X-band microwave study of $CdCr_2Se_4$ doped with In and $Cd_{1-x}In_xCr_2Se_4$ thin films

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The ferromagnetic resonance technique was applied to study the magnetic properties of $CdCr_2Se_4$ doped with In and $Cd_{1-x}In_xCr_2Se_4$ ($x \approx 0.07$) polycrystalline thin films. The films were obtained by evaporation in a high-vacuum system. The spin-wave resonance was observed for $CdCr_2Se_4$ thin films doped with In and the exchange-interaction constant was found. A slow relaxation mechanism could account for the magnon-scattering process. The increase in indium content of more than a few atomic percent affects the magnetic properties of the spin system. In this case from the temperature dependence of the position of the uniform mode in the ferromagnetic resonance experiment one can conclude that the spin-glass state is achieved at low temperatures.

I. INTRODUCTION

There is not much data available in literature on the preparation of polycrystalline thin films of chromium chalcogenide spinels and their magnetic properties.[1,2] The purpose of our paper is to present a method of $Cd_{1-x}In_xCr_2Se_4$ polycrystalline film preparation in the range of indium concentration x from 0 to 0.07. Undoped $CdCr_2Se_4$ is a ferromagnetic p-type semiconductor.[3,4] Small percentage substitutions (of about 1%) of Cd by trivalent elements such as In or Ga render the material n type while the similar substitution by monovalent elements, i.e., Ag or Au increases p-type conductivity. Experimental data on the electron transport and metal-semiconductor transition for $CdCr_2Se_4$ doped with In will be presented elsewhere.[5]

In order to study the magnetic properties, we used the ferromagnetic resonance (FMR) technique in the temperature range from 4.2 to 300 K. The spin-wave resonance (SWR) experiment at different temperatures (up to 150 K) enabled us to determine the exchange-interaction constant A. $CdCr_2Se_4$ crystallizes in a cubic spinel structure. All B sites (octahedral sites) are occupied by magnetic ions while all A sites (tetrahedral sites) are occupied by nonmagnetic (diamagnetic) ions. The number of Cr^{3+} nearest neighbors (in the vicinity of Cr^{3+} at B site) is 6. The nearest-neighbor exchange-interaction constant A is positive (it yields ferromagnetic interaction). The number of Cr^{3+} next nearest neighbors is 30 and the sign of the interaction constant B may be either positive or negative.[6]

The temperature dependence of a peak-to-peak linewidth gives the information on magnon-scattering processes in the polycrystalline state. The spin-glass behavior could also be predicted for the increased indium concentration.[7] The existence of a spin-glass state in $Cd_{1-x}In_xCr_2Se_4$ is caused by an interaction disorder resulting from statistical substitution of Cd cation by In.

II. EXPERIMENT

Thin $Cd_{1-x}In_xCr_2Se_4$ films with In concentration x between 0 and about 0.07 were deposited in a high-vacuum system. Four independent sources of Cd, Cr, Se, and In were used during the evaporation process.[8] Deposition rate was a known function of temperature of the sources. The three-layer structure was prepared as follows. A thin layer of Cr (≈ 50 Å) was deposited onto a Corning glass substrate preheated to about 520 K in order to improve the film adhesion. The Cd-Cr-Se-In film was evaporated at the substrate temperature of about 350 K onto the Cr layer. A thin layer of Cr was then deposited at 350 K in order to inhibit diffusion of Cd and Se during the subsequent annealing process. "As-deposited" samples were in the amorphous state. The film thickness was measured after deposition by means of Talysurf 4 profilometer. Thickness of the samples was also controlled during deposition process by the measurement of sample resistivity. The process of crystallization was studied in a Kristalloflex 4H x-ray-diffraction apparatus at different temperatures and for different annealing time intervals. The x-ray diffraction pattern was recorded *in situ* after each stage of heat treatment had been completed. It was found that the samples reached the polycrystalline state after being annealed at 790 K for 1 h. The composition of samples was analyzed by means of x-ray microprobe (ARL SEMQ microanalyzer) and Auger spectroscopy (Riber LAS-620). The temperature dependence of saturation magnetization was found from the FMR data. Microwave spectrometer at X band was applied for FMR and SWR measurements. The temperature was varied from 4.2 to 300 K. The magnetic interaction-exchange constant was derived from SWR spectrum. SWR and FMR data were taken for the external magnetic field rotating from the direction parallel to the film normal (perpendicular geometry) to the direction parallel to the film plane (parallel geometry). The temperature dependence of the uniform mode (FMR) and its linewidth for perpendicular and parallel geometry were investigated.

III. RESULTS AND DISCUSSION

We distinguish between two kinds of samples in relation to indium concentration: $Cd_{1-x}In_xCr_2Se_4$ with $x \leq 0.01$ and $Cd_{1-x}In_xCr_2Se_4$ with $x \approx 0.07$.

A. $Cd_{1-x}In_xCr_2Se_4$ with $x \leq 0.01$

Figures 1 and 2 present the resonance data for $CdCr_2Se_4$ doped with In at 40 K for parallel and perpendicular geometry, respectively. These figures show that SWR with five volume modes for each temperature up to about 150 K (the transition temperature from the ferromagnetic to the paramagnetic state) was obtained in case of perpendicular geometry (see Fig. 2). This allows us to calculate the exchange-interaction constant A from the spin-wave resonance data.

The dispersion relation for spin waves is given as

$$(\omega/\gamma)^2=\left[\frac{1}{M_s\sin^2\theta}\frac{\partial^2 E}{\partial\varphi^2}+\frac{2A}{M_s}k^2\right]\left[\frac{1}{M_s}\frac{\partial^2 E}{\partial\theta^2}+\frac{2A}{M_s}k^2\right]-\left[\frac{1}{M_s\sin\theta}\frac{\partial^2 E}{\partial\varphi\partial\theta}\right], \quad (1)$$

where $\omega=2\pi\nu$, ν is the microwave frequency, and γ is the gyromagnetic factor.[9] The wave vector of the microwave magnetization is denoted as k. In the limiting case of strongly pinned spins on both surfaces we get $n=1,3,5,\ldots$ for the allowed values of the wave vector $k=n\pi/L$, where L is the film thickness. The magnetic anisotropy energy density $E(\varphi,\theta)$ depends on the direction of static magnetization M_s (see Fig. 3). The energy is the sum of the following contributions:

$$E=E_H+E_d+E_K\ , \quad (2)$$

where

$$E_H=-M_sH(\sin\theta\sin\theta_H\sin\varphi+\cos\theta\cos\theta_H) \quad (3)$$

is the energy of magnetic field H applied at θ_H, $E_d=2\pi M_s^2\cos^2\theta$ is the demagnetization energy, $E_K=K\sin^2\theta$ is the energy of uniaxial magnetic anisotropy, and K is the magnetic uniaxial anisotropy constant. We set $K=0$ as no magnetic anisotropy showed up in our experiment (polycrystalline state) apart from the demagnetization contribution. From the equilibrium conditions $\partial E/\partial\varphi=0$ and $\partial E/\partial\theta=0$ one gets $\varphi=\pi/2$.

For the perpendicular geometry, when $\theta_H=\theta=0$, we have

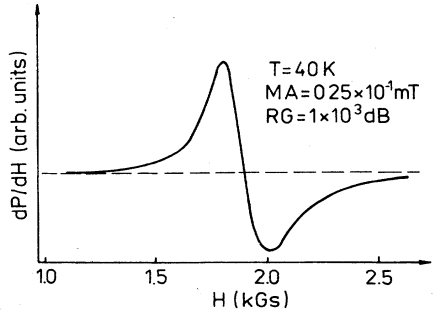

FIG. 1. Spin-wave-resonance spectra for $CdCr_2Se_4$ thin film doped with In for $T=40$ K and $\theta_H=90°$.

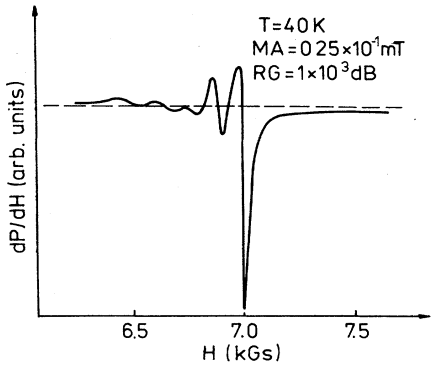

FIG. 2. Spin-wave-resonance spectra for $CdCr_2Se_4$ thin film doped with In for $T=40$ K and $\theta_H=0°$.

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

and for the uniform mode $k=0$,

$$(\omega/\gamma)_\perp=H_\perp-4\pi M_s\ . \quad (5)$$

In case of parallel geometry $\theta_H=\theta=90°$, hence

$$(\omega/\gamma)_\parallel^2=[H_n+(2A/M_s)(n\pi/L)^2]\times[H_n+4\pi M_s+(2A/M_s)(n\pi/L)^2]\ . \quad (6)$$

For the uniform mode

$$(\omega/\gamma)_\parallel^2=H_\parallel(H_\parallel+4\pi M_s) \quad (7)$$

SWR was performed for perpendicular geometry, i.e., $\theta_H=\theta=0$. The exchange constant A may be found from the best fit of the predicted quadratic dependence of H_n versus mode number n (see Fig. 4) to the experimental data. In the real case that dependence ($H_n\sim n^2$) cannot be used for lower-order modes because of microscopic fluctuation of magnetic parameters. Figure 4 shows the dependence of H_n on n^2 at two given temperatures. The linear relationship is seen (for higher-order modes); therefore from the slope of the line, the value of $(2A/M_s)(\pi/L)^2$ was found. The values of A are indicated in Fig. 4.

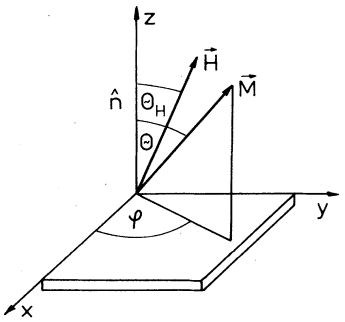

FIG. 3. Coordinate system.

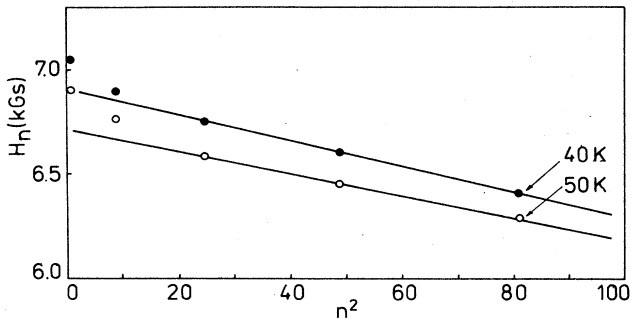

FIG. 4. Dependence of the resonance-field position H_n on the mode number n for $CdCr_2Se_4$ sample doped with In ($L=5000$ Å), $A=(2.3\pm0.2)\times10^{-12}$ J/m for $T=40$ K, $A=(2.4\pm0.2)\times10^{-12}$ J/m for $T=50$ K.

The temperature dependence of the resonance field of the uniform mode, for perpendicular and parallel geometry, are presented in Fig. 5. Ferromagnetic-paramagnetic transition temperature is also easily derived from Fig. 5. It is the temperature at which $H_\parallel=H_\perp$. The saturation magnetization M_s and its temperature dependence was obtained from the position of the uniform mode in perpendicular and parallel cases. From Eqs. (5) and (7), assuming that $(\omega/\gamma)_\perp=(\omega/\gamma)_\parallel$, one gets

$$4\pi M_s=H_\perp+0.5H_\parallel-[H_\parallel(H_\perp+1.25H_\parallel)]^{1/2}\ . \qquad (8)$$

From the experimental data [Fig. 5 and Eq. (8)] presented above the temperature dependence of M_s could be found (Fig. 6).

It should be pointed out that for magnetic material of this type the nonstoichiometry happens quite often on the microscopic scale. Therefore, one can expect that not only Cr^{3+} host ions but also Cr^{2+} ions could be created as a result of doping or because of the departure from stoichiometry. The annealing process in vacuum introduces Se vacancies; the charge is compensated by Cr^{2+} ions leading to the formula $Cd^{2+}\ Cr^{3+}_{2-2x}Cr^{2+}_{2x}Se^{2-}_{4-x}$. Doping with In should give $Cd^{2+}_{1-x}In^{3+}_xCr^{3+}_{2-x}Cr^{2+}_xSe^{2-}_4$. The spin is treated as consisting of ferromagnetic Cr^{3+} ions and paramagnetic impurities such as Cr^{2+} ions.[10] In

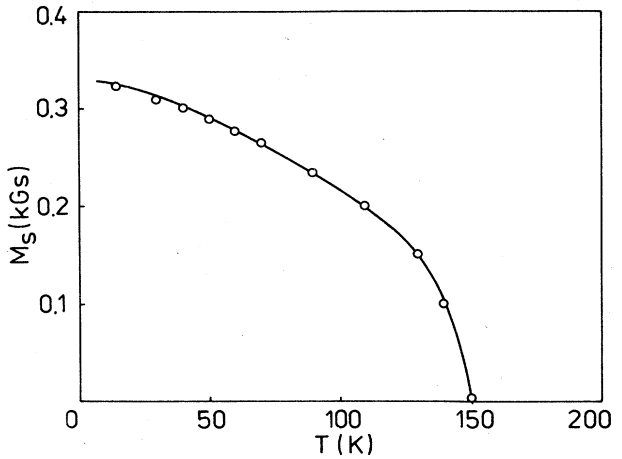

FIG. 6. Saturation magnetization of $CdCr_2Se_4$ sample doped with In versus T.

this system the scattering processes of magnons are more complex than in the case of a pure lattice comprised from the host magnetic ions only. The anisotropy of pure and stoichiometric single crystals of $CdCr_2Se_4$ is quite small, resulting in narrow lines in ferromagnetic resonance.[11] Some qualitative as well as quantitative information could be obtained from the temperature dependence of the linewidth of resonance spectrum ΔH. It is well known that ΔH is inversely proportional to the relaxation time τ. Figure 7 shows $\Delta H_\perp$ aNd $\Delta H_\parallel$ versus temperature.

We denote $\Delta H_\perp$ and $\Delta H_\parallel$ as peak-to-peak linewidth for perpendicular and parallel geometry. Two maxima are seen in Fig. 7, the first one occurs at low temperatures, while the second one at higher temperatures for $\Delta H_\perp$ and $\Delta H_\parallel$. As it was reported in Ref. 12 and 13 such behavior can be expected for slow or longitudinal relaxation mechanisms.

For slow relaxation, in the case of two levels, the linewidth ΔH may have two maxima as a function of temperature.[13]

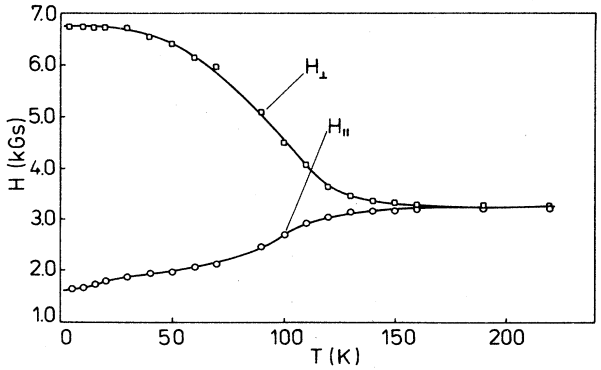

FIG. 5. Temperature dependence of resonance field for $CdCr_2Se_4$ thin film doped with In (perpendicular geometry $H_\perp$, parallel geometry $H_\parallel$).

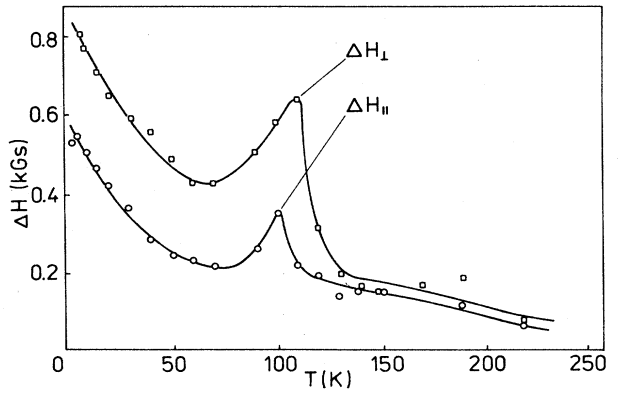

FIG. 7. Peak-to-peak linewidth ΔH vs temperature for $CdCr_2Se_4$ sample doped with In.

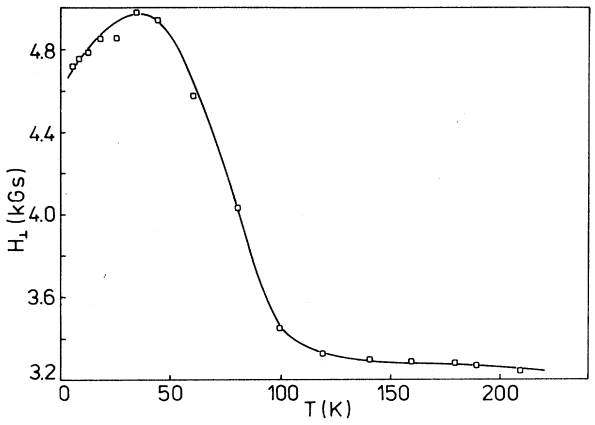

FIG. 8. Temperature dependence of resonance field H for $Cd_{1-x}In_xCr_2Se_4$ ($x \approx 0.07$).

B. $Cd_{1-x}In_xCr_2Se_4$ with $x \approx 0.07$

Indium ions dilute the ferromagnetic Cr^{3+} ions, and so Se vacancies need a larger amount of Cr^{2+} ions for charge compensation. As a result, the fluctuation of exchange magnetic constant of ferromagnetically coupled Cr^{3+} ions could happen which yields a spin-glass behavior at low temperatures. The same result may be produced if we assume that the magnetic moments of Cr^{2+} are coupled antiferromagnetically to Cr^{3+} moments. The temperature dependence of the uniform mode position, seen in Fig. 8, is similar to that reported for metallic glasses of thin-film Fe-B alloys in a spin-glass state.[14,15] Figure 8 shows the temperature dependence of the resonance field $H_\perp$ for $Cd_{1-x}In_xCr_2Se_4$ thin film with $x \approx 0.07$. There is a maximum at 40 K as it is expected for the spin-glass state. Similar data were presented for single crystals of $CdIn_{0.4}Cr_{1.6}S_4$ (Ref. 16) and the authors concluded that the sample was in the spin-glass state.

IV. CONCLUSIONS

The reported experimental data show that the proposed method of preparation gives $CdCr_2Se_4$ samples doped with In and $Cd_{1-x}In_xCr_2Se_4$ samples (with $x \approx 0.07$). Spin-wave resonance spectra could be obtained and it was possible to calculate the exchange-interaction constant A. In our case the value of $A = (2.3 \pm 0.2) \times 10^{-12}$ J/m derived from SWR data is in a good agreement with $A = 2.4 \times 10^{-12}$ J/m obtained by Baltzer[6] for the single crystal. The authors of Ref. 6 used the reduced Curie-Weiss and reduced Curie temperatures to perform a semiquantitative determination of exchange-interaction parameters. Therefore, it should be stressed that two quite different approaches give the same result. It could be concluded that the polycrystalline state does not affect the magnetic properties to a large extent. It is not the case when relaxation processes occur. As the exchange-interaction constant B for the next nearest neighbors is two orders lower than the interaction constant A for the nearest neighbors, we cannot determine the B value from SWR data. For our samples (polycrystalline) the value of the linewidth $\Delta H \sim 1/\tau$ is about one order of magnitude higher than that for monocrystalline bulk samples. The magnon-scattering process at grain boundaries affects ΔH in polycrystalline films.

At this stage of experiment we cannot explicitly establish whether $Cd_{1-x}In_xCr_2Se_4$ thin films (with $x \approx 0.07$) are in a spin-glass state at low temperatures or the magnetic moments of Cr^{2+} are coupled antiferromagnetically to the Cr^{3+} moments. The temperature dependence of saturation magnetization at low magnetic fields and low-temperature susceptibility measurements should be performed in order to solve that problem.

ACKNOWLEDGMENTS

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