

# EXAFS study of indium doped magnetic semiconductor CdCr<sub>2</sub>Se<sub>4</sub>

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## Abstract

An EXAFS study of indium substituted CdCr<sub>2</sub>Se<sub>4</sub> magnetic semiconductors is presented. Thin films of the compositions Cd<sub>1-y</sub>Cr<sub>2-2x</sub>In<sub>y+2x</sub>Se<sub>4</sub> with 2x = 0.00, 0.11, 0.27 and y = 0.14, 0.11, 0.00, respectively, were prepared by the radio frequency (RF) sputtering technique. From the Cr–K edge and Se–K edge EXAFS spectra the information on the local atomic environments around Se and Cr sites was obtained. With indium substitution the second nearest neighbour shell of the Cr site, which consists of Cr and possibly In ions, splits into two shells. The splitting increases with the increasing amount of indium. Direct current magnetisation measurements have shown that the samples with y = 0 or x = 0 are in the spin glass state and the samples with x ≠ 0 and y ≠ 0 are in the randomly canted state. These changes of magnetic properties are attributed to the differences of local environments as observed in the EXAFS measurements.

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## 1. Introduction

The chalcogenide spinel CdCr<sub>2</sub>Se<sub>4</sub> belongs to the family of magnetic semiconductors. This is an n-type semiconductor, which exhibits magnetic properties at low temperatures, depending on the cations substitution [1,2]. Magnetic interactions are responsible for the modification of the band structure and also for the transport properties and optical properties of the compounds. These are crucial for applications of the materials, e.g. in infrared detectors.

In this paper, thin film samples of the composition Cd<sub>1-y</sub>Cr<sub>2-2x</sub>In<sub>y+2x</sub>Se<sub>4</sub> with varying substitution 2x and y were studied. Films were deposited by the radio frequency (RF) sputtering technique on quartz glass substrates in controlled temperature conditions. The deposition device is equipped with a three-cathode system and a rotating sample holder. As-deposited samples are in the amorphous state and

form a multilayer structure of Cr (50 Å)/Cd–Cr–In–Se/Cr (50 Å). Heat treatment provides homogeneous polycrystalline films with the required composition. The composition of samples was analysed by means of an X-ray microprobe (ARL SEMQ microanalyser) and the thickness of the films was measured by Talysurf 4 profilometer. The measured compositions of the three investigated samples were Cd<sub>0.86</sub>Cr<sub>2</sub>In<sub>0.14</sub>Se<sub>4</sub>, Cd<sub>0.82</sub>Cr<sub>1.83</sub>In<sub>0.35</sub>Se<sub>4</sub> and CdCr<sub>1.73</sub>In<sub>0.27</sub>Se<sub>4</sub> with a thicknesses larger than 3000 Å. Other details of the preparation procedure are described in Ref. [3]. From the X-ray diffraction (XRD) pattern the lattice parameter *d* was determined. Fig. 1 presents the dependence of the lattice parameter on the indium content (y + 2x). As it is seen from the figure the lattice parameter is sensitive to the amount of substituted elements, particularly for y + 2x < 0.3.

In the crystallographic structure of the spinel CdCr<sub>2</sub>Se<sub>4</sub> magnetic Cr<sup>3+</sup> ions occupy octahedral sites. A long range ferromagnetic order appears below the Curie temperature of 130 K, despite the existence of antiferromagnetic interaction between third-nearest-neighbours [2]. However the interac-

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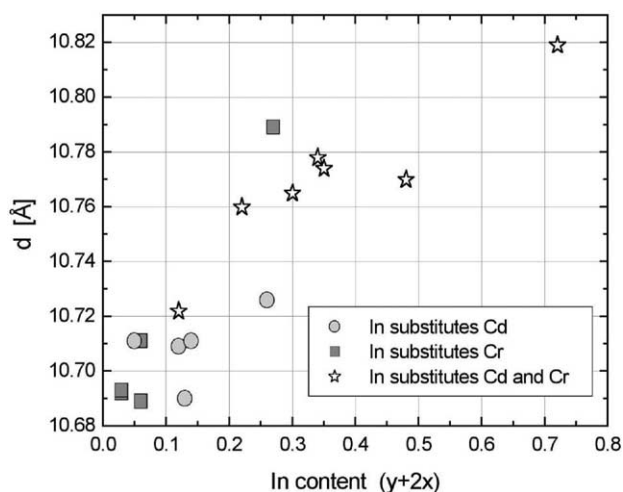


Fig. 1. The dependence of the lattice parameter  $d$  measured at room temperature on the indium content.

tion between the six equivalent nearest-neighbour Cr ions appears to be ferromagnetic [1].

EXAFS was used to investigate the structural changes upon indium substitution and relate them to the variation of magnetic properties of the compounds. Spectra were measured at the Cr–K edge and Se–K edge and the radial distributions of neighbouring atoms have been obtained. The results are discussed in relation with the data of direct current (d.c.) magnetisation measurements.

## 2. Experimental

X-Ray absorption measurements were carried out at beamline A1 at HASYLAB/DESY, Hamburg, Germany. Cr- and Se–K edge spectra were recorded at room temperature using a four crystal Si(111) monochromator. The energy resolution  $\Delta E/E$  was estimated to be about  $0.2 \cdot 10^{-4}$  for all measurements. The fluorescence detection mode was used for thin film samples and the transmission mode was applied for the  $\text{CdCr}_2\text{Se}_4$  powder reference sample. Three consecutive spectra at both edges for all the samples have been averaged in order to decrease the statistical errors of the detection. In the elaboration of the data the Viper program has been used [4].

The EXAFS spectra  $\chi(k)$  were obtained from the experimental spectra by subtraction of the atomic absorption background, approximated by Bayesian smoothing curve. The  $k^2\chi(k)$  function was Fourier transformed using the Hanning window in the range of  $k = 3\text{--}10 \text{ \AA}^{-1}$ . The modulus of the Fourier transform (FT) gives the pseudo-partial radial distributions around chromium and selenium sites. As it would be too difficult to derive the exact phase and amplitude corrections (calculated using multiple scattering theory) for indium doped samples a shift of the spectra in  $r$  space has been assumed. This shift,  $\delta r$ , was calculated using reference sample and XRD data and was estimated to be 0.5 and 0.6 Å for the

selenium and chromium radial distributions, respectively. It was taken to be equal to the shift of the first peak of the radial distribution function to the Cr–Se distance equal 2.69 Å for undoped  $\text{CdCr}_2\text{Se}_4$ . This procedure is in good agreement with linear phase correction function obtained from McKale's tables [5]. The sum of back Fourier transformed first and second shell distributions shows a good agreement with the experimental data of the thin film samples, Fig. 2, whereas for the powder sample the third shell contribution is also noticeable.

D.c. magnetization measurements have been carried out with a SQUID magnetometer in the temperature range from 4.2 to 160 K. The field cooling (FC) and zero field cooling (ZFC) magnetisation were measured at different external fields from 10 to 500 Oe in a similar way to that in Ref. [6].

## 3. Results and discussion

The radial distribution functions around the Cr site are presented in Fig. 3 and those around the Se site are shown in Fig. 4. The comparison of the radial distribution around Cr site shows that the most pronounced difference can be found in the second nearest neighbour shell where two peaks appear in the indium containing samples instead of one peak in the undoped material. The effect is attributed to a splitting of the second neighbour shell, which consists of Cr atoms at a unique distance from the absorbing central Cr atom in the undoped compound, whereas in the indium containing samples second neighbour Cr atoms appear at two different distances. In order to analyse the effect quantitatively, the radial distributions around the Cr site and the Se site were fitted in  $r$ -space with sets of gaussian lines. Examples of the fits are shown in Figs. 3 and 4. The distances corresponding to the individual lines, and thus, to the individual atomic neighbour shells are presented in Fig. 5 together with the crystal lattice parameter  $d$ .

It can be seen that the distance of the next neighbours of the Cr atoms, which are Se atoms, is nearly unchanged by the In doping, Fig. 5a. The second nearest neighbour shell containing Cr atoms at  $r_{\text{Cr-Cr}} = 3.79 \text{ \AA}$  in undoped  $\text{CdCr}_2\text{Se}_4$  shows the splitting which increases with doping from 0.4 Å for  $2x + y = 0.14$  sample to 0.5 Å for the  $2x + y = 0.27$  sample. Looking at the Se radial distribution function around the Se atoms one can find that the nearest neighbour shell, which consists of three Cr and one Cd atoms, shows a slight increase of the average distance with increasing indium content, Fig. 5b. This can be attributed to either an increase of the average distance of ions at the tetrahedral site (i.e. Cd or In) or the appearance of In ions, which are larger than the Cr ions, at the octahedral nearest neighbour sites.

Fig. 6 presents the FC and ZFC d.c. magnetisation of  $\text{Cd}_{0.86}\text{Cr}_{2.00}\text{In}_{0.14}\text{Se}_4$  thin film sample. The behaviour is typical for a spin-glass (SG) state [7,8]. A similar behaviour is observed for  $\text{Cd}_{1.0}\text{Cr}_{1.73}\text{In}_{0.27}\text{Se}_4$  where In substitutes chromium. This magnetic phase, of a topologically ordered

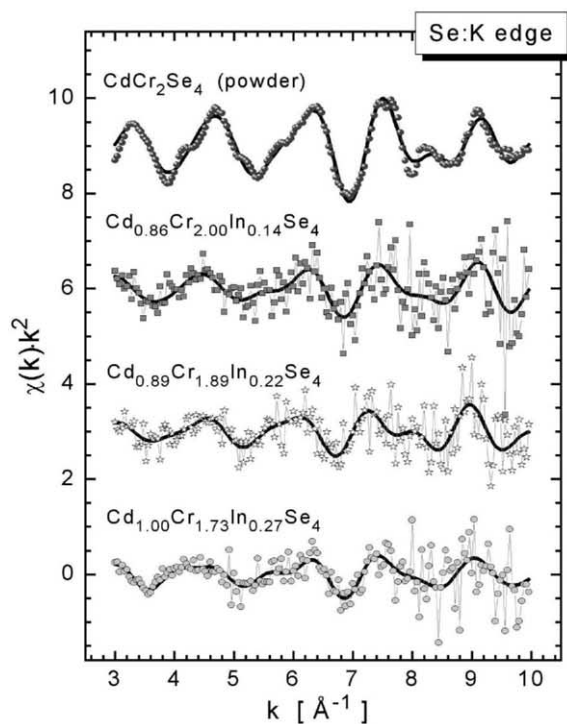
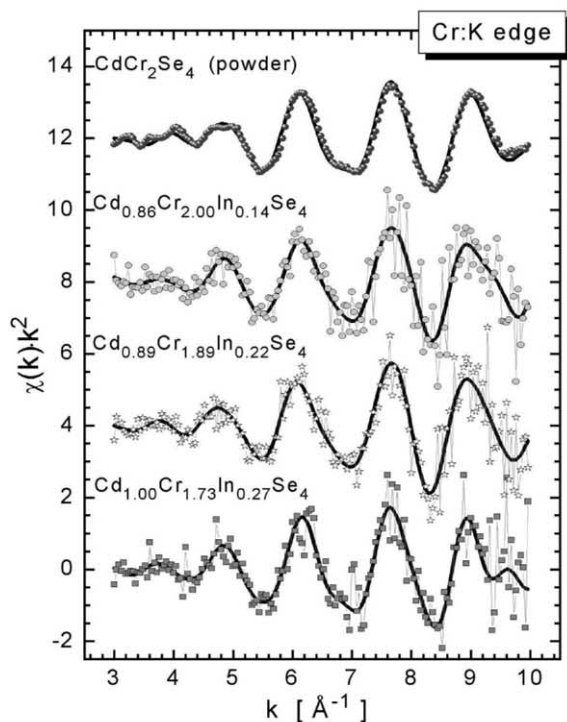


Fig. 2. The sum of back Fourier transformed first and second nearest neighbour shell distributions compared with experimental data for all the samples studied.

type, possesses finite randomly distributed spin clusters. The system is characterised by different magnetic excitation and coupling interactions from those in the ferromagnetic state. This is a consequence of a competition of ferromag-

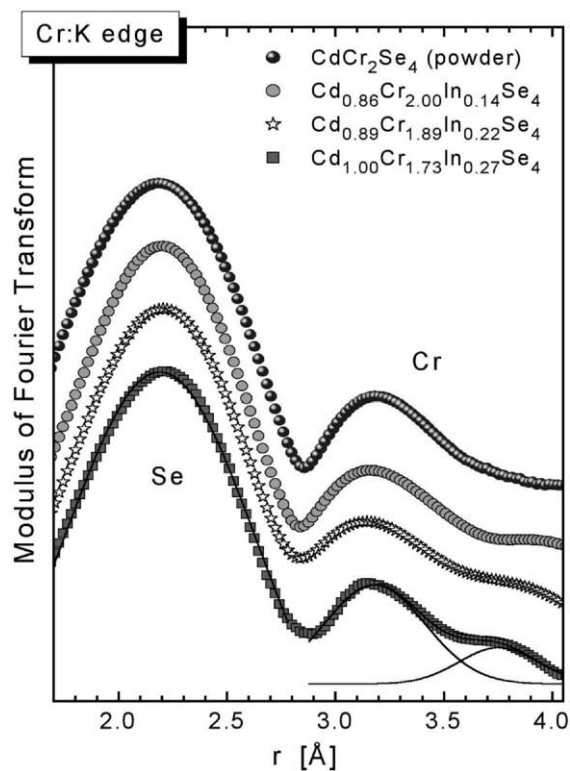


Fig. 3. The radial distributions around the chromium atom for all the samples studied.

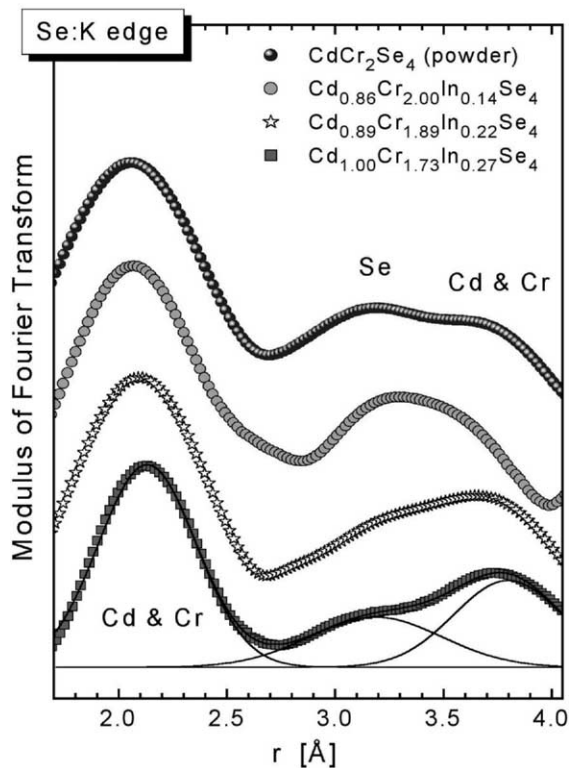


Fig. 4. The radial distributions around the selenium atom for all the samples studied.

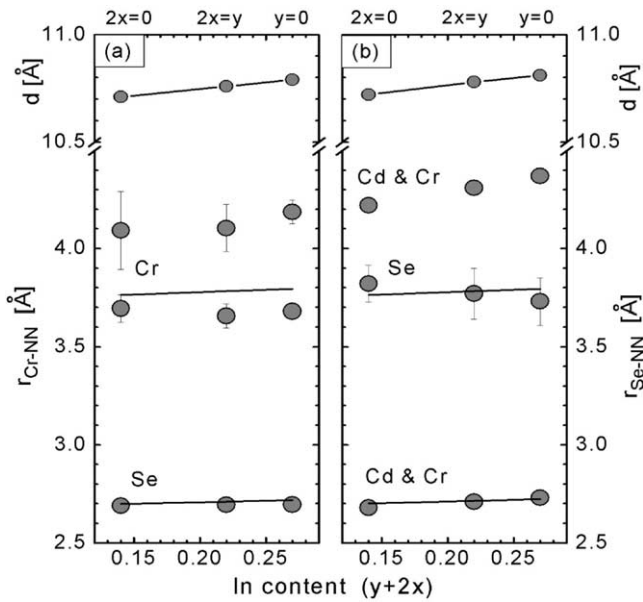


Fig. 5. The evolution of the interatomic distances with the indium content compared to the lattice parameter. The distances to the first and second nearest neighbours calculated from lattice parameter  $d$  are marked with lines. Estimated errors for the second neighbour shell are indicated by error bars.

netic interactions between nearest-neighbours and antiferromagnetic interaction between next nearest neighbours. The SG state is also characterised by an unidirectional magnetic anisotropy, which originates from the microscopic anisotropy of the Dzyaloshinskii–Moriya interaction [9]. This interaction aligns the remanent magnetisation in the direction of the initial applied field. Such a behaviour is confirmed by the FC and ZFC d.c. magnetisation measurements.

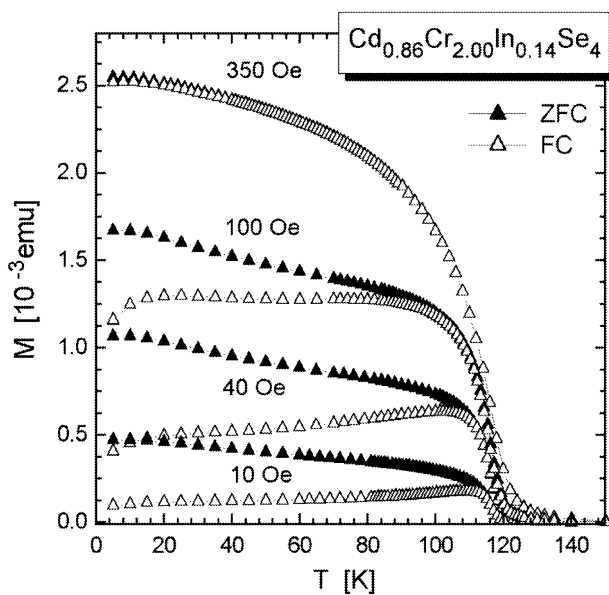


Fig. 6. Zero field cooling and field cooling d.c. magnetisation of  $\text{Cd}_{0.86}\text{Cr}_{2.00}\text{In}_{0.14}\text{Se}_4$ .

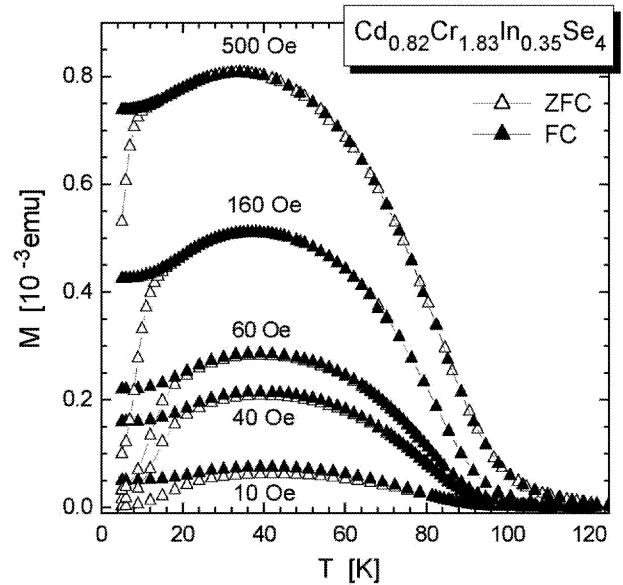


Fig. 7. Zero field cooling and field cooling d.c. magnetisation of  $\text{Cd}_{0.82}\text{Cr}_{1.83}\text{In}_{0.35}\text{Se}_4$ .

When In substitutes both Cd and Cr, i.e. in  $\text{Cd}_{0.82}\text{Cr}_{1.83}\text{In}_{0.35}\text{Se}_4$ , the magnetic behaviour is characteristic of a randomly canted structure [8,10], Fig. 7. This structure consists of two magnetic sublattices. At low temperatures, for diluted compounds, where  $\text{In}^{3+}$  substitutes  $\text{Cr}^{3+}$  sites, the antiferromagnetic interaction is enhanced, leading to a randomly canted state, which is macroscopically uniform.

#### 4. Conclusions

A comparison of the magnetic data with the EXAFS results shows that the magnetic properties of the compounds depend on the local atomic environments. The lack of presence of a long range ferromagnetic order in the In doped samples compared to the undoped compound which exhibits a ferromagnetic order can be attributed to a distortion of the local environment of the Cr site. This is indicated by the observed splitting of the second nearest neighbour shell which contains chromium. The splitting of the second nearest neighbour coordination shell which introduces the difference of exchange integrals between Cr atoms is presumably the reason of appearance of a canted magnetic state.

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