Ref. 4 concerning observed linewidths. We believe this discrepancy to be due to multiphonon effects, which are clearly present in the data shown in Fig. 1, especially at temperatures near 300 K, as the broad, intense background upon which the coherent peaks are observed. This conjecture could most readily be checked by repeating the incoherent measurements at very small values of momentum transfer; such measurements are currently in progress.

In conclusion, we have determined the phonon dispersion relations of $PdD_{0.63}$ by coherent neutron scattering. The results are in accord with the electronic band-structure calculations[14] and in complete disagreement with calculations[5] based upon the rigid-band model. The temperature dependence of the observed neutron groups shows clear evidence of strong anharmonicity, part of which may be due to the fact that the present sample is not stoichiometric. Efforts are in progress to load the crystal with higher concentrations of deuterium.

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*Permanent mailing address.

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Spin-Dependent Energy Transfer in CaF_2:Ce, Mn

J. L. Patel,* B. C. Cavenett, J. J. Davies, and W. E. Hagston
Department of Physics, University of Hull, Hull, England

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The ground-state magnetic resonance of Mn^{2+} in CaF_2:Ce, Mn can be observed by monitoring the change in either the Mn^{2+} or Ce^{3+} luminescent intensity. This spin-dependent luminescence is evidence for an exchange-coupled energy-transfer process between the cerium sensitizer and the manganese activator.

Energy-transfer processes involving exchange interactions between magnetic ions in luminescent systems have been proposed by several workers including Leach,[1] Birgeneau,[2] and, more recently, Soules *et al.*[3] In particular, Soules *et al.* have studied Sb-to-Mn transfer in fluorophosphate phosphors using the well-established technique of investigating the concentration dependence of the quantum yield and of the emission decay curves. They compare their results with theoretical calculations for dipole-dipole, dipole-quadrupole, and exchange mechanisms by using the theories of Dexter[4] and of Inokuti and Hirayama[5] and conclude that an exchange interaction between Sb and Mn ions explains the observed results. Progress with these methods is limited by the need for order-of-magnitude calculations and the use of a large number of experimental parameters; what has been lacking is a magnetic experiment which directly demonstrates the spin dependence of the energy-transfer processes implied by an exchange interaction. We report in this Letter such an investigation in which we have studied the transfer of energy from the Ce^{3+} sensitizers to the Mn^{2+} activators in single crystals of CaF_2.[1,6] Using microwave pumping in a magnetic field we have induced changes in the spin population of the Mn^{2+} ground state and shown that both the Ce and the Mn luminescent intensities are spin dependent. The results show that the energy-transfer process involves an exchange interaction between the Ce and the Mn ions.

When an Mn^{2+} ($3d^5$) ion is substituted as an impurity in cubic symmetry, the electronic transitions between the ground state $^6A_1$ and the higher levels are spin forbidden. Consequently, the optical absorption and fluorescence spectra of this ion are weak. Ginther[6] has shown that incorporating Ce^{3+} into CaF_2:Mn^{2+} sensitizes the Mn^{2+} luminescence so that absorption in the intense uv bands of the cerium results in an efficient transfer of energy to the manganese, which decays to the ground state giving a broad emission band centered at 520 nm at 1.8 K. As well as the green Mn^{2+} emission a blue cerium emission consisting of three bands centered at 315, 340, and 375 nm is also observed and, since the strength of the 375-nm cerium emission band depends on the concentration of manganese[6] and because the weak Mn^{2+} optical absorption is also in this region,[1] the energy-transfer process is interpreted as being resonant in nature. This 375-nm emission band has been associated with Ce^{3+} ions in C_{3v} symmetry.[7] The most suitable crystals for our experiment were prepared with 5×10^{-3} g atom Ce and 5×10^{-2} g atom Mn per mole and showed a strong Mn^{2+} luminescence.[8]

The experiments consisted of detecting changes in the intensity of emitted light as paramagnetic-resonance transitions were induced. The crystals of CaF_2:Ce, Mn were placed in a silica-filled microwave cavity operating in the cylindrical TE_{012} mode at 9.4 GHz. The crystals were in contact with the liquid helium at 1.8 K and were optically excited with a Wotan HBO-200 mercury lamp. By using appropriate filters, a linear polarizer, and an S20 photomultiplier the luminescence was monitored in a direction normal to the magnetic field. The microwaves were square-wave chopped at a frequency in the range 60 to 1500 Hz with a p-i-n modulator and changes in luminescent intensity were detected by using a lock-in amplifier.

When the Mn^{2+} emission is monitored and the magnetic field is swept the luminescence intensity changes at resonance as shown in Fig. 1(a). The magnitude of the signal is independent of polarizer angle and the g value and hyperfine splitting are isotropic and correspond to those observed for the ground state of isolated Mn^{2+} ions by using conventional EPR detection.[9] With the available microwave power of approximately 200 mW the signal represents a decrease of 0.25% in the emitted intensity when the microwaves are on and shows no sign of saturation. An estimate of the expected intensity change based on the assumption that it is limited by the Boltzmann distributions of the cerium and manganese spin system suggests that the maximum expected effect will be of the order of 1–2%, assuming complete saturation of one of the manganese hyperfine components and no inhomogeneous broadening due to fluorine hyperfine interactions. In practice, the fluorine inhomogeneous broadening will reduce the maximum observable change by preventing complete saturation of the whole EPR envelope, so that the experimentally observed value of 0.25% represents a large effect.

Our experiments show that altering the spin distribution in the Mn^{2+} ground-state levels changes the Mn^{2+} luminescent intensity. This could be explained if the EPR transitions occur in the ground state of a Mn^{2+} ion which is coupled to a Ce^{3+} ion by a spin-dependent interaction. The transfer of energy from Ce^{3+} to Mn^{2+} would then be sensitive to the manganese ground-state spin and the Mn^{2+} luminescence would in turn be affected by the change in the energy-transfer rate. The coupling between the Ce and Mn spins has been investigated by an experiment in which one monitors the *cerium* emission rather than the Mn^{2+} emission. The Mn^{2+} ground-state EPR is

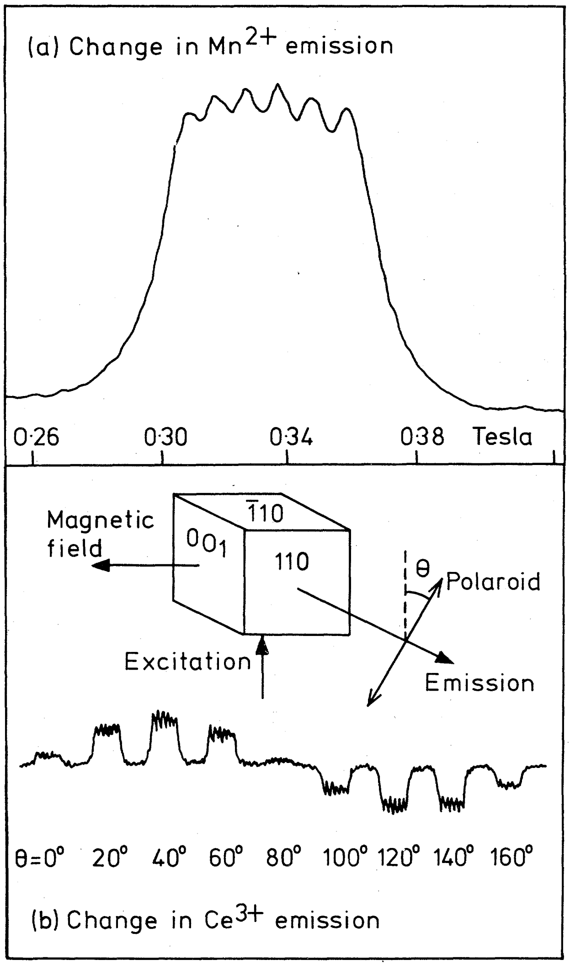

FIG. 1. (a) Mn^{2+} ground-state resonance detected by monitoring the Mn^{2+} luminescence at 1.8 K. The signal represents a decrease of 0.25% in the Mn^{2+} emission intensity. (b) Mn^{2+} ground-state resonance detected by monitoring the Ce^{3+} luminescence through a polaroid analyzer set at successive angles, θ, as specified. The inset shows the directions of observation and of the magnetic field. The maximum signal, which occurs at approximately $\theta = 45°$, corresponds to a decrease of 1.5% in the Ce^{3+} emission intensity. A corresponding increase in the intensity occurs at approximately $\theta = 135°$.

again observed [Fig. 1(b)] but in this case the signal is due to changes in the cerium luminescent intensity. As expected, it is the 375-nm emission which overlaps the Mn^{2+} absorption that is primarily responsible for the observed magnetic resonance, suggesting that the Ce^{3+} centers involved are in trigonal symmetry, but the other two emissions also show small resonance effects which will be discussed in more detail elsewhere. The sign and magnitude of the EPR-induced changes in the emitted cerium light depend on the crystal orientation and the polarization of the emitted light. For example, the signals of Fig. 1(b) were obtained with the magnetic field along [001] and the direction of observation along [110] when the analyzer was rotated through successive angles of 20°. [The inset of Fig. 1(b) shows the relative directions in detail.] Reversal of the magnetic field reverses the sign of the signals. To explain these and the polarization properties for other crystal orientations it is necessary to invoke transitions in the emitting cerium ions which contain both σ and π components of polarization. When the wave functions of Ce^{3+} in various symmetries are examined,[10] it is apparent that Ce^{3+} in cubic or tetragonal symmetry cannot lead to the observed results: Only trigonal or lower symmetry can account for the observations. Therefore, from the polarization data and the fact that the 375-nm emission gives the largest optically detected resonance, we conclude that the cerium centers involved have trigonal symmetry.

As noted above, the Mn^{2+} EPR as detected by the Mn^{2+} emission displays no detectable polarization properties, so that the Mn^{2+} ions must be situated in a field of cubic symmetry.[11] From this it follows that the interaction between the cerium and manganese ions which leads to the observed optically detected resonance cannot be of the electric multipole type. The argument is as follows. Figure 2 represents the energy levels of two Kramers doublets in the presence of a magnetic field. P_1 is the probability of a transition from state φ_a to state ψ_a induced by an electric multipole interaction E_m, with similar definitions for P_2, P_2', and P_1'. For cubic symmetry, even in the presence of a magnetic field, states

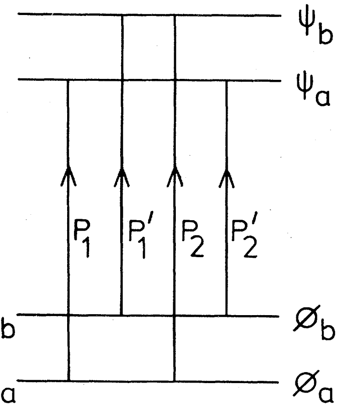

FIG. 2. Simplified energy-level scheme used to discuss the Mn^{2+} excitation. See text for discussion.

φ_a and ψ_a become, under time reversal, φ_b and ψ_b, respectively, and the electric multipole operator remains invariant. Since $P_1 \propto |\langle\varphi_a|E_m \times|\psi_a\rangle|^2$, etc., the time-reversal argument shows that $P_1 = P_1'$ and $P_2 = P_2'$. The total transition probabilities from φ_a and φ_b are therefore equal, so that the total excitation rate depends only on the sum of the populations $(N_a + N_b)$ of these states. In the present case of energy transfer from cerium to manganese, microwave-induced population changes in the Mn^{2+} ground state, equivalent in the above model to inducing transitions between φ_a and φ_b while leaving $N_a + N_b$ constant, would leave the rate of excitation of the Mn^{2+} ions unchanged and hence would not affect the Mn^{2+} or the Ce^{3+} emission intensities. Thus the observation of spin-dependent changes in the luminescence of both these ions cannot be accounted for in terms of an electric multipole interaction. We therefore conclude that a spin-exchange interaction is responsible for transfer of energy from the cerium to the manganese ions. The interaction must be relatively weak since in neither case is the observed spectrum that of a strongly coupled Ce-Mn pair. However, the width of the hyperfine structure in the optically detected Mn^{2+} ground-state resonance is greater than that observed in the conventionally detected spectrum where each hyperfine component is well resolved. Since in the optical case only those Mn^{2+} ions interacting with Ce^{3+} ions are detected, it is concluded that the extra broadening is due to the Ce-Mn interaction. This broadening gives $J_{ex} \sim 0.01$ cm^{-1} for the exchange interaction which is comparable to $J_{ex} = 0.03$ cm^{-1} obtained by Soules *et al.*[3] for Sb-to-Mn exchange.

Dexter[4] has discussed energy-transfer processes involving spin exchange between sensitizer and activator ions and finds that the selection rules allow spin-flip transitions. In our case, this makes possible the excitation of the Mn^{2+} activator which was previously forbidden by the spin selection rules for electric dipole transitions. We note too that since our experimental system is similar to that used by Berggren, Imbusch, and Scott[12] for Cr^{3+}-to-Cr^{3+} pair energy transfer in Al_2O_3 our interpretation could well explain their results in terms of the exchange interaction proposed in a later paper by Birgeneau.[2] If so, it should be possible in Al_2O_3:0.5% Cr to observe the pair ground-state magnetic resonance by monitoring the single-ion emission in analogy with our own results. (In CaF_2:Ce, Mn we exclude energy transfer to Mn^{2+} pairs since if Mn-Mn interactions were important in the energy-transfer process the optically detected EPR spectrum would be that characteristic of the ground state of exchange-coupled Mn^{2+} pairs.[13])

The experiments described above directly demonstrated for the first time a case in which exchange interactions are responsible for the energy transfer between sensitizer and activator ions. The results confirm that the action of the cerium sensitizer is to remove the spin-forbidden nature of the manganese transitions and this is expected to be a valid description of sensitizer action for Mn^{2+} in technologically important materials such as the halophosphate phosphors.[3]

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*Present address: Department of Physics, University of Lancaster, Lancaster, England.

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