Exchange-interaction constant of polycrystalline $CdCr_2Se_4$ thin films doped with In

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(Received 4 December 1989; revised manuscript received 10 April 1990)

The magnetic properties of indium-doped polycrystalline thin films of $CdCr_2Se_4$ were studied. The magnetic-exchange-interaction constant A and the saturation magnetization M_s were determined as functions of the temperature (4.2–300 K) by means of the spin-wave resonance and the ferromagnetic resonance, respectively. We show that M_s follows the Bloch law; i.e., $M_s(T)=M_s(0)(1-BT^{3/2})$. The decrease in the spin-wave stiffness constant D with increasing temperature is proportional to $T^{5/2}$.

I. INTRODUCTION

The magnetic properties of chalcogenide spinels of $CdCr_2Se_4$ are very sensitive to In doping.[1] It is, therefore, interesting to investigate how the indium content affects the magnetic properties of $Cd_{1-x}In_xCr_2Se_4$ polycrystalline thin films. In this paper we report results that extend our previous study[2] to include the temperature dependences of the fundamental magnetic parameters such as the saturation magnetization M_s and the exchange interaction constant A. Our aim is to show that $Cd_{1-x}In_xCr_2Se_4$ is a ferromagnetic semiconductor that can be described by a simple spin-wave theory for $T<T_C$ (T_C is Curie temperature).

The experimental techniques that are used for measurements of the magnetic properties of thin films require higher sensitivities than standard methods applied in the studies of bulk ferromagnetism. The obvious reason is the small total mass of ferromagnetic material in the film form. Our previous experience[2] suggests that the spin-wave resonance (SWR) is the most suitable technique in the determination of the exchange interaction constant A of thin films. The SWR with well-resolved volume modes may be obtained by a low-energy excitation at a microwave frequency (the microwave spectrometer) for appropriate boundary conditions of surface spins. The dispersion relation of volume modes may then be used to calculate the exchange constant A.[2] The saturation magnetization can be derived from the ferromagnetic resonance (FMR) spectra in the perpendicular and parallel geometries.

The FMR is a very sensitive technique and can be applied to weakly ferromagnetic materials. Thus, it is not surprising that this method is so powerful when dealing with thin-film semiconductors.

II. EXPERIMENT

Thin Cd-In-Cr-Se films were deposited by vacuum evaporation from four independent sources of Cd, In, Cr, and Se.[2,3] The temperature of each source was monitored individually, thus providing the control of the deposition rate of each element. Therefore, we were able to vary the film composition in a wide range. Thin Cd-In-Cr-Se films were deposited at 350 K onto a Corning glass substrate covered with a 50 Å-thick Cr layer. "As-deposited" films were in an amorphous state. An appropriate heat treatment was necessary for the film recrystallization.[4] In order to prevent the diffusion of Se and Cd during the heat treatment the samples were overcoated with a thin layer of chromium ($\approx$50 Å). The heat treatment was carried out in a Kristalloflex 4H x-ray diffraction apparatus. The annealing temperature was varied from 300 to 850 K. Different annealing time intervals were chosen. X-ray diffraction patterns were recorded *in situ* after each stage of the heat treatment had been completed.

The film thickness was determined by means of a Talysurf-4 profilometer. The composition and homogeneity of the samples were analyzed by means of x-ray microprobe [using an Applied Research Laboratories (ARL) SEMQ microanalyzer] and Auger spectroscopy (using a Riber LAS-620). The magnetic parameters of the samples such as the saturation magnetization M_s, the spectroscopic splitting factor g, and Curie temperature T_C were found from the FMR data. The deposition procedure and the measurements are described in detail in Ref. 2.

III. RESULTS AND DISCUSSION

The SWR was detected for $Cd_{1-x}In_xCr_2Se_4$ ($x\approx0.01$) thin films in the temperature range from 30 to 110 K. It is well known that the SWR is observed when the surface spins satisfy appropriate boundary conditions. The quantitative analysis based on the Rado-Weertman model yields

$$k_n=n\pi/L\ ,$$

where k_n is a wave vector of a microwave component of the magnetization, n is an odd integer, and L stands for a film thickness. This condition is fulfilled in the limiting case of completely pinned surface spins. For a perpendicular configuration, i.e., when the external magnetic field

$H_\perp$ is applied along the normal to the film plane, the dispersion relation can be written in the following form:

$$(\omega/\gamma)_\perp = H_\perp^n - 4\pi M_s + (2A/M_s)(n\pi/L)^2 , \quad (1)$$

where $\omega = 2\pi\nu$, ν is a microwave frequency, γ is the gyromagnetic factor, and n is a spin-wave mode number.

We are not able to control the evaporation process to such an extent as to create the appropriate boundary conditions for the surface spins. Therefore, from a large number of samples with the same composition we have chosen those that show a volume mode excitation in the SWR experiment.

Figure 1 presents the dependence of $H_\perp^n$ on n^2 at different temperatures (30–90 K) for $Cd_{1-x}In_xCr_2Se_4$ ($x \approx 0.01$) thin films with $L = 500$ nm. The saturation magnetization M_s and its temperature dependence were determined from the magnetic balance technique and the FMR (for details see Ref. 2).

The linear relationship between $H_\perp^n$ and n^2 is clearly seen in Fig. 1 for higher-order modes. This allows us to extract the value of $(2A/M_s)(\pi/L)^2$ from the slope of the line [see Eq. (1)]. The exchange constant A and its temperature dependence can also be found provided that the saturation magnetization M_s and the film thickness L are known.

Figure 2 demonstrates the saturation magnetization as a function of $T^{3/2}$ together with the linear fit to the data. As expected from the simple spin-wave theory,[5] M_s decreases with increasing temperature at low temperatures according to the Bloch law:

$$M_s(T) = M(0)(1 - BT^{3/2} - \cdots) . \quad (2)$$

The coefficient B and the spin-wave stiffness constant D are related by

$$B = (0.1174/m)[g\mu_B/M(0)](k_B/4\pi D)^{3/2} , \quad (3)$$

where k_B is the Boltzmann constant, μ_B is the Bohr magneton and m is the number of lattice points per unit cell.

The dispersion relation for magnons is of the form

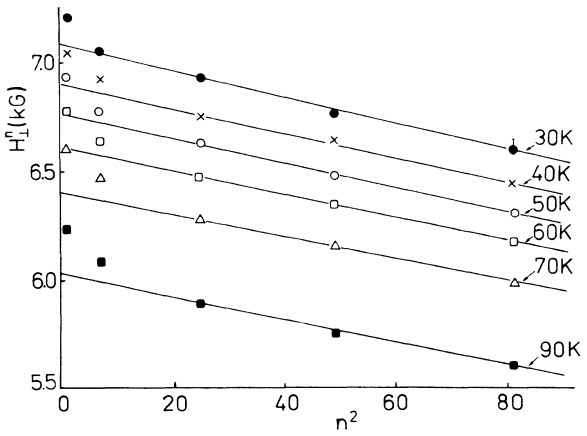

FIG. 1. Dependence of the resonance position $H_\perp^n$ on n^2 at different temperatures for a $Cd_{1-x}In_xCr_2Se_4$ sample with thickness $L = 500$ nm.

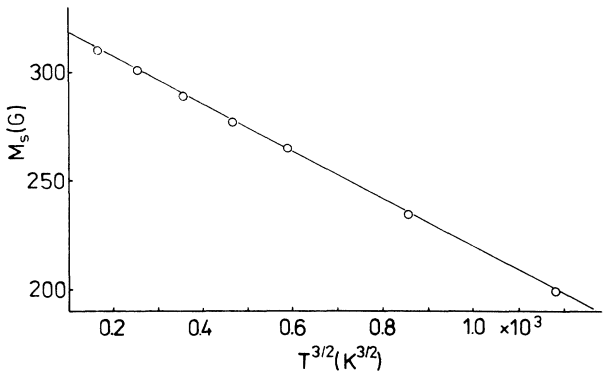

FIG. 2. Saturation magnetization M_s vs $T^{3/2}$ for $Cd_{1-x}In_xCr_2Se_4$ sample.

$$\hbar\omega \sim Dkn^2 . \quad (4)$$

The temperature dependence of D at low temperatures is very important for classification of models of magnetically ordered materials. Therefore, the experimental determination of $D(T)$ for thin films of chalcogenide is an important issue.

The relationship between the exchange constant A and the spin-wave stiffness constant D is given by

$$D = (2A/M_s)g\mu_B . \quad (5)$$

The temperature dependence of D can be derived from the previously established temperature dependences of M_s and A.

Figure 3 presents a plot of the spin-wave stiffness constant D versus $T^{5/2}$. The experimental data suggest that D is proportional to $(1 - CT^{5/2})$ for T lower than 60 K. This result seems to be quite satisfactory because, according to the spin-wave theory of ferromagnetism, the linear relationship between D and $T^{5/2}$ is expected at low temperatures only.

In addition, the value of the spin-wave stiffness constant D can be derived from the Bloch law [on the basis of Eqs. (2) and (3)]. The extrapolation of lines shown in Figs. 2 and 3 to 0 K yields $D^M = (171 \pm 5)$ meV Å^2, and $D^{SWR} = (175 \pm 7)$ meV Å^2, where D^M is determined from

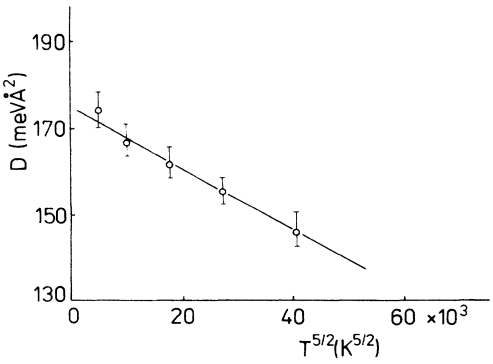

FIG. 3. The temperature dependence of the spin-wave stiffness constant D.

the temperature dependence of the saturation magnetization and D^{SWR} is derived from the SWR data. The agreement between D^{M} and D^{SWR} is good. Moreover, both D^{M} and D^{SWR} are close to those reported for a $CdCr_2Se_4$ single crystal.[6]

IV. CONCLUSIONS

Comprehensive studies of the both magnetic properties and mechanisms of the electron transport are required for a complete characterization of $Cd_{1-x}In_xCr_2Se_4$ thin films. Our investigations reveal that this material is a ferromagnetic semiconductor. The critical temperature at which the metal-semiconductor transition occurs is very sensitive to the electrical and magnetic parameters of the samples.

In this paper we discuss the fundamental magnetic parameters of the polycrystalline $Cd_{1-x}In_xCr_2Se_4$ thin films, since the magnetic properties are easily affected by a deviation from stoichiometry.

The saturation magnetization of chalcogenide thin-film spinels of Cd-Cr-Se is smaller than that predicted for stoichiometric samples. In the case of indium-doped Cd-Cr-Se materials the saturation magnetization decreases, while the indium concentration increases. As the magnetic behavior of such systems is limited by the existence of Cr^{2+} and/or Cr^{3+} ions[1,6] these effects can be accounted for by the formation of defects in cation and/or anion sublattices. The following mechanisms of defect formation lead to a decrease in the saturation magnetization: (i) In^{3+} ion substitution for Cd^{2+} resulting in the mixed-valency compound of $Cd_{1-x}{}^{2+}In_x{}^{3+}Cr_{2-x}{}^{3+}Cr_x{}^{2+}Se_4^{2-}$, (ii) In^{3+} ion substitution for Cd^{3+} that gives $Cd^{2+}In_{2x}{}^{3+}Cr_{2-2x}{}^{3+}Se_4{}^{2-}$, and (iii) introduction of Se vacancies that in the absence of In doping yield mixed-valency compound of $Cd^{2+}Cr_{2-2y}{}^{3+}Cr_{2y}{}^{2+}Se_{4-y}{}^{2-}$.

In all cases (i)–(iii) the saturation magnetization decreases with an increased departure from stoichiometry. At high indium concentration ($x \approx 0.07$) spin-glass behavior is expected, which manifests itself in the temperature dependence of both the resonance field and its linewidth.[2,7]

The magnetic properties of $Cd_{1-x}In_xCr_2Se_4$ indicate that, as far as the magnetic behavior is concerned, this material may be described by the spin-wave model below the Curie temperature.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Z. Obuszko for the magnetic balance measurements and W. Powroźnik for the preparation of the thin films. This work was partially supported by Central Research Program CPBP 01.08.B3.3.

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