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MAGNETIC ANISOTROPY OF V^{++} IN CdS*

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The magnetization measurements at magnetic field up to 6 T obtained from newly grown hexagonal $Cd_{1-x}V_xS$ ($x \approx 0.0004$) are presented. The strong anisotropy of magnetization is observed at low temperatures ($1.6 < T < 20$ K). The data are well described by the crystal field model calculations taking into account static trigonal Jahn–Teller distortion and spin–orbit coupling.

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The strong s,p–d exchange interaction is one of the most characteristic features of diluted magnetic semiconductors (DMS) [1]. DMS based on transition metal (TM) ions with less than half filled d shell are particularly interesting for a possible ferromagnetic p–d exchange. So far, among all the studied II–VI systems, only the chromium based crystals revealed ferromagnetic p–d exchange [2] (Cr^{++} electronic configuration is d^4). The recent growth of CdS heavily doped with vanadium calls for examining the situation in DMS with V^{++} ions (electronic configuration is d^3). Since the information about spin alignment is indispensable for understanding exchange interaction we thought it is worthwhile to study magnetization of this new material.

The ground term of the V^{++} (d^3) ion is ^4F, which means that the total spin momentum of the ion is $S = 3/2$ and total orbital momentum is $L = 3$. The cubic crystal field splits this 7-fold orbitally degenerate term into two orbital triplets: $^4T_1$ and $^4T_2$ and an orbital singlet $^4A_2$ (see Fig. 1a). The ground orbital triplet $^4T_1$ undergoes static Jahn–Teller distortion of trigonal symmetry [3,4] yielding further splittings. Thus in the cubic symmetry there exist four equivalent possible distortion axes corresponding to one of the (111) crystal axes and four different kinds of centers are expected. In wurtzite structure, the hexagonal crystal field may be regarded as a trigonally distorted (along c axis) cubic field. In this case one of the Jahn–Teller distortion axes coincide with the hexagonal stress direction. This way the degeneracy of the four V center types is lifted. If the energy of the center

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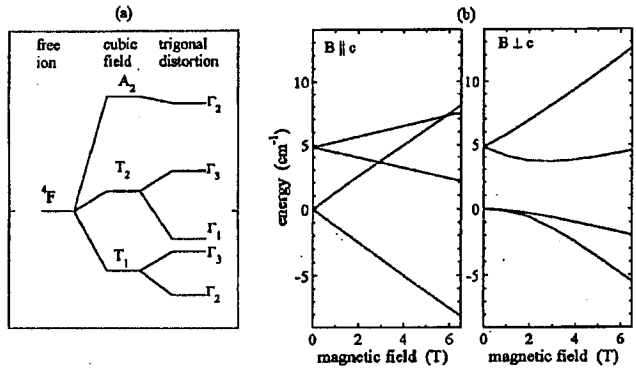

Fig. 1. (a) The schematic diagram of energy levels of V^{++} ion in cubic crystal field with trigonal distortion. (b) The calculated magnetic field dependence of the four lowest energy levels (Γ_2 term) of V^{++} ion for magnetic field parallel and perpendicular to the trigonal distortion.

distorted along c axis is lower than the energy of the other ones, this center will be favored against the other ones and in the extreme case only this one type of centers will be present in the crystal. Otherwise the three types of centers (each distorted at the angle of 70.5° to the hexagonal stress) will be present. In the first case the anisotropy of a single ion may lead to the huge anisotropy in the macroscopic magnetization. We recall that the presence of differently distorted types of centers have been observed for Cr^{++} for which tetragonal Jahn–Teller distortion occurs [5]. However, in this case the hexagonal stress is at the same angle to all of the Jahn–Teller distortion axes and no centers are favored. The averaging over three types of centers reduces the observed macroscopic anisotropy [6].

In this communication we present results of magnetization measurements obtained from the hexagonal $Cd_{1-x}V_xS$ crystals, grown by the modified (high pressure) Bridgman technique. Single phase crystals were obtained only for rather low vanadium concentration (below 0.1 mol %). Magnetization was measured at low temperatures (1.6–30 K) as a function of magnetic field (up to 6 T). In Fig. 2 the experimental data at magnetic field aligned either parallel or perpendicular to the hexagonal c axis are displayed (the diamagnetic contribution of the host lattice is subtracted). At 2 K magnetization is strongly anisotropic. For the magnetic field parallel to the c axis the magnetization saturates at about 3 T, while for B perpendicular to the c axis it is almost linear up to 6 T. As a result, more than 50% of anisotropy is observed at 2 T. Anisotropy decreases with increasing temperature and at 20 K is less than 20%.

To describe the data we performed numerical calculations within a simple crystal field model with the Hamiltonian as follows:

$$\mathcal{H} = \mathcal{H}_{\rm cf} + \mathcal{H}_{\rm tr} + \mathcal{H}_{\rm so} + \mathcal{H}_{\rm B}, \tag{1}$$

where the $\mathcal{H}_{\rm cf}$ describes the cubic crystal field, $\mathcal{H}_{\rm so}$ is the spin–orbit coupling, $\mathcal{H}_{\rm B}$ is magnetic field Zeeman term and $\mathcal{H}_{\rm tr} = B_2^0 O_2^0 + B_4^0 O_4^0$ (B_l^k parameters and O_l^k

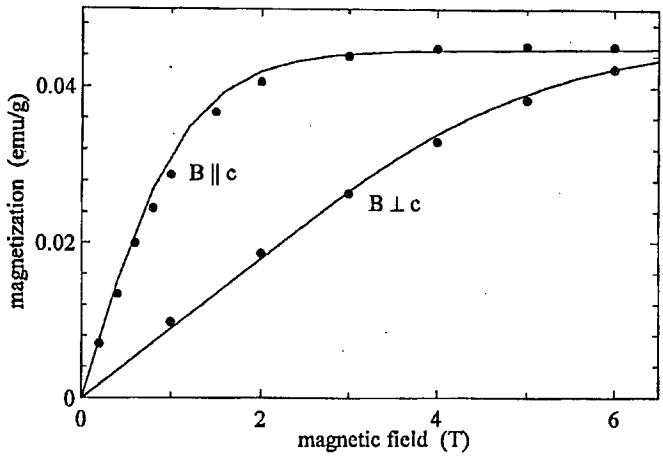

Fig. 2. Magnetization measured for $Cd_{1-x}V_xS$ at $T = 2$ K for magnetic field parallel and perpendicular to the c axis. The solid lines represents the result of numerical calculation. The scaling of the absolute value provides $x = 0.00043$.

operators are defined in Ref. [3]) is trigonal distortion. Since the observed huge anisotropy can be hardly described with the three kinds of centers with different Jahn–Teller distortions we assumed the opposite situation for which only the centers distorted along c axis are present in the crystal. Thus the two distortions are of the same symmetry and may be described by the one common term in the Hamiltonian $\mathcal{H}_{\rm tr}$. We used the basis composed of 28 states: $|l_z, s_z\rangle$, where l_z and s_z are the z components of orbital and spin momenta, respectively. The full 28×28 Hamiltonian matrix was numerically diagonalised supplying eigenenergies and eigenstates which were then used to calculate the magnetization.

The Hamiltonian contains four free parameters: Dq, which roughly corresponds to one tenth of cubic crystal field splitting, λ — the spin–orbit parameter and two parameters describing the trigonal distortion (so-called B_2^0 and B_4^0). The crystal field splitting was determined for V^{++} in CdS by Pappalardo et al. [7]: $10Dq = 4200$ cm^{-1}. The EPR studies of V^{++} center were performed for cubic ZnS [4] returning the spin–orbit splitting of the ground Γ_2 term into two spin doublets as 4.04 cm^{-1}. The authors also conclude that the first excited orbital state is a doublet Γ_3. Assuming that V^{++} in CdS is not drastically different than in ZnS we have chosen the spin–orbit and trigonal distortion parameters to provide the similar spin–orbit splitting of the ground Γ_2 term, to obtain Γ_3 as a first excited term and to obtain the best matching with our data. The results of calculations of the four lowest energy levels versus magnetic field are plotted in Fig. 1b for $\lambda = 40$ cm^{-1}, $B_2^0 = -112$ cm^{-1} and $B_4^0 = -1.87$ cm^{-1}. The calculated magnetization for magnetic field parallel and perpendicular to the distortion axis (which coincides with c axis) is compared with experimental data in Fig. 2. The absolute value of the calculated magnetization was scaled to match the saturation value. The obtained scaling factor corresponds to the vanadium concentration $x = 0.00043$.

The very good description of the data provided by the model strongly suggests that all the vanadium centers in the crystal are Jahn–Teller distorted along c crystal axis.

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