

# EFFECT OF $\text{Cr}^{2+}$ IONS ON THE MAGNETIC ANISOTROPY OF CHROMIUM CHALCOGENIDE SPINELS

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## ABSTRACT

Crystal field theory is used to calculate the single-ion contribution of impurity  $\text{Cr}^{2+}$  ions to the magnetic anisotropy of chromium chalcogenide spinels. These crystals are magnetic semi-conductors ( $\text{Cr}^{3+}$  are the host ions) and impurity magnetic ions are created to charge compensate for defects or by intentional doping. We find a symmetry breaking of the anisotropy from cubic, at high temperatures, to non-cubic at low temperatures. In ferromagnetic resonance experiments (FMR), for an applied magnetic field in the (110) plane, the salient feature of the non-cubic component of the anisotropy is the asymmetry of the angular dependence of the resonance field about the [110] direction, a "signature" of the presence of  $\text{Cr}^{2+}$  ions in the system. We report FMR data of single crystals of the ferromagnetic semiconductor  $\text{CdCr}_2\text{Se}_4$  with 0.1 mole % Ag, where this effect is seen. The values of the non-cubic anisotropy constants obtained from the fitting of the data are consistent with our theoretical predictions. Moreover, the values of the cubic anisotropy constants suggest a competition of contributions from  $\text{Cr}^{2+}$  and  $\text{Cr}^{4+}$  impurity ions.

## 1. INTRODUCTION

The effect of Cr ions of different valences,  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$ , on the magnetic anisotropy and ferromagnetic resonance (FMR) linewidth of chromium chalcogenide spinels has been intensively investigated after the discovery<sup>1</sup> of magnetism in these compounds. In particular,  $\text{CdCr}_2\text{Se}_4$  exhibits ferromagnetism (Curie temperature around 130K), and when perfectly stoichiometric and at low temperatures it is an electrical insulator. The anisotropy due to the  $\text{Cr}^{3+}$  host ions is found<sup>2</sup> to be extremely small and the resonance line very narrow. In addition, however,  $\text{CdCr}_2\text{Se}_4$  also exhibits semi-conducting behavior<sup>3</sup> as a result of a lack of stoichiometry (as grown), by thermal treatment or by intentional doping. The combination of semiconducting and magnetic properties has been the most attractive feature of these chromium chalcogenide compounds. The non-stoichiometry causes the appearance of impurity magnetic ions which manifest in anomalous peaks of the resonance field and of the FMR linewidth along some particular crystallographic directions.

Several studies have been made to identify the impurity magnetic ions responsible for the above-mentioned anomalies. It was first suggested by Berger and Pinch<sup>4</sup> that  $\text{Cr}^{2+}$  ions could be formed to charge compensate for  $\text{Se}^{-2}$  vacancies, and qualitatively explain the variation of anisotropy from sample-to-sample. However, it has also been

suggested<sup>5</sup> that accidental  $\text{Fe}^{2+}$  impurities are responsible for the anisotropy anomalies, after identification<sup>6</sup> of similar effects in  $\text{CdCr}_2\text{S}_4$  doped with Fe. On the other hand, in Ag-doped  $\text{CdCr}_2\text{Se}_4$  ( $\text{Ag}^{1+}$  substituting for  $\text{Cd}^{2+}$ ), it was verified<sup>7</sup> a change in sign of the first anisotropy constant  $K_1$  (from positive to negative) and attributed to the formation of  $\text{Cr}^{4+}$  ions, which could equally be created to charge compensate for Cd vacancies. Further investigations<sup>8</sup> showed that vacuum annealing of Ag-doped  $\text{CdCr}_2\text{Se}_4$  altered the sign of  $K_1$  (now from negative to positive). This change was ascribed<sup>8</sup> to the formation of  $\text{Cr}^{2+}$  ions, which occurred as Se vacancies appeared in the crystal, whereas subsequent annealing in Se atmosphere<sup>8</sup> reversed the anisotropy sign as the vacancies filled up, though the value of  $K_1 (<0)$  was much less in magnitude than the initial one. The presence of  $\text{Cr}^{4+}$  ions has also been suggested as responsible for the low temperature peaks of the FMR linewidth of Ag-doped  $\text{CdCr}_2\text{Se}_4$ <sup>7,9</sup> and of "as grown"  $\text{HgCr}_2\text{Se}_4$ <sup>10,11</sup>, as well as to explain<sup>10-13</sup> the negative anisotropy of  $\text{HgCr}_2\text{Se}_4$ . It should be mentioned that variations in sign occur<sup>14</sup> depending on the degree of deviation from stoichiometry.

In this work we shall calculate the  $\text{Cr}^{2+}$  single-ion contribution to the anisotropy of spinel chalcogenides. In particular, we find a symmetry breaking of the anisotropy from cubic, at high temperatures, to non-cubic at low temperatures. In FMR experiments, for an applied magnetic field in the (110) plane, the salient-feature of the non-cubic component of the anisotropy is the asymmetry of the resonance field  $H_{\text{RES}}^{(\theta)}$  about the [110] direction, a "signature" of the presence of  $\text{Cr}^{2+}$  ions in the system. In Fig. 1 we report FMR data<sup>11</sup> for the angular dependence of the  $H_{\text{RES}}^{(\theta)}$  of single crystals of  $\text{CdCr}_2\text{Se}_4$  with 0.1 mole % Ag at  $T = 4.2\text{K}$ , where this effect is seen. Regardless of the Ag doping, the contribution of  $\text{Cr}^{2+}$  ions is sizable, probably due to the large amount of Se defects. The asymmetry of the  $H_{\text{RES}}^{(\theta)}$  about the [110] direction has been observed<sup>4,5,15</sup> in several FMR studies of both  $\text{CdCr}_2\text{Se}_4$  and  $\text{CdCr}_2\text{S}_4$ , but either ignored or attributed<sup>15</sup> to small deviations from the sample sphericity. However, it cannot produce such a big effect, which has in fact an intrinsic origin and constitute the main result of this paper.

In section II we discuss the level structure of the  $\text{Cr}^{2+}$  ions, and the single-ion contribution to the anisotropy of chalcogenide spinels is calculated in section III. These results are used to interpret our data in section IV. Finally, some conclusions are presented in section V.

## 2. LEVEL STRUCTURE OF Cr<sup>2+</sup> IONS IN CHALCOGENIDE SPINELS

The chromium chalcogenides<sup>1</sup> have a normal spinel structure. The Cr ions (B sites) are surrounded by an octahedron of selenium ions. Each B site lies on an axis of three-fold symmetry which is parallel to one of the body diagonals of the cubic crystal. The local symmetry about a B site is not cubic but trigonal. Four kinds of B sites may be distinguished according to which of the four directions [111], [ $\bar{1}\bar{1}\bar{1}$ ], [1 $\bar{1}\bar{1}$ ] and [ $\bar{1}\bar{1}1$ ] is parallel to the trigonal axis. The selenium positions are displaced slightly from those of a regular octahedron. Two contributions to the trigonal field may be distinguished. The cations (Cd ions occupying tetrahedral positions, or A sites) tend to make the potential greatest along the trigonal axis. The anions (Se ions) oppose the effect of the cations<sup>16</sup>.

Since  $kT_c \approx 400\text{cm}^{-1}$ , to calculate the temperature dependence of the anisotropy we need the energy levels within this range, i.e., the level structure of the orbital ground state. Starting from the  $(2L+1)(2S+1)$  fold-degenerate state,  $3d^4 - ^5D$ ,  $L=2$ ,  $S=2$  of Cr<sup>2+</sup>, we consider medium crystal field and use the perturbative method of Bleaney and Stevens<sup>17</sup>. The cubic crystal field splits the <sup>5</sup>D state into a  $\Gamma_5$  triplet and a  $\Gamma_3$  doublet orbital ground state. The trigonal field does not remove the orbital degeneracy, and its effect is calculated to first order in perturbation theory. We have now to include the spin-orbit interaction and the action of the molecular field of the Cr<sup>3+</sup> host ions on the spin of the Cr<sup>2+</sup> impurity ion, both to first order. For simplicity, we shall neglect the Zeeman interaction and the spin-spin interactions. The ten-fold  $\Gamma_3$  state finally splits with eigenvalues

$$E_{\alpha,i} = 0 \text{ (doublet)}, \quad (1)$$

$$E_{\alpha,i} = \pm \left(\frac{5}{2} \pm \frac{3}{2}\right)^{1/2} A(1 \pm \eta\beta_{3i})^{1/2}, \quad (2)$$

$$A = [(\Delta E_x)^2 + 8\left(\frac{\lambda v}{\Delta}\right)^2]^{1/2}, \quad (3)$$

$$\eta = \frac{4\sqrt{2} \Delta v \lambda \Delta E_x}{\Delta^2 (\Delta E_x)^2 + 8\lambda^2 v^2}, \quad |\eta| < 1, \quad (4)$$

where  $\alpha$  runs over the ten-fold level structure and  $i$  over the four distinct B sites,  $\Delta E_x$  is the exchange energy between the Cr<sup>2+</sup> ions and the host Cr<sup>3+</sup> ions,  $\lambda$  is the spin-orbit coupling,  $\Delta$  is the cubic crystal-field splitting,  $v$  is the trigonal component and  $\beta_{3i}$  is the direction cosine of the magnetization with respect to the coordinate system in which the  $z$  axis is one of the four [111] directions (local axis of deformation). It should be mentioned that in calculating the energy eigenvalues, the angular momentum was quantized along the local axis of deformation and the spin along the direction of magnetization.

Our results for the level structure of the Cr<sup>2+</sup> ions differ from those obtained by Hoekstra and van Stapel<sup>5</sup>. In the latter the orbital ground state splits by the combined

action of spin-orbit coupling and trigonal field, in second order, whereas the exchange (molecular) field is taken to be infinite. Contrary to the later assumption, we take the molecular field of the order of the spin-orbit coupling and their effect is calculated in first order using wave functions including first-order corrections from the trigonal field. Comparison with experimental data in section IV indicates that our viewpoint is more adequate to describe the anisotropy of CdCr<sub>2</sub>Se<sub>4</sub>.

## 3. Cr<sup>2+</sup> SINGLE-ION ANISOTROPY IN CHALCOGENIDE SPINELS

In order to calculate the anisotropy due to the Cr<sup>2+</sup> ions let us determine their contribution to the free energy per unit volume:

$$F(T=0K) = \frac{N}{4} \sum_{i=1}^4 E_{0,i}, \quad (5)$$

$$F(T) = -\frac{NKT}{4} \sum_{i=1}^4 \ln Z_i, \quad (6)$$

$$Z_i = \sum_{\alpha} \exp\left(\frac{-E_{\alpha,i}}{KT}\right), \quad (7)$$

where  $E_{0,i}$  is the ground state energy,  $E_{\alpha,i}$  is given by Eqs. (1-4),  $N$  is the number of impurity Cr<sup>2+</sup> ions per cm<sup>-3</sup> and a statistical distribution over the distinct B sites is assumed.

It is clear that Eq. (2) implies level crossing of the two low-lying energy levels according to the sign of  $\beta_{3i}$ . Using values for  $A$  and  $\eta$  ( $<0$ ) which fit our data this effect is illustrated in Fig. 2, where  $\beta_{3i}$  is related to the cosine directions  $\alpha_j$  of the magnetization with respect to the [100], [010] and [001] axes of the crystal. For an applied field in the (110) plane, it is assumed that the crystal is magnetized to saturation,  $\alpha_j = M_j/M_s$ , where  $M_j$  are the magnetization components,  $M_s$  is the saturation magnetization, and  $\theta$  is the angle between the direction of magnetization and the [100] crystal axis. Level crossing occurs along the [112] direction at site  $\gamma_1$ , along the [110] direction at sites  $\gamma_2$  and  $\gamma_3$ , and along the [112] direction at site  $\gamma_4$ .

Using the ground-state energy in the form

$$E_{0,i} = -2A(1 - \eta|\beta_{3i}|)^{1/2}, \quad (8)$$

we obtain the following zero-temperature free energy expressions, according to the  $\theta$  interval:

$$-([100]) \quad 0 < \theta < \arctg \frac{1}{\sqrt{2}} \quad ([112]) \quad (9)$$

$$F_1(T=0) = \frac{K_0}{2} \alpha_3 + \frac{K_M}{2} \alpha_3^3 + \frac{K_f}{2} (\alpha_3^5 - 5\alpha_1^2 \alpha_2^2 \alpha_3) +$$

+ cubic anisotropy

$$-([112]) \quad \arctg \frac{1}{\sqrt{2}} < \theta < \frac{\pi}{2} \quad ([110]);$$

$$([110]) \frac{\pi}{2} < \Theta < \pi - \arctg \frac{1}{\sqrt{2}} ([112])$$

$$F_{2,3}(T=0) = \frac{k_0}{2} (\alpha_1 + \alpha_2 \pm \alpha_3) + \frac{K_M}{2} (\alpha_1^3 + \alpha_2^3 \pm \alpha_3^3 \pm 3\alpha_1 \alpha_2 \alpha_3) + \frac{K_F}{2} (\alpha_1^5 + \alpha_2^5 \pm \alpha_3^5) + \alpha_1 \alpha_2 \alpha_3 (\pm \alpha_1 \alpha_2 + \alpha_3 + \alpha_1 + \alpha_2 \alpha_3) + \text{cubic anisotropy}, \quad (10)$$

$$-([11\bar{2}]) \pi - \arctg \frac{1}{\sqrt{2}} < \Theta < \pi$$

$$F_4(T=0) = -F_1 + \text{cubic anisotropy}, \quad (11)$$

where  $K_0$  is given by a power series in  $\eta$  and has no effect on the resonance field.

$$K_M = \frac{NA}{12\sqrt{3}} \eta^3, \quad (12)$$

$$K_F = \frac{7NA}{288\sqrt{3}} \eta^5, \quad (13)$$

and the cubic anisotropy is given by

$$F_{\text{cubic}} = K_1(0) s + K_2(0) p, \quad (14)$$

$$s = \alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2, \quad (15)$$

$$p = \alpha_1^2 \alpha_2^2 \alpha_3^2, \quad (16)$$

$$K_1(0) = \frac{5\sqrt{3}}{36} \eta^4 + \frac{21\sqrt{3}}{36} \eta^6, \quad (17)$$

$$K_2(0) = \frac{7}{18} \eta^6. \quad (18)$$

On the other hand using Eqs. (6), (7) and (1)–(4), and dropping constant terms, we obtain the free energy at finite temperatures:

$$F(T) = -\frac{NkT}{4} \sum_{i=1}^4 \ln \{ 1 + \cosh [2\gamma(1+\eta\beta_{3i})^{1/2}] + \cosh [2\gamma(1-\eta\beta_{3i})^{1/2}] + \cosh [\gamma(1+\eta\beta_{3i})^{1/2}] + \cosh [\gamma(1-\eta\beta_{3i})^{1/2}] \}, \quad (19)$$

where  $\gamma = A/kT$ . For  $kT < A$ ,  $F(T)$  is given by the zero-temperature expressions plus logarithmic (temperature dependent) corrections. Therefore, for  $kT < A$ , including  $T = 0$ , the free energy has non-cubic components proportional to the cubic and fifth power of the magnetization components. For  $kT > A$ , however, the cubic symmetry is recovered:

$$F(T) = K_1(T) s + k_2(T) p, \quad (20)$$

where

$$K_1(T) = NkT \left[ \frac{2}{9} \left(\frac{T}{9}\right)^2 - \frac{4}{27} \left(\frac{T}{9}\right)^3 + \frac{6}{81} \left(\frac{T}{9}\right)^4 - \frac{8}{243} \left(\frac{T}{9}\right)^5 \right], \quad (21)$$

$$K_2(T) = NkT \left[ \frac{16}{27} \left(\frac{T}{9}\right)^3 - \frac{64}{81} \left(\frac{T}{9}\right)^4 + \frac{160}{243} \left(\frac{T}{9}\right)^5 \right], \quad (22)$$

$$r = \frac{17}{8} \gamma^4 \eta^2, \quad (23)$$

$$q = 5 + 5\gamma^2 + \frac{17}{8} \gamma^4, \quad (24)$$

The effect of the magnetic anisotropy on the resonance field is considered through the effective field

$$\vec{H}_a = -\frac{\partial F}{\partial \vec{M}}, \quad (25)$$

which can be written in the form

$$\vec{H}_a = -\vec{N} \cdot \vec{M}, \quad (26)$$

thus defining an effective demagnetization tensor. For spherical samples, the resonance field is calculated from Kittel's equation

$$\left(\frac{\omega}{\gamma}\right)^2 = [H + (N_x - N_z)M_s] [H + (N_y - N_z)M_s], \quad (27)$$

where  $\gamma$  is the spectroscopic ratio. In evaluating  $\vec{N}$  we used the coordinate system in which  $\vec{M}$  is quantized along the  $z$  direction, and assumed  $M_x, M_y \ll M_z \approx M_s$ . These standard approximations influence differently the free energy expressions in Eqs. (9–11), resulting in resonance fields with small discontinuities along the directions where level crossing occur (see Figs. 1 and 2). To avoid this problem we would have to calculate the low-lying energy states in higher order of perturbation theory, as indicated in Fig. 2, to obtain the level splitting and a unique expression for the zero-temperature free energy.

#### 4. COMPARISON WITH EXPERIMENTAL DATA

In the experiments we have used a spherical sample with diameter  $\Phi = 0.30$  mm made from single crystals of 0.1 mole % Ag-doped  $\text{CdCr}_2\text{Se}_4$ . The sphere was polished using abrasive powder with an average particle size near  $0.5 \mu\text{m}$ , and oriented by X-ray diffraction to within  $1^\circ$ . FMR resonance experiments were performed in the 3 cm wavelength range in a nonresonant system. In this system

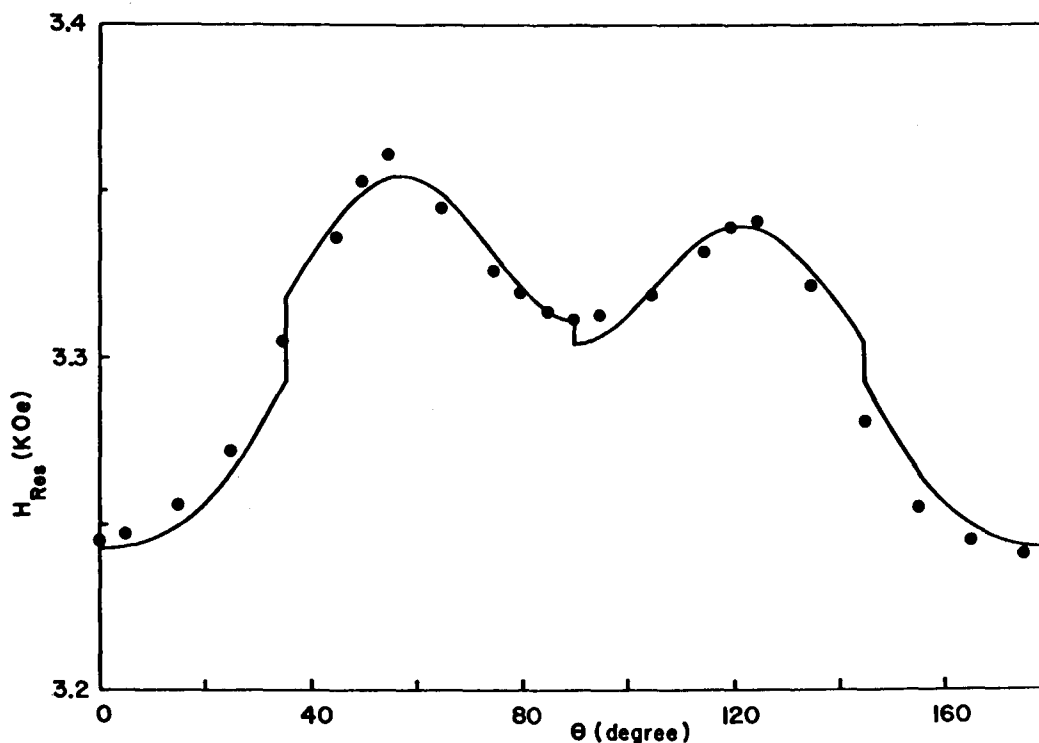


Fig. 1 - Angular dependence of  $H_{RES}^{(\theta)}$  for  $CdCr_2Se_4$  with 0.1 mole % Ag (diameter  $\phi = 0.30$  mm) at 9.2 GHz and 4.2K.  $\theta$  is the angle between the static magnetic field and the [100] direction in the (110) plane. The curve is a fitting including additional non cubic anisotropy components due to  $Cr^{2+}$  impurity ions (values in Oersted):  $(\omega/\gamma) = 3298.5$ ,  $(K_M/M_S) = 6.2$ ,  $(K_f/M_S) = -3.8$ ,  $(K_1/M_S) = 4.1$  and  $(K_2/M_S) = 71.4$ .

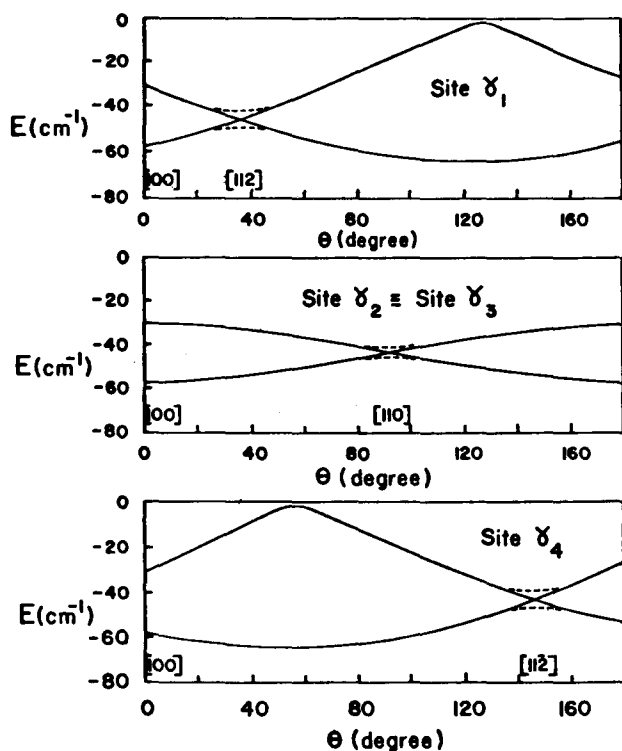


Fig. 2 - Low-lying energy levels of  $Cr^{2+}$  ions in chromium chalcogenide spinels. The parameters used are those of the fitting of Fig. 1. Level crossing occurs along the [112] direction at site  $\gamma_1$ , along the [110] direction at sites  $\gamma_2$  and  $\gamma_3$ , and along the [112] direction at site  $\gamma_4$ . The dotted lines illustrate the level splitting obtained in higher order of perturbation theory.

the sample is placed in a section of a shorted waveguide, at the antinode of the R.F. magnetic field, mounted on a thin sapphire rod of the cryostat. The external magnetic field lies in the (110) plane of the crystal, so that FMR can be observed along the principal crystallographic directions. Resonance data were obtained in the temperature range 4.2 to 130K using a heterodyne receiver to improve the signal-to-noise ratio.

Fig. 1 shows the angular dependence of the resonance field  $H_{RES}^{(\theta)}$  at 4.2K. The salient feature is the asymmetry of the  $H_{RES}^{(\theta)}$  about the [100] direction, being a consequence of the non-cubic anisotropy component. In Fig. 1 we also present a fitting of the data, where the discontinuities in the theoretical curve reflect the level-crossing approximation used to calculate  $H_{RES}^{(\theta)}$  from Eqs. (25-27). We have used the zero-temperature expressions for the free energy, Eqs. 9-11, since at 4.2K the logarithmic corrections are negligible.

It is clear that the asymmetry of the  $H_{RES}^{(\theta)}$  is justified by the presence of  $Cr^{2+}$  ions, in agreement with the theoretical results derived in sections III and IV. Though we do not have a complete knowledge of the parameters involved, we can test the consistency of the values of the anisotropy constants obtained in the fitting of Fig. 1.  $K_M$  and  $K_f$  were found to be negative, in accord with the sign<sup>17</sup> of the cubic crystal-field splitting  $\Delta$ . Also,  $K_f$  is smaller than  $K_M$  as predicted by Eqs. (12), (13) and (4). Taking<sup>17</sup>  $\lambda = 58cm^{-1}$ ,  $(v/\Delta) \approx (-1/10)$  and assuming a typical concentration of  $10^{19}$   $Cr^{2+}$  ions per  $cm^3$ , we find  $\Delta_{EX} \approx$

$\approx 70\text{cm}^{-1}$ , which is the correct order of magnitude for the exchange energy. In fact, it may be greater than this estimate because the observed asymmetry persists in the entire ferromagnetic region. On the other hand, the values of  $K_1$  and  $K_2$  are not in agreement with Eqs. (17) and (18), which suggest  $K_1 > K_2$ . This means that a complete explanation of the cubic component requires to include the contributions of  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$  ions. One should recall that the contribution of the former to  $K_1$  is negative<sup>7-13</sup> and may justify the low value of this anisotropy constant. Further work is in progress and will be the object of a future report.

## 5. CONCLUSIONS

In this paper we have calculated the  $\text{Cr}^{2+}$  single ion contribution to the anisotropy of chromium chalcogenide spinels. In particular we find a symmetry breaking of the anisotropy from cubic, at high temperatures, to non-cubic at low temperatures. In FMR experiments, for an applied magnetic field in the (110) plane, the salient feature of the non-cubic component of the anisotropy is the asymmetry of the angular dependence of the resonance field about the [110] direction, a "signature" of the presence of  $\text{Cr}^{2+}$  ions in the system. We used our theoretical results to interpret our data for the angular dependence of the resonance field of  $\text{CdCr}_2\text{Se}_4$  with 0.1 mole % Ag (see Fig. 1).

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The values of the non-cubic anisotropy constants obtained from the fitting in Fig. 1 are consistent with the theoretical predictions based on  $\text{Cr}^{2+}$  effects. These impurity ions are created in the crystal to charge compensate for Se defects.

Moreover, neglecting the contribution of the host  $\text{Cr}^{3+}$  ions, the values obtained for the cubic anisotropy constants suggest a competition of contributions from  $\text{Cr}^{2+}$  and  $\text{Cr}^{4+}$  impurity ions. The later are formed to charge compensate for Cd vacancies or due to the Ag doping, as evidenced<sup>7-12</sup> in several FMR studies.

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