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Raman spectroscopy of $Cd_{1-x}Cr_xS$

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Spin-flip Raman scattering and magnetization measurements are reported for the diluted magnetic semiconductor $Cd_{0.998}Cr_{0.002}S$. The data at $T = 1.9$ K and in magnetic fields $B \leqslant 10$ T give the s-d exchange constant $N_0\alpha = 0.22$ eV.

I. INTRODUCTION

Diluted magnetic semiconductors[1] (DMS) with Cr as the magnetic ion attracted considerable attention recently due to the unique character of the p-d exchange interaction between p-like holes in the valence band and localized d-type electrons in the Cr^{2+} ion. Unlike other DMS with Mn, Co, or Fe, for which the p-d exchange is antiferromagnetic (i.e., preferred orientation of the valence-band electron spin and the spin of the magnetic ion is antiparallel), for Cr DMS this interaction is ferromagnetic.[2–5] This conclusion was based on the magnetic-field-induced exciton splitting in $Zn_{1-x}Cr_xS$,[3] $Zn_{1-x}Cr_xSe$,[2] and $Zn_{1-x}Cr_xTe$.[4]

In typical exciton spectroscopy the exciton line splits into four components when a magnetic field is applied. The energy separations between these four components are used to determine the exchange constants $N_0\alpha$ for the conduction band and $N_0\beta$ for the valence band.[6] In the case of Cr DMS, however, the available Cr concentration x was rather low ($x < 0.01$), which resulted in small exciton splittings.[7] Consequently, not all the exciton lines could be resolved and only the difference $N_0\alpha - N_0\beta$ could be evaluated. This $N_0\alpha - N_0\beta$ was found to be negative for all Cr DMS studied so far (contrary, $N_0\alpha - N_0\beta > 0$ for all non-Cr DMS[1]). Since the driving mechanism for conduction-electron exchange is a potential (direct) exchange, it is reasonable to expect a positive $N_0\alpha$, which is indeed the case for all Mn, Co, and Fe DMS.[1] Moreover, the magnitude of $N_0\alpha$ is largely independent of the magnetic ion and host lattice, $N_0\alpha = 0.2$–0.25 eV.[1,8–12] It was therefore speculated that $N_0\alpha$ in Cr DMS is essentially the same as for other DMS. Thus, assuming $N_0\alpha = 0.2$ eV, the (positive) value of $N_0\beta$ was determined for several Cr DMS.[2–4] Although the assumption concerning $N_0\alpha$ is reasonable, it was not supported by any experimental data on Cr DMS. The sign and magnitude of $N_0\alpha$ can be obtained from a spin-flip Raman experiment,[8–13] but for all the Zn-based Cr DMS no Raman scattering was observed until now. In this paper we report the results of Raman scattering on recently grown $Cd_{1-x}Cr_xS$. These data give the value of $N_0\alpha$.

II. EXPERIMENT

The single crystals of $Cd_{1-x}Cr_xS$ were grown by the modified high-pressure Bridgman method. High-purity CdS and Cr powders were used as the starting ingredients. Single-phase hexagonal crystals (i.e., without chromium sulfide precipitations) were obtained only for rather low Cr concentration ($x < 0.005$). Such a low Cr content could not be determined precisely using conventional methods (e.g., atomic absorption or wet chemical analysis). Instead, x was estimated from the measured magnetization of the samples and the calculated magnetic moment of the Cr ion.[14,15] The details of this method will be discussed below. The magnetization was also used to check the homogeneity of the Cr concentration, which turned out to be better than 10% across the sample. No ferromagnetic precipitates were observed in the magnetization. The present study was on a single-phase crystal of $x \approx 0.002$. The sample was cleaved just before the experiment. No other surface preparation was made.

Raman scattering was measured at 1.9 K in the backscattering geometry. We used an argon laser for below-the-band-gap excitation (2.409 eV and 2.539 eV). Laser powers of typically 5 mW gave intensities of 2 W/cm^2. The exciting beam and the scattered light were linearly polarized (incident perpendicular to the scattered). The measurements were performed in the Voigt geometry (light propagation vector perpendicular to the magnetic field B). The magnetic field was parallel to the hexagonal crystal axis. Raman spectra were taken using a double monochromator equipped with a photon counting system. Raman shifts larger than 0.5 meV could be observed. Magnetic fields up to 10 T were produced by a split-coil, radial-access Bitter magnet.

The magnetization was measured at 1.9 K and $B < 5.5$ T using a superconducting quantum interference device (SQUID) magnetometer. The magnetic-field orientation was

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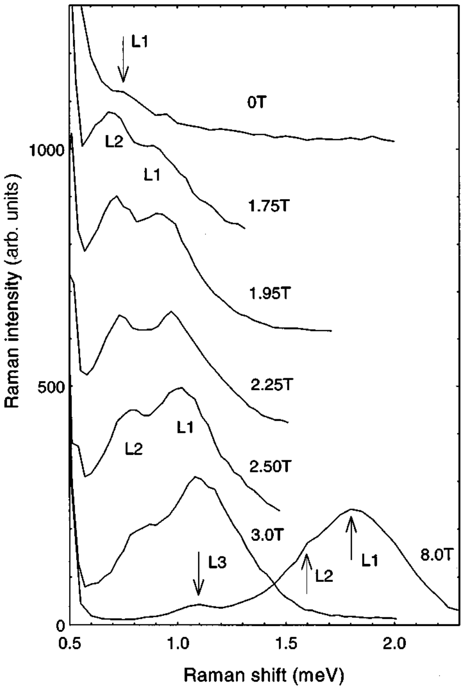

FIG. 1. Raman spectra for $Cd_{0.998}Cr_{0.002}S$, measured at $T=1.9$ K in the Voigt configuration. The magnetic field B is parallel to the crystal hexagonal axis. All the spectra except for $B=3.0$ T and 8.0 T (for which the intensity, in counts/sec, is meaningful) are shifted upward for clarity.

the same as in the optical experiment.

III. RESULTS AND DISCUSSION

At zero magnetic field a weak line, with a Raman shift of 0.75 meV, is observed (Fig. 1, line $L1$). We attribute this line to the internal Cr^{2+} transition from the ground level to the first excited level. We recall that the Cr^{2+} lowest energy levels in II-VI compounds are well described by an effective spin Hamiltonian for spin $S=2$.[16] At $B=0$ the dominant term in this Hamiltonian is the axial anisotropy term DS_z^2, which results in a doublet (or semidoublet[14]) ground level, followed by another doublet at energy $3D$, and a singlet at energy $4D$ above the ground level.[16] For CdS the parameter D was estimated from electron paramagnetic resonance data: $D=-0.224$ meV.[16] The predicted energy of the excited doublet ($3D=0.67$ meV) is in reasonable agreement with the Raman shift of line $L1$ at $B=0$, which supports the identification of this line as an internal Cr^{2+} transition. From the present data for the Raman shift, $D=-0.25\pm0.02$ meV.

In fields somewhat above 1 T another Raman line (line $L2$ in Fig. 1), which is stronger than line $L1$, is observed. (Below 1 T line $L2$ is masked by the scattered laser light.) Although the energy of line $L2$ varies more strongly with B than that of line $L1$, the lines do not cross. Instead they exhibit a typical anticrossing behavior near 2 T, with intensity transfer from $L2$ to $L1$ (Fig. 1). At higher magnetic fields line $L1$ dominates the Raman spectrum (Fig. 1). In addition to line $L2$, another line ($L3$) is also visible in high fields. This weak line is believed to originate from intra-Cr transitions. The magnetic-field variation of the Raman shift of the observed lines is displayed in Fig. 2.

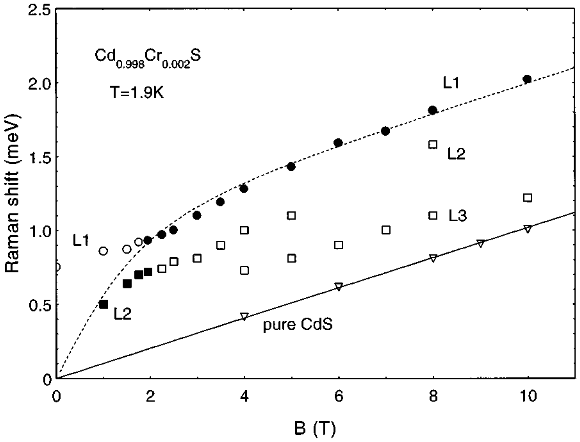

FIG. 2. Raman shift as a function of magnetic field B. The full points represent strong line intensity, whereas the empty points show weak lines. The triangles show the measured Raman shift for pure CdS. The solid line corresponds to $g^*=1.76$. The broken line shows the SFRS energy shift calculated from Eq. (1) with $N_0\alpha=0.22$ eV and $g^*=1.76$.

The strong line (line $L2$ at low fields, line $L1$ at high fields) is identified as spin-flip Raman scattering (SFRS) from donor electrons. Such a scattering was observed earlier for Mn, Fe, and Co DMS.[8–13] In the spin-flip Raman process, scattering occurs via bound magnetic polaron (BMP) states, i.e., donor electrons coupled by s-d exchange to the magnetic ion states.[17] In the case of permanent magnetic moment ions (Mn^{2+} and Co^{2+}), the BMP leads to a zero-field splitting of the donor electron ground level, which manifests itself as a zero-field Raman shift.[17] On the other hand, for induced-magnetic-moment ions (Fe^{2+}) there is no splitting in the absence of magnetic field. Instead, a pronounced interaction between the BMP and the low energy levels of the magnetic ion results in anticrossing effects.[18] The Cr-based DMS exhibit both effects, since the Cr^{2+} ion has a permanent magnetic moment (multiplet ground level), but the excited states are close enough to interact with the BMP levels.

The problem of the BMP in Cr DMS has not been treated theoretically thus far, and will be studied separately. The data interpretation in the present paper is based on earlier works on BMP's in Mn and Fe DMS. In particular, detailed calculations of the BMP in Fe DMS show that outside the anticrossing region the energy of the SFRS line can be approximated by the s-d exchange splitting for conduction-band electrons:[19,18]

$$E_{\mathrm{SFRS}}=E_{s-d}+g^*\mu_B B=N_0\alpha x(-\langle S\rangle)+g^*\mu_B B, \qquad (1)$$

where $N_0\alpha$ is the s-d exchange constant defined in a conventional way,[6] $\langle S\rangle$ is the average spin of the Cr ion along the magnetic-field direction, g^* is the conduction-band g factor for pure CdS, and μ_B is the Bohr magneton. Equation (1) is an approximation since it neglects the term resulting from the difference between the local magnetization within the donor orbit and the average magnetization in the bulk. (This difference contains two contributions: one from the BMP, and another from magnetic-moment thermal fluctuations.[19]) The neglected term roughly scales with the magnetic ions concentration x and with the deriva-

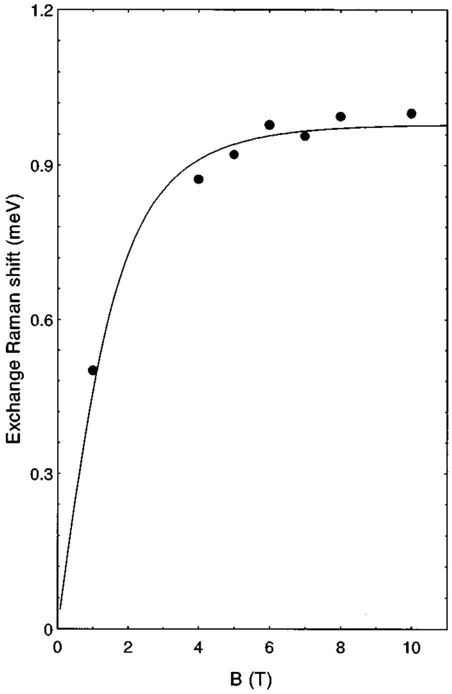

FIG. 3. The exchange-induced part, E_{s-d}, of the spin-flip Raman shift as a function of B at 1.9 K. These results were obtained from the data in Fig. 2, assuming Eq. (1). The data in the anticrossing region are not shown. The solid line represents the fit to Eq. (4) with $N_0\alpha = 0.22$ eV.

tive $\partial M/\partial B$. Based on an analogy with the BMP in $Cd_{0.977}Mn_{0.023}S$, for which the considered correction of the Raman shift was about 1 meV at $B=0$,[12] one expects the correction in the present material to be about 0.1 meV at $B=0$. This correction should decrease rapidly with increasing magnetic field, due to the decrease of $\partial M/\partial B$ as $\langle S\rangle$ approaches saturation.

The measured contribution of pure CdS to E_{SFRS} is shown in Fig. 2. From the linear behavior of the Raman shift versus magnetic field the effective g factor is $|g^*| = 1.76$, in good agreement with the earlier data[20] ($g^* = +1.78$). Figure 2 shows that at 10 T the energy shift E_{SFRS} for SFRS in the sample with Cr concentration $x \approx 0.002$ is nearly double the energy shift in pure CdS (Fig. 2). This means that both the Zeeman splitting and the splitting due to the s-d exchange are of the same sign, i.e., $N_0\alpha$ is positive. In Fig. 3 we show the s-d exchange contribution to the Raman shift, $E_{s-d} = N_0\alpha x\langle S\rangle$, obtained as a difference between the SFRS energy shifts for the samples with and without Cr.

The product $x\langle S\rangle$ can be obtained experimentally from the macroscopic magnetization M per unit mass. Assuming that all Cr ions, for the present low Cr concentration, can be regarded as isolated (noninteracting with other Cr ions), one obtains

$$M = -\frac{\mu_B x}{m}\langle L+2S\rangle = \frac{\mu_B x}{m}\frac{(-\langle S\rangle)}{k}, \tag{2}$$

where $k = \langle S\rangle/\langle L+2S\rangle$ and m is the average mass of the $Cd_{1-x}Cr_xS$ molecule. The parameter $k = 1/2$ for spin-only magnetic moment, but $k > 1/2$ for Cr^{2+} ion due to the contribution of the orbital angular momentum to the magnetic moment.[2,3] The parameter k was found to be nearly independent of the host lattice. Since a calculation of k for Cr in CdS is not presently available, the value for Cr in ZnS ($k = 0.53$) was adopted for the present case.

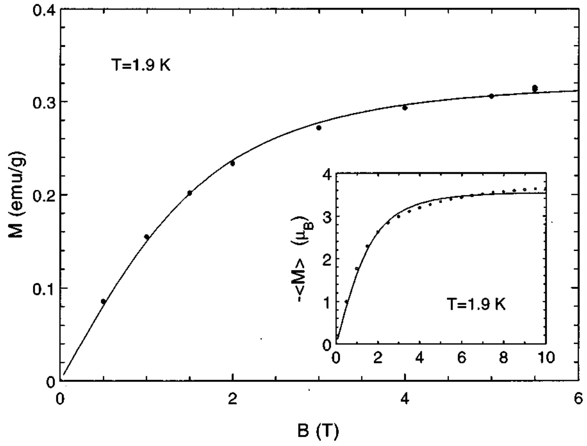

FIG. 4. Magnetization M as a function of magnetic field B for $Cd_{0.998}Cr_{0.002}S$ at $T = 1.9$ K and with B parallel to the hexagonal axis. The solid line represents Eq. (3) with $a = 0.160$ emu/g and $b = 0.64$ K. The inset shows the calculated average magnetic moment of a Cr^{2+} ion in cubic ZnS for $B\|[111]$ (Ref. 14). The solid line in the inset represents Eq. (3) with $a = 1.77\mu_B$ and $b = 0.64$ K.

To determine the average spin $\langle S\rangle$ from Eq. (2), the magnetization of the very same sample was measured at 1.9 K. The direction of B was the same as in the Raman measurements. The data, corrected for diamagnetic susceptibility of pure CdS ($\chi_d = -3.7\times10^{-7}$ emu/g)[21] are shown in Fig. 4. The observed field variation is typical for Cr-based DMS.[14]

It is useful to represent the magnetization curve in Fig. 4 by an analytical expression. Early calculations of $\langle M\rangle$ and $\langle S\rangle$ for a Cr^{2+} ion in other II-VI host materials[14] show that both are well represented by an effective Brillouin function

$$\langle M\rangle, \langle S\rangle \approx aS\mathscr{L}_S(B, T+b), \tag{3}$$

where $\mathscr{L}_S(\ )$ is the Brillouin function for $S=2$, and a and b are phenomenological parameters. An example of a fit of a calculated magnetization curve to an effective Brillouin function, in this case for Cr in ZnS,[14] is shown in the inset of Fig. 4. The fit, represented by the solid line in the inset, gives the parameters $a = 1.77\mu_B$ and $b = 0.64$ K. (These a and b are merely phenomenological parameters, which also depend somewhat on the field range in the fit. If Cr were an ideal spin the parameters would have been $a = 1.93\mu_B$ and $b = 0$ K.) A fit of the measured magnetization curve for the present sample was made holding the parameter b fixed at 0.64 K. The fit, shown as a solid line in the main part of Fig. 4, gave $a = 0.160$ emu/g. Using this value and Eq. (2), the Cr concentration of the present sample was estimated as $x = 0.0024$.

Usually the exchange parameter $N_0\alpha$ is derived from the proportionality between the exchange contribution to the Raman shift, E_{s-d}, and the magnetization M [Eqs. (1) and (2)].[8–13] However, in the present case the SFRS energy shift should be described by Eq. (1) only outside the anticrossing region. For this reason $N_0\alpha$ was obtained by restricting the fit of the Raman-shift data to fields $B \geqslant 4$ T. The fit was to the function

$$E_{s-d} = \left(N_0 \alpha \frac{km}{\mu_B} \right) M. \tag{4}$$

The fit to Eq. (4) requires knowing the values of M at the fields where the Raman data were taken. Since the magnetization was measured only at $B < 5.5$ T, it was assumed that the effective Brillouin function obtained from a fit of M vs B below 5.5 T described the magnetization in the entire field range, up to 10 T. This function was then used to generate the values of M for the fit to Eq. (4). The fit to Eq. (4), based on Raman data for $B \geqslant 4$ T only,[22] gave $N_0\alpha = (0.22 \pm 0.02)$ eV. The values of E_{s-d} generated from the fit to Eq. (4) are represented by the solid line in Fig. 3. The value $N_0\alpha = 0.22$ eV for $Cd_{1-x}Cr_xS$ is very close to those for $Cd_{1-y}Mn_yS$ (0.22 eV),[8] $Cd_{1-z}Co_zS$ (0.18 eV),[11] and CdFeS (0.20 eV) (Ref. 10). Apparently for CdS-based DMS the s-d exchange interaction is nearly independent of the magnetic ion. Although this conclusion is probably true for other host lattices, it remains to be verified experimentally.

Previously, the p-d exchange value for several Cr DMS[2–4] were determined after making an assumption concerning $N_0\alpha$. The present work gives experimental justification of this assumption.

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[22] The derivative $\partial M/\partial B$ of the experimental magnetization decreases by more than an order of magnitude when B changes from zero to 4 T. Therefore, the BMP correction to Eq. (1) should be smaller than 0.01 meV for the magnetic-field range used for the fit, and can be neglected.