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EPR of Gd^{3+}-doped $Pr_xLa_{1-x}F_3$ Single Crystals

1. INTRODUCTION

Electron paramagnetic resonance (EPR) studies of Gd^{3+} - doped PrF_3 single crystals have been previously reported by Jones et al. [1], by Sharma [2] , by Misra et al. [3] and by Korczak and Subotowicz [4] . While the first three of these studies [1-3] have been mainly confined to the determination of spin Hamiltonian parameters, along with reports of EPR linewidths at certain fixed temperatures, i.e., at room, liquid-nitrogen and liquid-helium temperatures, the last publication [4] has reported a detailed study of EPR linewidths at 4.2, 77 and between 100 - 293 K. So far, no detailed study of EPR linewidths has been made at liquid-helium temperatures, i.e. below 77 K, on Gd^{3+}-doped $Pr_xLa_{1-x}F_3$ crystals.

It is interesting to study EPR of Gd^{3+}-doped $Pr_xLa_{1-x}F_3$ ($0 \leqslant x \leqslant 1$) single crystals, in which some of the paramagnetic host Pr^{3+} ions have been replaced by diamagnetic La^{3+} ions. Thus, one can study systematically the effect of paramagnetic host ions on Gd^{3+} EPR linewidths as a function of x representing the fraction of Pr^{3+} ions in the host lattice. The motivation of the studies presented here is to study, in detail, the EPR linewidths as a function of temperature over the entire range 4.2 - 293 K for various values of x, to understand the role of the paramagnetic host lattice and that of the main interactions.

2. SAMPLE PREPARATION AND CRYSTAL STRUCTURE

Mixed crystals of Gd^{3+}-doped $Pr_xLa_{1-x}F_3$ were prepared, using the Bridgman-Stockbarger method, from LaF_3 and PrF_3 of 99.9% purity, obtained from Koch-Light laboratories Ltd., as described by Korczak and Mikołajczak [5] . The crystals contained 0.1% of Gd^{3+} ions. The crystals possess hexagonal structure, space group $C^3_{6v}(P6_3cm)$ [3] .

X-band ($\approx$ 9.5 GHz) measurements were made using a VARIAN spectrometer (model V4506); the details of the experimental arrangement have been described by Misra and Korczak [6] . The crystals were placed in a TE_{102} cavity inside an ANDONIAN cryostat for low-temperature measurements.

3. SPECTRA AND LINEWIDTHS

The EPR spectra of all Gd^{3+}-doped $Pr_xLa_{1-x}F_3$ crystals are the same in appearance, i.e. the same as that shown in Fig. 1 [4] for PrF_3 host at 77 K for the orientation of the Zeeman field $\overline{B}$ being parallel to the magnetic $\hat{z}$ axis, which is parallel to the c axis of the crystals. Fig. 1 also defines the various allowed transition $M \leftrightarrow M-1$ ($M = -\frac{7}{2}, -\frac{5}{2}, \ldots, \frac{5}{2}, \frac{7}{2}$); the spin of Gd^{3+} is $S = \frac{7}{2}$. For greater details of spectra, see[3].

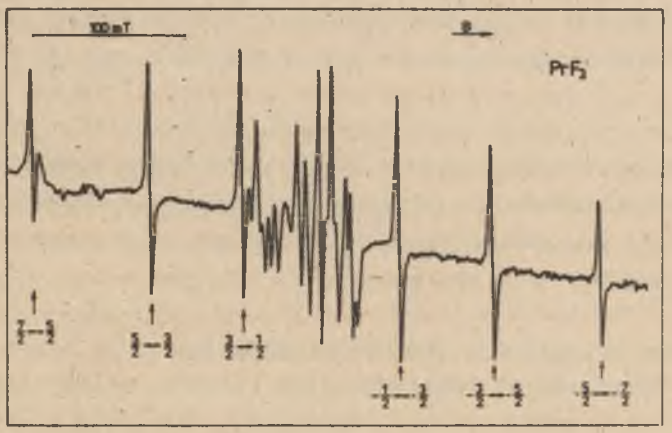

Fig. 1 EPR spectrum for Gd^{3+}-doped PrF_3 single crystal at 77 K ($\vec{B} \parallel \hat{z}$)

A. Dependence of spectra on the fraction (x) of Pr^{3+} ions.

At all temperatures the peak-to-peak first-derivative linewidths, ΔB, for the various transitions, increased for

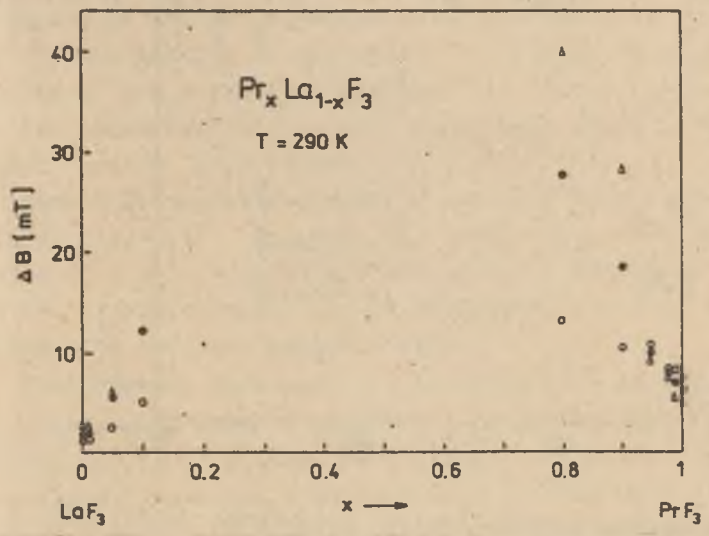

Fig. 2 The EPR linewidths ΔB versus x of the $M \longrightarrow M-1$ transitions for Gd^{3+} in $Pr_xLa_{1-x}F_3$ at T=290K (o $M=-\frac{1}{2}$, • $M=-\frac{3}{2}$, Δ $M=-\frac{5}{2}$).

increasing x from 0 to 0.1 and decreased for increasing x from 0.8 to 1.0. This is displayed in Fig. 2 for $\bar{B} \parallel \hat{z}$ at 290 K. ΔB for $0.1 < x < 0.8$ were too large to be observed. This may be due to the fact that for these intermediate values of x the Gd^{3+} ions get clustered together so that the linewidths are considerably increased. The clustering takes place because these values of x are significantly different from those of, either the pure LaF_3, or the pure PrF_3, lattices.

B. Temperature variation of EPR linewidths.

At any temperature, the linewidths for the various transitions are not significantly different for different orientation of $\bar{B}$ with respect to the crystal axes. Further, for $x \leqslant 0.8$, they hardly vary with temperature. However, for $x \geqslant 0.9$ a considerable variation of linewidths with temperature is observed, being about the same for all values of x in this range, as verified for x = 0.9, 0.95, 0.98, 0.99 and 1.0. The variation for x = 0.95 is shown in Fig. 3, which shows clearly that as

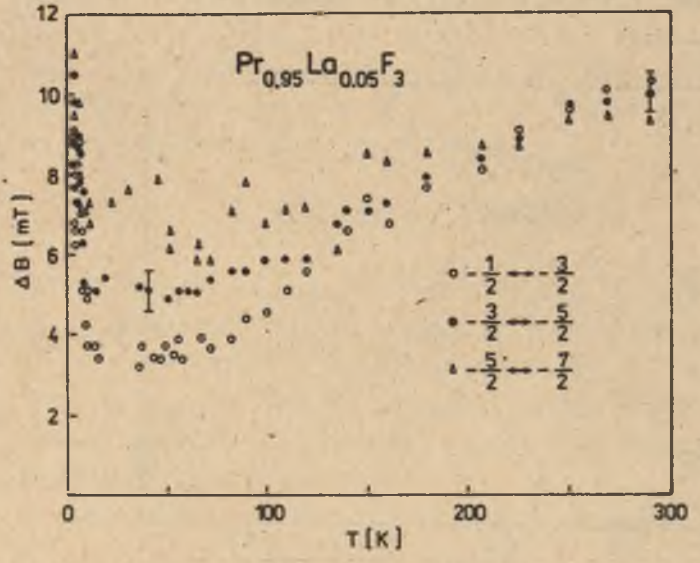

Fig. 3 The temperature variations of linewidths ΔB of Gd^{3+} in $Pr_{0.95}La_{0.05}F_3$ ($\bar{B} \parallel \hat{z}$)

the temperature is decreased from room temperature the linewidth decrease monotonically to about 30 K, at which temperature they rebound to increase sharply below 5 K to approach infinity at about 3-4 K.

Generally, in paramagnetic hosts the linewidth increases with decreasing temperature due to dipole-dipole interaction [7], e.g., in $YbCl_3.6H_2O$[8], $LiYbF_4$ [9]. However, in $Pr_xLa_{1-x}F_3$ crystals, for $x \geq 0.9$, the linewidths decrease with decreasing temperature up to about 30 K, below which they increase drastically with decreasing temperature. This behaviour is similar to that is observed in metallic hosts, e.g., $La_{3-x}V_xS_4$ ($x = 0.21$)[10] which could occur if there is a formation of clusters of Gd^{3+} that exhibit metal-like behaviour. This behaviour is explained as follow. Above about 30 K the linewidth behaves Korringa like, i.e., it is proportional to temperature (T):

$$\Delta B \sim \frac{1}{T_2} = \frac{\gamma \pi n^2(E_F)}{(\gamma+1)N^2} F_d \langle J^2 \rangle_F kT \qquad (1)$$

In eq. (1), k is Boltzmann constant, T_2 is spin-spin relaxation time, $\gamma = T_{df}/T_{dL}$ is the bottleneck factor (T_{df} = conduction- - electron-localized-spin relaxation time and T_{dL} = conduction--electron-lattice relaxation time), $\langle J^2 \rangle_F$ is the average of the square of the d-f exchange integral over the Fermi surface, $n(E_F)$ is the density of states of the conduction band at the Fermi level for one spin direction, the factor F_d is associated with the degeneracy of the host S-d levels and N is the number of host ions per unit volume.

When T is decreased to below about 30 K an extra linewidth contribution, ΔB^*, probably due to the increased dipole interaction when short-range magnetic ordering begins to set in. When the magnetic transition is approached at about 3-4 K, ΔB^* increases to infinity asymptotically.

The observed behaviour of ΔB above 30 K in $Pr_xLa_{1-x}F_3$ ($x \geq 0.9$) is not exactly linear as predicted by eq.(1). The temperature dependence is, in fact, between exponentially decreasing with increasing T and linear, as seen from Fig. 3. This kind of behaviour has been observed in singlet-ground-state monopnicttides TmX and PrX (X is one of the group-VA elements - P, As, Sb, Bi) of NaCl structure [11] , and explained to be governed by

$$\Delta B \sim kT(\chi_T - \chi_{iso}) \qquad (2)$$

In eq. (2) χ_T and χ_{iso} are the isothermal and isolated susceptibilities of the host paramagnetic ion respectively. Eq. (2) implies that the population fluctuation in the excited states of the Pr^{3+} ion contribute to the line broadening of the Gd^{3+} impurity. Thus, the observed behaviour of ΔB in $Pr_xLa_{1-x}F_3$ hosts above about 30 K can be explained to be due to the combined mechanisms, described by eqs. (1) and (2). On the other hand, below about 30 K ΔB behaviour is predominantly due to increased dipole-dipole interaction and the final arrival at the magnetic transition at about 3-4 K.

4. CONCLUDING REMARKS

The EPR linewidth behaviours for $Pr_xLa_{1-x}F_3$ ($x \geqslant 0.9$) at low temperature can be explained to be due to the exchange interactions and the behaviour of the isothermal susceptibility of the host Pr^{3+} ions. For $x \leqslant 0.8$ the dilution by the diamagnetic La^{3+} ions of the paramagnetic host lattice, constituted by Pr^{3+} ions is sufficient to suppress almost entirely the effects of the paramagnetic lattice.

The more detailed analysis of the data is in progress and will be published shortly.

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