Spin-flip Raman scattering in the semimagnetic semiconductor CdS:Mn

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A giant spectral shift has been detected for Raman scattering involving spin flip of a donor-impurity electron in CdS:Mn crystals in a magnetic field. There is a strong correlation between the spin of the donor electron and the magnetic moments of the manganese atoms, which can be seen in the nonzero spectral separation of the Stokes and anti-Stokes components of the spin-flip Raman scattering at $H = 0$. This separation amounts to 0.15–0.20 of the maximum separation, observed in saturating fields, and it decreases with increasing temperature.

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The exchange interaction of band electrons with localized *d*-electrons of manganese in manganese-doped $A^{II}B^{VI}$ compounds causes a giant splitting of the spin states in the valence and conduction bands, as can be seen in several magnetooptic effects.[1,2] A promising method for studying such compounds is spin-flip Raman scattering by free and quasibound carriers, since this method yields direct information on the magnitude of the paramagnetic splittings.[3,4] In the case of spin-flip Raman scattering by bound electrons of a shallow donor impurity, correlations between the spin state of the donor and the spin states of the magnetic impurity subsystem may be important. Correlations of this sort should directly affect the shift of the Raman-scattering line.

The CdS:Mn crystals studied in the present experiments were grown from the melt by the Bridgman method. The manganese concentration was $n_{Mn} = 10^{20}$ cm^{-3}. Samples with dimensions of $5 \times 5 \times 1$ mm were cut with the C_6 hexagonal axis running perpendicular to the large face. The samples were mechanically and chemically polished and then immersed in liquid helium inside a superconducting solenoid. The experiments were carried in the Voigt geometry in fields up to 50 kOe. The standard $x(yx)z$ arrangement, with right-angle scattering, was used (see the inset in Fig. 1). The spectral instrument was a DFS-24 double monochromator with a dispersion of

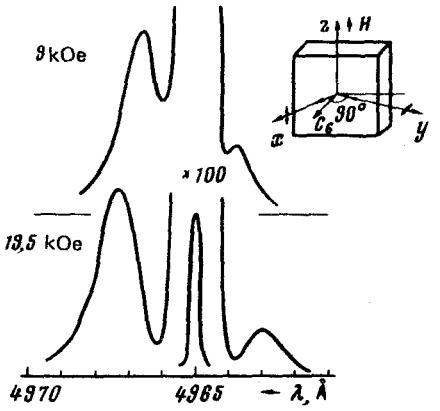

FIG. 1. Spectrum of spin-flip Raman scattering in a CdS:Mn crystal with $n_{Mn} = 10^{20}$ cm^{-3}. The scattering was excited by the line $\lambda = 4965$ Å at a power $P = 400$ mW. The inset shows the experimental geometry.

4.5 Å/mm. A resolution no worse than 0.5 cm^{-1} was achieved in operation with slits 20 × 20 μm in size. The light source was a cw Ar^+ laser with a power ~2 W. The CdS crystals used in these experiments had a donor impurity concentration ~10^{16} cm^{-3}, according to estimates based on Hall measurements at room temperature.

In manganese-doped $A^{II}B^{VI}$ semiconducting compounds, the exchange interaction of conduction electrons with the localized magnetic moments of manganese can be described by the Heisenberg exchange Hamiltonian[2]

$$H_{ex} = \sum_{\mathbf{R}_i} J^e(\mathbf{r} - \mathbf{R}_i)\mathbf{S}_i\vec{\sigma}, \tag{1}$$

where $\mathbf{S}_i$ is the spin of the manganese atom at lattice site $\mathbf{R}_i$, $\vec{\sigma}$ is the electron spin, and J^e is the exchange-interaction constant. Interaction (1) leads to a strong exchange field, which substantially changes the energies of the electronic states with different spins:

$$E_{\pm 1/2} = \mu_B g H \sigma_z + G^e \sigma_z. \tag{2}$$

Here G^e is the effective field associated with the exchange interaction, given by

$$G^e = J^e \langle S^z_{Mn} \rangle n_{Mn} = J^e n_{Mn} B_{5/2}(\mu_B gH/kT), \tag{3}$$

where $B_{5/2}(t)$ is the Brillouin function for a spin $S = 5/2$. The effective field depends on the concentration of the magnetic-impurity atoms, n_{Mn}, and on the average projection of the magnetic moment localized at these atoms, $\langle S^z_{Mn} \rangle$. The effect of the exchange field G^e may be considerably greater than that of the external magnetic field H, so that the spin splitting will have a characteristic dependence on the temperature and the magnetic field in addition to having an anomalously high value.

Spin-flip Raman scattering in CdS:Mn crystals can be observed at several laser lines: $\lambda = 4880, 4965, 4017$, and 5145 Å, which correspond to a spectral region near the fundamental absorption edge of CdS. The spin-flip Raman-scattering line in the CdS:Mn crystal is much broader than that in pure CdS (8 cm^{-1} and 0.5 cm^{-1}, respectively), apparently because of a spatial inhomogeneity of the manganese distribu-

tion in the crystal (Fig. 1). The magnitude of the shift varies in a nonlinear way with the magnetic field, reaching values ~ 30 cm^{-1} in saturating fields. Although the sample was in superfluid helium at $T = 1.8$ K, the donor spin temperature estimated from the intensity ratio of the Stokes and anti-Stokes components was considerably higher ($T_s = 8$ K for the spectra in Fig. 1). With increasing temperature the average magnetic moment $\langle S^z_{Mn} \rangle$ decreases [in accordance with (3)], so that the spectral shift of the spin-flip Raman-scattering line, $\Delta\nu(H)$, also turns out to be sensitive to a warming of the crystal. With increasing T_s, the $\Delta\nu(H)$ dependence becomes less steep, and saturation eventually sets in at strong magnetic fields (curves 1–4 in Fig. 2). This behavior is particularly noticeable in measurements with the shortest laser line ($\lambda = 4880$ Å), which falls in a region of strong absorption (curve 4 in Fig. 2), in which saturation cannot be reached at the magnetic fields used. As the laser power is reduced, the line shift increases, while the intensity ratio of the Stokes and anti-Stokes components falls off; at low excitation levels, only the Stokes component is found in the Raman-scattering spectrum. Comparison with the spin-flip Raman scattering in pure CdS (curve 5 in Fig. 2) indicates that at a manganese concentration $\sim 10^{20}$ cm^{-3} the effective field G^e is much more influential than the direct effect of the magnetic field, and it becomes predominant.

On the whole, the behavior of the spin-flip Raman scattering in CdS:Mn crystals can be described satisfactorily in the approximation of an effective molecular field, but there is one result which does not fit in this picture. A careful study of the line shift $\Delta\nu(H)$ of the spin-flip Raman scattering in weak fields (in which this shift can accurately be approximated as linear) shows (Fig. 3) that the shift in the limit $H \to 0$, $\Delta\nu(0)$, remains nonzero. In particularly favorable cases it is possible to resolve the Stokes and anti-Stokes components of the Raman-scattering line at $H = 0$. A similar behavior has been observed[4] in $Cd_{1-x}Mn_xSe$. With increasing spin temperature of the magnetic-impurity subsystem, the residual shift $\Delta\nu(0)$ decreases, but even at extremely high temperatures it amounts to 7–10% of the shift in a saturating magnetic field (see the inset in Fig. 3). This behavior implies a strong correlation between the spin of the donor electron and the magnetic moments of those manganese atoms which lie within the wave function of the donor.

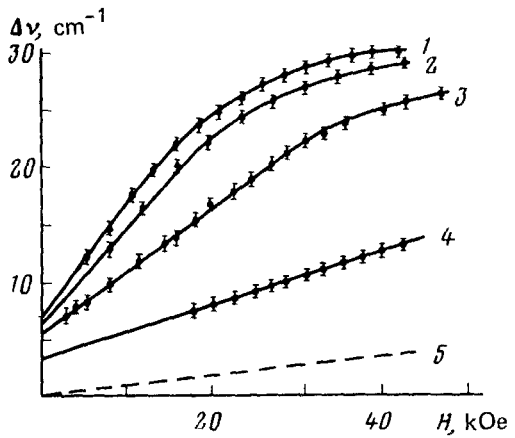

FIG. 2. The shift $\Delta\nu(H)$ of the Stokes component of spin-flip Raman scattering in CdS:Mn vs the magnetic field for various laser lines. 1–$\lambda = 5145$ Å; 2–$\lambda = 5017$ Å; 3–$\lambda = 4965$ Å; 4–$\lambda = 4880$ Å, $P = 100$ mW. Curve 5–Spin-flip Raman scattering in CdS without a manganese impurity.

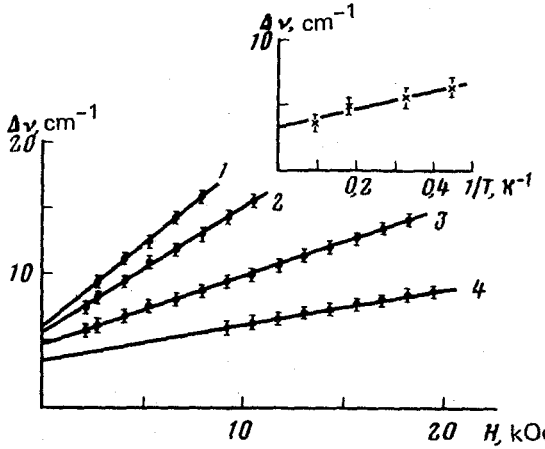

FIG. 3.
The shift $\Delta\nu(H)$ of the spin-flip Raman-scattering line in CdS:Mn in weak magnetic fields. 1–λ = 5145 Å, P = 200 mW; 2–λ = 5017 Å, P = 200 mW; 3–λ = 4965 Å, P = 100 mW; 4–λ = 4965 Å, P = 400 mW. The inset is a plot of the residual shift $\Delta\nu(0)$ against the reciprocal temperature of the magnetic-impurity subsystem. The temperature was determined from the slopes of curves 1–4.

Let us examine this nonzero separation of the Stokes and anti-Stokes components at $H = 0$. In the case of a localized donor state, an electron interacts effectively with only a few tens of manganese atoms. The spin relaxation of manganese in the CdS lattice is very slow ($\tau_s \sim 10^{-2}$ s; Ref. 5). Under these conditions the electron spin manages to adiabatically follow the resultant spin of the manganese atoms in the orbit of the donor and to assume the energetically most favorable configuration. On the other hand, the magnitude of the splitting between different-spin states is determined by the absolute value of the resultant spin, $|\mathbf{S}_0|$, of the manganese atoms: $\mathbf{S}_0 = \Sigma\mathbf{S}_i$. The shape of the spin-flip Raman-scattering line at $H = 0$ then reflects a statistical distribution of the magnetic moments localized in the donor volume with respect to the modulus of the resultant spin, $|\mathbf{S}_0|$. The exchange interaction in (1) leads to an effective interaction of a ferromagnetic type between different manganese atoms, with the result that the peak of this distribution is shifted toward higher values of the total spin S_0; the effect can be seen in the spin-flip Raman-scattering spectrum as an increase in the initial spectral shift $\Delta\nu(0)$ with decreasing temperature.

Magnetic order does not arise in the donor–(magnetic impurity) system with which we are concerned here. The spectral shift of the spin-flip Raman-scattering line at $H = 0$ tells us only that there are strong correlations between the spin of the donor electron and the spin state of the manganese atoms which lie within the orbit of this electron. However, if the donor concentration is raised above the Mott transition, we can produce a system of delocalized electrons, which form an impurity band. Magnetic ordering can occur in such a system,[6] and spin-flip Raman scattering may prove an effective tool for studying these phenomena.

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