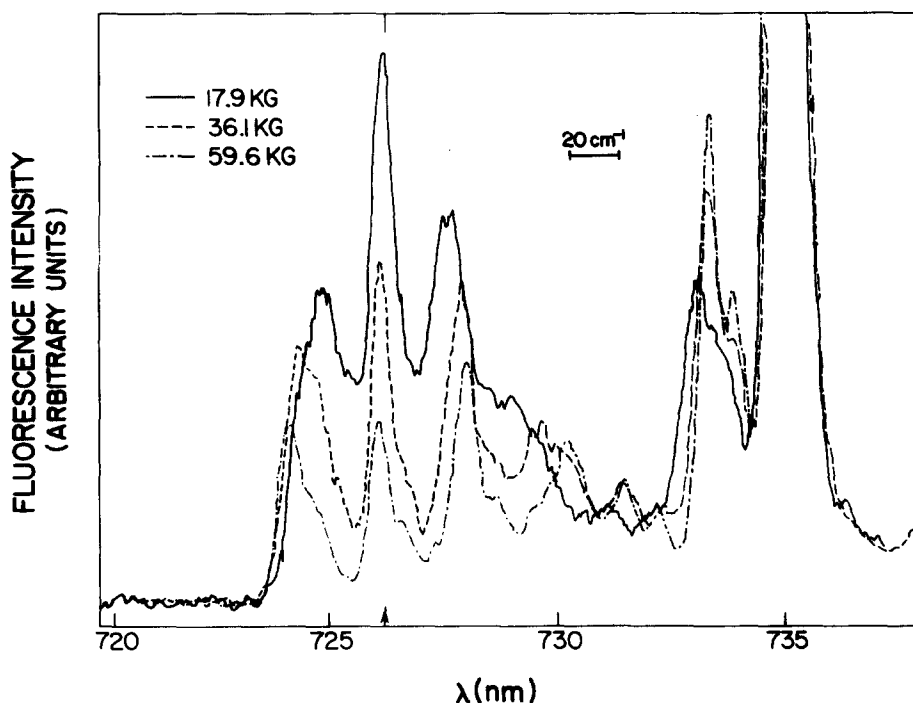
Fig. 1. Cr^{3+} fluorescence at 4.2 K at $H = 17.9$ kG (—), 36.1 kG (- - -) and 59.6 kG (---). The arrow shows the position of the $-1/2 \rightarrow -1/2$ line at zero field.

limited to the 100 Å band pass of an Oriel interference filter centered at 5500 Å. The beam was chopped at 13 Hz and the fluorescence recorded following synchronous detection. The entrance and exit slits were adjusted at 100 and 30 μm respectively and the resulting wavelength resolution was about 1 Å. The magnetic fields were measured by monitoring the magnet current to within 0.1%.

The measurements were performed at 4.2 K and the spectra obtained at 17.9, 36.1 and 59.6 kG are shown in Fig. 1.

3. RESULTS AND DISCUSSION

One of the main features of the high field spectrum as compared with the zero field one, is the increase of the splitting between the four fluorescent components which at high fields appear as four almost equally spaced lines having comparable intensities. Figure 2 shows the average value of the splittings as a function of H. The estimated linewidth at 60 kG is found to be 20% smaller than at zero field. Another interesting feature shown in Fig. 1 is the appearance of increasingly resolved shoulders on the low energy side of each of the main lines.

Finally the strong lines from Cr^{3+} pairs show also the effect of the increasing magnetic field. Their intensity grows with field as the single ion ones become smaller.

In the following we shall discuss the splitting of the main four single ion fluorescence lines, and describe a simple model which can account for the present results.

We will assume that the Cr^{3+} interacts through exchange only with its 8 nearest neighbor Gd^{3+} ions. Thus, in the presence of the external field H the interaction Hamiltonian for the Cr^{3+} ion reads

$$\mathcal{H} = -\kappa S_0 \sum_{i=1}^{8} S_i - g\mu_B S_0 \cdot H \qquad (1)$$

where S_0 is the Cr^{3+} spin operator, S_i is the spin operator of the Gd^{3+} ion at poisition i and κ is the exchange coupling constant.

Within a molecular field approximation one would simply replace S_i by its mean thermodynamical average $\langle S \rangle_{T,H}$ at temperature T in the field H. This would lead to an effective field along the direction of H, given by $H_\parallel^e = H + (8\kappa/g\mu_B)\langle S \rangle_{H,T}$, where $H_\parallel^e = 0$ for $H = 0$. However, the experimental zero field splitting indicates that S_0 is also acted upon by the instantaneous exchange field which results from the sum of the fluctuating components $\sqrt{(S^2 - \langle S \rangle_{HT}^2)}$ of the Gd^{3+} spins normal to the magnetic field [5]. Thus, assuming no correlation between the fluctuations of the 8 Gd^{3+} spins, we can approximate equation (1) by

$$\mathcal{H} \simeq -g\mu_B S_0 \cdot H^e = -(S_\parallel^0 H_\parallel^e + S_\perp^0 H_\perp^e)g\mu_B \qquad (2)$$
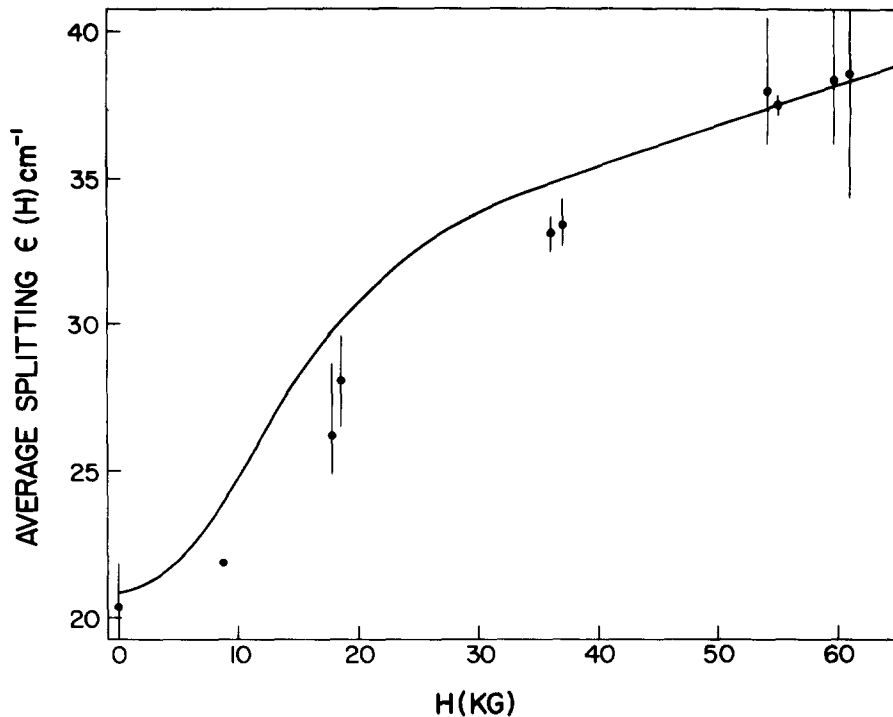
where

Fig. 2. Average splitting of the single ion Cr^{3+} fluorescence peaks vs H at 4.2 K. The error bars in the experimental points extend from the minimum to the maximum splitting at each field. The full line is the splitting calculated from equation (5).

$$H_{\parallel}^e = H + \frac{8\kappa}{g\mu_B}\langle S \rangle_{H,T} \tag{3}$$

and

$$H_{\perp}^e = \sqrt{8}\kappa\,[S^2 - \langle S \rangle_{H,T}^2]^{1/2}/g\mu_B. \tag{4}$$

Therefore the splitting is given by $-g\mu_B|H^e|$, that is

$$\epsilon(T,H) = \kappa S\left\{\left(8\sigma + \frac{g\mu_B}{\kappa S}H\right)^2 + 8(1-\sigma^2)\right\}^{1/2} \tag{5}$$

where $\sigma = \langle S \rangle_{T,H}/S$.

The full line in Fig. 2 is a plot of equation (5) for $\kappa = 2.1$ cm^{-1} [2]. The pertinent values of σ were extracted from the experimental data of [4]. The agreement is remarkably good considering the simplicity of the model and that no adjustable parameters are used. Furthermore, the experimental results give direct evidence that the Cr^{3+}–Gd^{3+} exchange interaction is ferromagnetic.

The above model can also account for the 20% observed reduction in the linewidths. In this model the linewidths originate from the fluctuating component of the exchange field $H_{\perp}^e$. Thus, the ratio of linewidths at zero and 60 kG, is given by

$$\frac{\Gamma_{60}}{\Gamma_0} \simeq \frac{\sqrt{(1-\sigma_{60}^2)}}{\sqrt{(1-\sigma_0^2)}} \simeq 0.8. \tag{6}$$

It was pointed out previously that small shoulders appear on the low energy side of each line as the magnetic field is increased. The fact that the shoulders are better resolved at high fields may result from the larger separation and reduced linewidths of the main components.

It is interesting to notice that the energy of the $-1/2 \rightarrow -1/2$ transition changes by about 3 cm^{-1} in going from 0 to 60 kG.

If equation (1) is also used to analyze the magnetic field shift of the lower excited state component, one finds from the above mentioned result, that the exchange coupling constant in the excited state is $\kappa' = 1.2$ cm^{-1}. The fact that this value of κ' differs from the 3.2 cm^{-1} extracted in [2] from the splitting of the ^2E absorption band, may indicate a change of the exchange interaction in the excited state following the relaxation of the lattice associated with the Frank–Condon effect, responsible for the relative shift of the absorption and emission bands reported in [2].

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