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Ferrimagnetism of $Cu_{0.45}Co_{0.55}Cr_2S_{4-y}Se_y$

M. Gogołowicz, S. Juszczyk, and J. Warczewski
Institute of Physics, Silesian University, ul. Uniwersytecka 4, PL-40-007 Katowice, Poland

T. Mydlarz
International Laboratory of High Magnetic Fields and Low Temperatures, ul. Próchnika 95, PL-53-529 Wrocław, Poland

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Powdered samples of the new ferrimagnetic spinel series $Cu_{0.45}Co_{0.55}Cr_2S_{4-y}Se_y$ for $0.0 \leq y \leq 1.5$ have been obtained. The results of measurements of magnetization isotherms in applied fields up to 14 T at 4.2 and 77 K, the magnetization curves in pulsed fields in the temperature range of 77 K $\leq T \leq$ 300 K, the Curie temperature, the anisotropy field, and the asymptotic Curie-Weiss temperature are summarized. The magnetic moment, the temperature Θ_{CW}, and the Curie constant exhibit anomalous behavior in the concentration range of $0.5 < y < 1.0$. It turns out that the magnetic properties of these spinels can be explained if one assumes the existence of monovalent Cu ions and of Cr ions in two valence states: Cr^{3+} and Cr^{4+}, the concentration ratio $[Cr^{3+}]$:$[Cr^{4+}]$ being equal to 1.55:0.45. The terms of the molecular-field approximation were used to explain the magnetic properties of the compounds under study. The ground-state energy and the exchange integrals for three types of interactions between the nearest neighbors Cr^{n+}-X^{2-}-Cr^{m+}, Co^{2+}-X^{2-}-Co^{2+}, and Cr^{n+}-X^{2-}-Co^{2+} have been calculated.

I. INTRODUCTION

Spinels with the general formula $Cu[Cr_2]X_4$, where X=S,Se, have been found to be metallic conductors and ferromagnets with relatively high Curie temperatures, $T_C = 420$ K for X=S and 434 K for X=Se.[1] These properties are in contrast with those of the other chromium chalcogenide spinels, which are semiconductors with magnetic critical temperatures much lower than room temperature, e.g., $ZnCr_2Se_4$ with $T_N = 22$ K and $MnCr_2S_4$ with $T_C = 77$ K.[1,2] Recently, a new class of magnetic spinels with the general formula $Cu_xM_{1-x}Cr_2X_4$, where M=Zn,Mn and X=S,Se, has been obtained. In these spinels different transitions occur, for example, antiferromagnetism to ferromagnetism in $Zn_{1-x}Cu_xCr_2Se_4$ (Ref. 3) or ferrimagnetism to ferromagnetism in $Mn_{1-x}Cu_xCr_2S_4$ (Ref. 4), as well as a change of the character of the electrical conductivity.

The chalcogenide spinels with copper and chromium are of interest to many authors. The magnetic and electrical properties of the spinel series $Co_{1-x}Cu_xCr_2S_4$ have been studied by Belov *et al.*[5] and of the spinel series $Co_{1-x}Cu_xCr_2Se_4$ by Smirnov *et al.*[6] The spinels $Co_{1-x}Cu_xCr_2S_4$ are formed over the entire range of x, between $x = 0.0$ and $x = 1.0$. The compound with $x = 0.0$ is a ferrimagnetic semiconductor and that with $x = 1.0$ is a ferromagnetic metallic conductor with high Curie temperature $T_C = 377$ K. The concentration $x = 0.5$ is a transition point for these properties. With increasing x, the following observations were made: a nonlinear decrease of the magnetic moment per molecule at 4.2 K, as well as increase of T_C and Θ_{CW} for $\Theta_{CW} > T_C$.

The compounds $Co_{1-x}Cu_xCr_2Se_4$ crystallize with the spinel structure only for $x \leq 0.2$; for $0.8 \leq x \leq 1.0$, they exhibit the monoclinic structure of the type Cr_3S_4. A transition from the cubic spinel structure to the monoclinic structure has been observed in this system at a pressure on the order of 10^{-2} Pa. Belov *et al.*[7] have observed a drastic influence of the concentration y on the magnetic properties of the spinel series $CuCr_2S_{4-y}Se_y$. The magnetic moment μ at $y = 1$ is 25 times smaller than μ at both $y = 0$ and $y = 4$. Similar behavior was exhibited by T_C and Θ_{CW}. Also, the electrical conductivity revealed a semiconductive character at $y \simeq 1$, whereas its character is metallic for $y \neq 1$.

Considerable changes of the magnetic properties related to the variation of the concentration of the anions have been observed also in the spinel series $CuCr_2Se_{4-y}Br_y$, $CuCr_2Se_{4-y}Cl_y$, and $CuCr_2Te_{4-y}J_y$.[8,9] In these compounds, for example, the values of T_C and Θ_{CW} decrease with increasing y, whereas the magnetic moment increases when Se→Br and is constant when Se→Cl.

The aim of this work is to study the influence of the substitution of sulphur ions by selenium ions on the magnetic properties of the spinel series $Cu_{0.45}Co_{0.55}Cr_2S_{4-y}Se_y$. The choice of the composition of the cations follows from the reported change of the magnetic properties near $x = 0.5$ in an isostructural spinel series $Co_{1-x}Cu_xCr_2S_4$.[5]

II. EXPERIMENT

Polycrystalline samples of $Cu_{0.45}Co_{0.55}Cr_2S_{4-y}Se_y$ (y=0.0, 0.5, 0.8, 1.0, 1.2, 1.3, 1.4, and 1.5) were prepared by heating stoichiometric quantities of mixed elements of Cr (99.9% pure), Co (99.9%), Cu (99.99%), S (99.999%), and Se (99.999%) in sealed evacuated quartz tubes at 1023–1123 K for 10 days and then cooling in the furnace.[10] For $y > 1.5$ a mixture of spinel and defect NiAs-type phases is formed.

The structure of the samples was verified by x-ray measurements on a HZG-4/*A* diffractometer with Cu $K\alpha$ radiation, using corundum as an internal standard.[10] The results of the x-ray studies provide data for the determination of the temperature dependence of the lattice parameter a, the anion parameter u, the x-ray Debye temperature Θ_M, the spontaneous magnetostriction ω_m, the bulk modulus K as well as the Born index n of the repulsive energy, and the lattice energy U. From these x-ray measurements it is concluded, that[10]

(i) All compounds under study are the normal spinels with a strong probability for the Cr ions to be in the octahedral [B] positions.

(ii) The lattice parameter increases with increasing selenium concentration y and does not obey Vegard's law.

(iii) Between anions and cations in tetrahedral positions the covalent bond dominates with a small ionic-bond contribution in the case of $y=1.5$.

(iv) Between anions and cations in octahedral positions the ionic bond dominates with a small covalent-bond contribution in the case of $y=1.5$.

The magnetic properties of these compounds were studied using different techniques:

(i) The sample was placed in high magnetic stationary fields up to 14 T at 4.2 and 77 K, and measured with an induction magnetometer.

(ii) The sample was placed in high-pulsed magnetic fields up to 15 T within the temperature range 77–300 K and measured with the induction method.

(iii) The sample was placed in medium dc magnetic fields up to 0.6 T within the temperature range of 77–600 K and measured with a Faraday-Obuszko-type magnetic balance.

(iv) The sample was placed in weak mutual magnetic inductions of the order of 10^{-5} T within the temperature range 77–300 K and measured with the induction method.[11]

The powdered samples were prepared for the magnetic field measurements as described by Krok *et al.*[3] In order to check the reproducibility of results for every concentration y, three different types of samples depending on heating regime have been measured.

III. RESULTS

A. Magnetization curves

Figures 1(a) and 1(b) show typical behavior of the magnetization as a function of the applied magnetic field for selenium concentrations $y=0.0$ and 0.8 and for the temperature range 4.2–300 K. The other magnetization curves determined for all the y values in the 0.0–1.5 interval exhibit similar shapes. The curves at 4.2 and 77 K were obtained in stationary magnetic fields and all the other curves in pulsed magnetic fields. It turns out that for all values of y saturation is reached at small values of magnetic field (about 2–3 T). The magnetic moment μ per molecule at 4.2 K (deduced from the isotherms of static magnetization at the applied field up to 14 T) exhibits an anomalous minimum at $y=0.8$ (see Fig. 2).

B. Critical temperature measurements

The temperature dependence of the magnetic susceptibility (for $T \le T_C$) is shown in Fig. 3. The behavior of all the samples is typical of a ferrimagnet without a compensation point. The value of T_C has been determined by extrapolation to the horizontal axis of the linear part of a curve after the signal reached a maximum. T_C decreases linearly from 272 K for $y=0.0$ to 226 K for $y=1.5$ (cf. Fig. 2).

C. Paramagnetic susceptibility

An example of the (χ_M^{-1} versus T) curve is given in Fig. 4. The paramagnetic Curie-Weiss temperatures were determined for all concentrations by extrapolation to the horizontal axis of the linear parts of the recipocal molar susceptibility χ_M versus temperature. The molar Curie constants have been determined from the slope of the

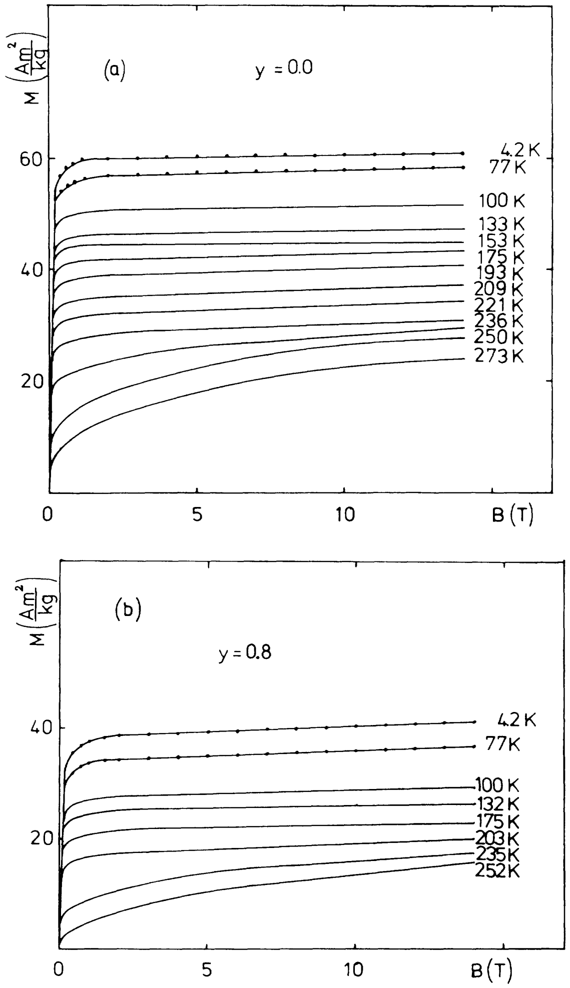

FIG. 1. Typical magnetization curves vs magnetic field for the samples chosen as representative: (a) $y=0.0$, (b) $y=0.8$. The curves at 4.2 and 77 K were obtained in stationary magnetic fields and all the other curves in pulsed magnetic fields.

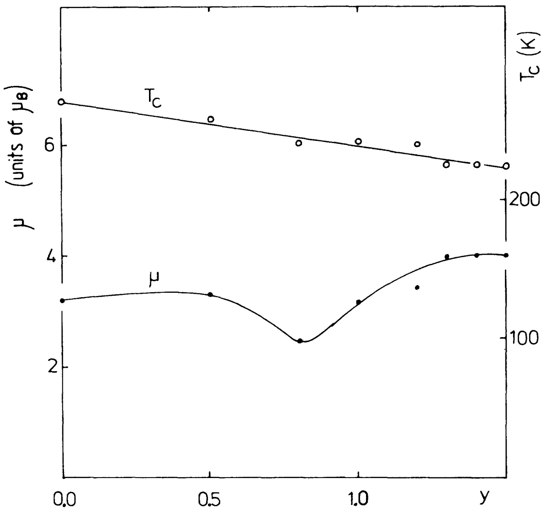

FIG. 2. The magnetic moment μ per molecule at 4.2 K (deduced from the isotherms of static magnetization at the applied field up to 14 T) and the Curie temperature T_C (determined from the magnetic susceptibility in an applied mutual induction $B=10^{-5}$ T) versus selenium concentration y.

linear parts. The factors σ and Θ' were obtained from the fitting of Eq. (10) to the experimental data of $\chi_M^{-1}=f(T)$. It is seen in Fig. 5 that Θ_{CW} and C_M also behave anomalously near $y=0.8$.

D. Magnetic anisotropy

Using the singular point detection (SPD) technique[12] the anisotropy measurements were carried out in a pulsed magnetic field. Figure 6 shows the concentration dependence of the anisotropy constants K_1 at 200 K (at this temperature the anisotropy constant exhibited a maximum). It is clear that the anisotropy constant is small.

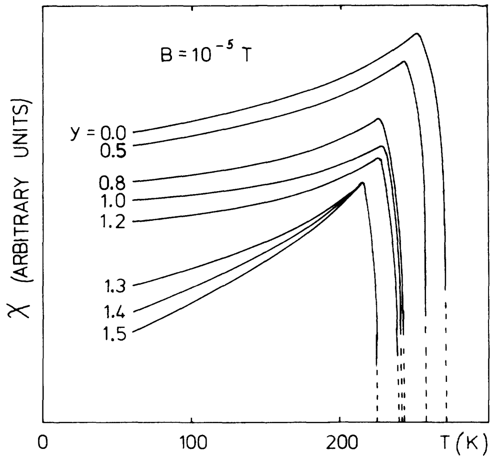

FIG. 3. The temperature dependence of the magnetic susceptibility (for $T \leq T_C$) for different concentrations y.

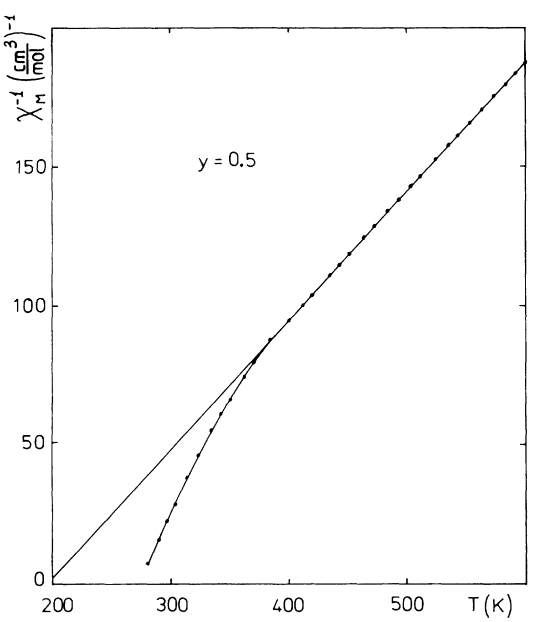

FIG. 4. Experimental curve for inverse molar susceptibility as a function of temperature for $y=0.5$. The curves for the other concentrations are similar.

Because the singularity points were observed already on the d^2M/dt^2 versus H curves, we can see that all compounds under study possess uniaxial anisotropy.

Marais *et al.*[35] report, that for $CoCr_2S_4$ the anisotropy constant K_1 is of the order of 3×10^4 J/m^3 at 77 K and relate this value to the presence of Co^{2+} ions. For $CuCr_2Se_4$ on the contrary, Nakatani *et al.*[14] have found a large negative value of the anisotropy constant K_1 of the order of -4×10^4 J/cm^3 at 77 K and relate this value to the presence of Cr^{4+} ions in this spinel.

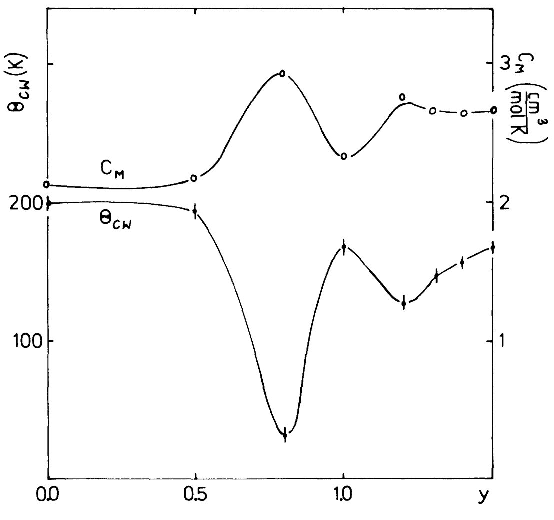

FIG. 5. The paramagnetic Curie-Weiss temperature Θ_{CW} and the molar Curie constant C_M [determined from $\chi_M^{-1}=f(T)$ curves] vs concentration y.

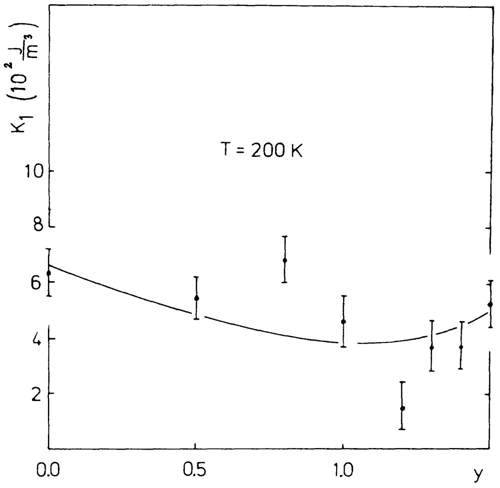

FIG. 6. The anisotropy constant K_1 at 200 K (at this temperature the anisotropy field exhibited a maximum) vs concentration y.

The small value of K_1 in the spinel series $Co^{2+}{}_{0.55}Cu^{1+}{}_{0.45}Cr^{3+}{}_{1.55}Cr^{4+}{}_{0.45}S_{4-y}Se_y$ can be explained as a resultant of the strong positive contribution of the Co^{2+} ions as well as of the strong negative contribution of the Cr^{4+} ions.

The experimental data are summarized in Table I.

IV. DISCUSSION

A. Qualitative features of the theoretical model for $Co_{1-x}Cu_xCr_2S_4$

Many experimental attempts have been made to clarify the valence states of the Cr ions in copper chalcogenide spinels (either $Cr^{3+}+Cr^{4+}$ or $Cr^{3+}+Cr^{3+}$ or $Cr^{3+}+Cr^{2+}$ or $Cr^{2+}+Cr^{4+}$). Neutron diffraction data[15,16] show that all Cr ions have a magnetic moment of about $3\mu_B$ and indicate their equivalence. Yokoyama *et al.*[17] estimated from the NMR spectra that all the Cr ions are trivalent. Riedel and Horvath[18] indicated that the cation-anion distances of $CuCr_2S_4$ correspond to the valence distribution $Cu^{2+}(Cr^{3+}Cr^{4+})S_4^{2-}$. Kovtun *et al.*[19,20] suggested the coexistence of tetravalent and trivalent Cr ions based on the analysis of NMR spectra. Nakatani *et al.*[14] showed from magnetic measurements of the $CuCr_2S_4$ single crystals, that the g factor of the Cr ions is close to 2.0, which suggests that all the Cr ions are trivalent. Kovtun *et al.*[21] reported that the observed intensity of neutron diffraction was reproducible for valence states of $Cu^{+}{}_{1-x}Cu^{2+}{}_x(Cr^{3+}{}_{1+x}Cr^{4+}{}_{1-x})X^{2-}{}_4$ with $x=0.25$ at 4.2 K and $x=0.0$ at 77 K. Yamashita *et al.*[22] showed from the analysis of the neutron diffraction data for a single crystal that the effective valence states of $CuCr_2Se_4$ is $Cu^{1.07+}(Cr^{3+}{}_{1.28}Cr^{4+}{}_{0.72})Se^{2-}{}_4$. Ando and Nishihara[23] estimated the coexistence of divalent and trivalent Cr ions from the Mössbauer spectra observed in the magnetic semiconductors $Fe_{1-x}Cu_xCr_2S_4$ ($0.0\leq x\leq 0.5$). Juszczyk *et al.*[24] interpreted the magnetic properties of the mixed crystal series $Zn_{1-x}Ga_{2x/3}Cr_2Se_4$ ($0.0\leq x\leq 0.5$) assuming the same coexistence of valence of the Cr^{3+} and Cr^{2+} ions. Gurevich *et al.*[25] concluded from the ferromagnetic resonance (FMR) data of the spinels $CdCr_2S_4$ and $CdCr_2Se_4$ that Cr ions coexist in divalent and trivalent states.

Several experimental studies have been carried out to determine whether the Cu ions are monovalent or divalent. Most authors[3,4,16,19–21,26–31] suggest that the valence of the copper ions is Cu^+.

Recently, the self-consistent-charge spin-polarized discrete variational X_α method was used by Horikawa *et al.*[29] and Ogata *et al.*[30] to calculate the electronic band structure in the spinels $CuCr_2X_4$ (X=S,Se,Te). The pure ionic model is not always appropriate for the electronic structure of these compounds and it is important to consider the covalent-bond contribution. Because these calculations are very time consuming, the simple ionic models are still helpful in many cases.

In order to determine the valence states and spin distribution in the compounds under study, these quantities have been first found for the spinel series $Co_{1-x}Cu_xCr_2S_4$. The experimental data obtained by Belov *et al.*[5] can be explained if one proposes the following valence-state distributions:

$$\text{(i) } Cu^{+}{}_xCo^{2+}{}_{1-x}(Cr^{3+}{}_{2-x}Cr^{4+}{}_x)S^{2-}{}_4 ,$$

$$\text{(ii) } Cu^{+}{}_xCo^{2+}{}_{1-x}(Cr^{2+}{}_{1-x/2}Cr^{4+}{}_{1+x/2})S^{2-}{}_4 .$$

TABLE I. The basic experimental data: the magnetic moment μ per molecule at 4.2 K, the effective moment per molecule μ_{eff}, the Curie temperature T_C, the paramagnetic Curie-Weiss temperature Θ_{CW}, the Curie molar constant C_M and the anisotropy constant K_1 at 200 K.

y	μ (units of μ_B) T=4.2 K	μ_{eff} (units of μ_B)	T_C (units of K)	Θ_{CW} (units of K)	C_M	K_1 (units of J/m^3) T=200 K
0.0	3.22	4.13	272	200.0	2.12	633
0.5	3.28	4.17	258	195.0	2.16	553
0.8	2.45	4.87	240	31.6	2.94	688
1.0	3.21	4.32	243	168.7	2.32	468
1.2	3.24	4.71	241.5	116.2	2.75	148
1.3	4.09	4.63	225.5	150.0	2.66	380
1.4	4.00	4.60	225.5	162.5	2.63	344
1.5	4.00	4.68	226.0	170.0	2.72	538

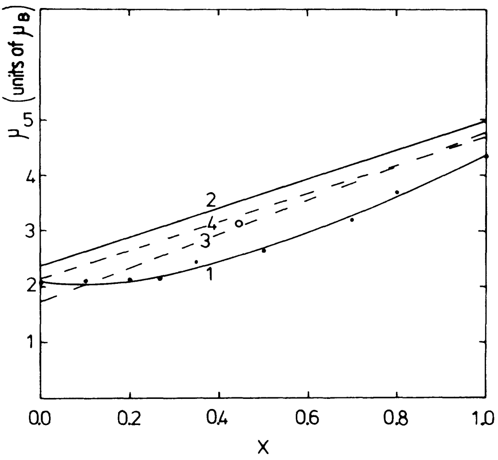

FIG. 7. The experimental and theoretical dependences of the magnetic moment μ vs copper concentration x [reported by Belov *et al.* (Ref. 5)] in comparison with our two models. 1 and 2 denote μ_{expt} and μ_{calc}, respectively, by Belov *et al.* (Ref. 5) for $Cu_x^{2+}Co_{1-x}^{2+}(Cr_2)S_4^{2-}$, 3 denotes μ_{calc} for $Cu_x^{+}Co_{1-x}^{2+}(Cr_{2-x}^{3+}Cr_x^{4+})S_4^{2-}$, 4 denotes μ_{calc} for $Cu_x^{+}Co_{1-x}^{2+}(Cr_{1-x/2}^{2+}Cr_{1+x/2}^{4+})S_4^{2-}$, ○ denotes an experimental point for the spinel series studied by us for $y=0.0$.

These formulas are based on the assumption that copper ions are monovalent and carry no magnetic moment.

It follows from the magnetization and paramagnetic susceptibility measurements[32,33] that there exist both Cr^{2+} and Cr^{3+} ions in the compound $CoCr_2S_4$. On the other hand, it is known from the polarized neutron diffraction studies[22] of single crystals of $CuCr_2Se_4$, that Cr^{3+} and Cr^{4+} ions are also present. In addition, if the p band of the anion is full, then the interaction between Cr^{3+} and Cr^{4+} must be ferromagnetic and increase strongly with increasing concentration of Cr^{4+}. Therefore, the Curie-Weiss temperature, the Curie temperature, and the electrical conductivity should also increase. The experimental results for magnetic moment versus copper concentration[5] for $Co_{1-x}Cu_xCr_2S_4$ confirm our proposition (i) of the Cr valence states, as indicated by the comparison with our two models shown in Fig. 7.

B. Exchange Hamiltonian

In our discussion of the magnetic properties of the $Cu_{0.45}Co_{0.55}Cr_2S_{4-y}Se_y$ spinel series, the antiferromagnetic coupling between the tetrahedral and octahedral sublattices is assumed. These properties are explained in terms of the molecular field approximation.

The total exchange Hamiltonian can be divided as follows:

$$H=H_{\text{SX}}+H_{\text{DX}}+H_{\text{BX}}+H_{\text{anis}}+H_{s\text{-}d}\ , \tag{1}$$

where,

$$H_{\text{SX}}=-\sum_{\substack{i,j\\(i\neq j)}} J_{ij}^{\text{SX}}\mathbf{S}_i\cdot\mathbf{S}_j \tag{2}$$

represents the superexchange interaction of the type Co^{2+}-X-Co^{2+}, Cr^{n+}-X-Cr^{m+}, and Cr^{n+}-X-Co^{2+}, with the numbers of nearest neighbors $z_{AA}=4$, $z_{BB}=6$, and $z_{AB}=12$. These interactions are described by the exchange integrals J_{AA}, J_{BB}, and J_{AB}, respectively. We present the following equation:

$$H_{\text{DX}}=-\tfrac{1}{6}x_3(1-x_3)\sum_{\substack{i,j\\(i\neq j)}} b_{ij}\mathbf{S}_{B_i}\cdot\mathbf{S}_{B_j}\ , \tag{3}$$

which is the double-exchange contribution due to the Cr ions, where x_3 is the concentration of Cr^{3+} ions (normalized in such a way that $x_3+x_4=1$, where x_4 is the corresponding quantity for the Cr^{4+} ions) and b_{ij} is the hopping integral ($b_{ij}=\langle i\,|\,V\,|\,j\rangle$) between the atomic t_{2g} states $|\,i\rangle$ and $|\,j\rangle$ for neighbors i and j. The factor $x_3(1-x_3)$ expresses the probability of finding one Cr atom in the state Cr^{3+} and the neighboring one in the state Cr^{4+}. Additionally, the spin contribution from a hopping electron between two Cr ions is averaged among the fixed spins, so that the average spin per site is $\bar{S}_B=S_3x_3+S_4x_4=1.39$ corresponding to spins: $S_3=\frac{3}{2}$ for Cr^{3+} and $S_4=1$ for Cr^{4+} ($x_3=1.55$ and $x_4=0.45$). We note that

$$H_{\text{BX}}=\sum_{\substack{i,j\\(i\neq j)}} p_{ij}(\mathbf{S}_{B_i}\cdot\mathbf{S}_{B_j})^2 \tag{4}$$

describes the biquadratic-exchange contribution due to Cr ions, containing both the double-exchange and superexchange parts. This interaction will be neglected in the following analysis because there is no evidence of the noncollinearity of the spin structure.

$$H_{\text{anis}}=-D\sum_i (S_i^z)^2 \tag{5}$$

corresponds to the uniaxial anisotropy with the easy axis $\langle 100\rangle$, mainly due to Co^{2+} ions,

$$H_{s\text{-}d}=-J_{s\text{-}d}\sum_i \mathbf{S}_j\cdot\mathbf{s}_i \tag{6}$$

represents the s-d interaction due to the presence of holes in the p band of the anions X^{2-} and is caused by defects such as vacancies or the overlap of the bands.

C. Ground-state energy

By taking into account the above formulas one can calculate the ground-state energy in the compounds under study. For the quantitative formulation we begin with the classical expression for the ground-state energy (per formula unit), corresponding to the Hamiltonian of Eq. (1). It is given by

$$\begin{aligned}E_G=&-\mathbf{M}\cdot\mathbf{H}-D\cos^2(\theta-\theta_0)-J_{AA}z_{AA}x_A^2S_A^2\\&-J_{BB}z_{BB}S_B^2-J_{AB}z_{AB}X_A\mathbf{S}_A\cdot\mathbf{S}_B\ ,\end{aligned} \tag{7}$$

where $x_A=0.55$, $S_B=1.39$, and $S_A=1.5$. In Eq. (7) we neglected the terms of (3), (4), and (6).

D. Exchange integrals

In the spinels under study the B sites are occupied by two types of ions, Cr^{3+} and Cr^{4+}, while the A sites are occupied by Co^{2+} ions. We denote by B_3 and B_4 the sublattices occupied by the trivalent and tetravalent Cr ions, respectively. For simplicity we assume that the interactions J_{AB_3} and J_{AB_4} can be represented by a single average integral J_{AB}, and $J_{B_3B_3}$, $J_{B_4B_4}$, and $J_{B_3B_4}$ by J_{BB}. The experimental temperature dependence of χ_M^{-1} was used to determine J_{AA}, J_{BB}, and J_{AB}. The expression for the paramagnetic susceptibility for the two-sublattice model was obtained as follows. In the paramagnetic phase the magnetization of a sublattice is given by

$$M_i=(C_{M_i}/T_i)(H_i+H_{\mathrm{ext}}) \quad i=A,B \ , \tag{8a}$$

where

$$C_{M_i}=N_i g_i^2 \mu_B^2 S_i(S_i+1)/3k_B \ , \tag{8b}$$

C_{M_i} being the molar Curie constant of the sublattice, N_i $(=x_i N_A)$ is the number of given atoms per mole (where x_i is the concentration of atoms and N_A the Avogadro's number), g_i is the Landé g factor, S_i is the spin, H_i $(=\sum_i N_{ij}M_j)$ is the molecular field (N_{ij} are the molecular-field constants), and H_{ext} is the external field. The molecular-field constants N_{ij} are connected with the exchange integrals J_{ij} by equation

$$N_{ij}=2z_{ij}J_{ij}/N_j g_i g_j \mu_B^2 \ , \tag{9}$$

where z_{ij} is the number of nearest neighbors in the jth sublattice to an atom in the ith sublattice, N_j is the number of atoms per mole in the jth sublattice, g_i and g_j are the Landé factors for the ions in the ith and jth sublattice, respectively, and μ_B is the Bohr magneton.

The reciprocal molar susceptibility versus T can be given by relation

$$\frac{1}{\chi_M}=\frac{H_{\mathrm{ext}}}{\sum_i M_i}=\frac{T-\Theta_{\mathrm{CW}}}{C_M}-\frac{\sigma}{T-\Theta'} \ , \tag{10}$$

where

$$C_M=\sum C_{M_i}$$

(taken from experiment, $C_M=C_M^{\mathrm{expt}}$),

$$\sigma=\frac{C_A C_B}{C_M^3}\{C_A^2(N_{AA}-N_{AB})^2+C_B^2(N_{BB}-N_{AB})^2 -2C_A C_B[N_{AB}^2-(N_{AA}+N_{BB})N_{AB} +N_{AA}N_{BB}]\} \ , \tag{10a}$$

$$\Theta'=-\frac{C_A C_B}{C_M}(N_{AA}+N_{BB}-2N_{AB}) \ , \tag{10b}$$

$$\Theta_{\mathrm{CW}}=\frac{1}{C_M}(C_A^2 N_{AA}+C_B^2 N_{BB}+2C_A C_B N_{AB}) \ . \tag{10c}$$

From Eqs. (10a)–(10c), in which σ, Θ', and Θ_{CW} were obtained from the experimental curves of $\chi_M^{-1}=f(T)$ (see the example in Fig. 4), the constants N_{AA}, N_{AB}, and N_{BB} were determined. Then, using Eq. (9), we calculated the exchange integrals J_{ij}. Because the experimental values of the Curie constants turned out to be lower than the calculated ones from Eq. (8b) ($C_M^{\mathrm{expt}}=\alpha C_M^{\mathrm{calc}}$), calculations were taken $C_{M_i}^{\mathrm{expt}}$ values. The g_i factors have been taken from experiment[3,34] $g_A=g_{\mathrm{Co}^{2+}}=2.7$, $g_{B_4}=g_{\mathrm{Cr}^{4+}}=1.86$, and $g_{B_3}=g_{\mathrm{Cr}^{3+}}=2.0$. For the B sublattice the total g factor per site has been assumed to be equal $g_B=g_{B_3}x_3+g_{B_4}x_4=1.97$.

To provide a further check on the exchange integrals so obtained we used them to calculate the Curie temperature T_C and compared the result with experiment, using

$$T_C=-\tfrac{1}{2}(C_A N_{AA}+C_B N_{BB}) +\tfrac{1}{2}[(C_A N_{AA}-C_B N_{BB})^2+4C_A C_B N_{AB}^2]^{1/2} \ . \tag{11}$$

Divergence between the values of T_C^{calc} and T_C^{expt} was of the order of 5%.

The exchange integrals are presented in Fig. 8. The accuracy of their values has been estimated to be about ±10%. In all cases the exchange integrals J_{AA} between tetrahedral sites are positive, the integrals J_{BB} between octahedral sites are small and negative. The 120° interactions between the sublattices A and B represented by J_{AB} are negative. In the spinels under study the superexchange interactions Cr-X-Cr and Cr-X-X-Cr take place. The former can be positive and the latter negative.[3] There appears to be competition between the positive and negative exchange interactions, leading to a small negative value of J_{BB}. All the exchange integrals exhibit anomalous behavior in the critical region of $0.5<y<1.0$.

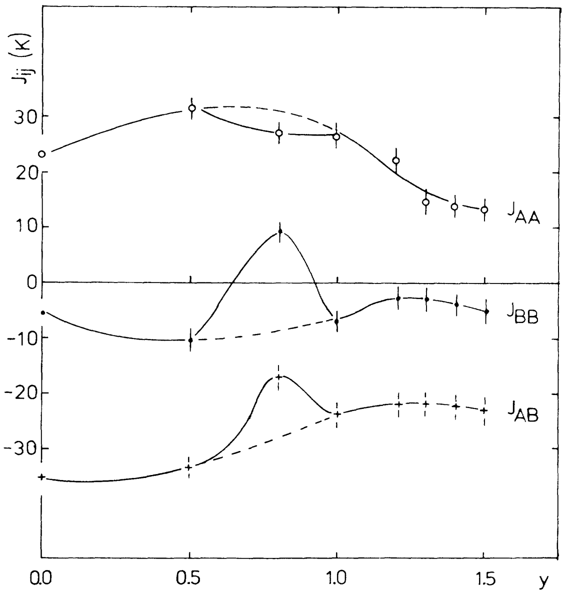

FIG. 8. The exchange integrals vs selenium concentration y: $J_{AA}(\mathrm{Co}^{2+}\text{-}X^{2-}\text{-}\mathrm{Co}^{2+})$, $J_{BB}(\mathrm{Cr}^{n+}\text{-}X^{2-}\text{-}\mathrm{Cr}^{m+})$, and $J_{AB}(\mathrm{Cr}^{n+}\text{-}X^{2-}\text{-}\mathrm{Co}^{2+})$.

The changes of the magnetic moment μ, the paramagnetic Curie-Weiss temperature Θ_{CW}, and the high-field susceptibility χ_{hf} (Ref. 35) caused by the variation of selenium concentration (y) follow from three reasons which are strongly connected to each other. They are the following:

(i) Substitution of S ions by the Se ions takes place in a statistical way and therefore the tetrahedral and octahedral surroundings are not equivalent to each other. Different values of electronegativity of anions (S and Se) and of their ionic radii may cause irregular changes in the ligand field in the crystal volume.

(ii) The bonds in these compounds are of intermediate character between ionic and covalent—as follows from the x-ray measurements.[10] Therefore, there probably occurs a transfer of a part of electrons from anions to cations, which causes a change of their valence. It leads to a change of indirect exchange interactions.

(iii) An inequality of ionic radii of anions causes an increase of the average distance between the magnetic ions (Co^{2+}, Cr^{3+}, and Cr^{4+})—the lattice parameter increases with increasing selenium concentration y. But, at the same time, the overlap of the orbitals in the interaction Cr^{n+}-X-Co^{2+} becomes greater, which causes an increase of indirect, antiferromagnetic interactions between these cations. It leads to the lowering of the total magnetic moment.

The greatest influence of these mechanisms on the magnetic behavior is observed for $y = 0.8$, where the greatest increase of the lattice parameter takes place. It is in agreement with the shape of the experimental dependence of μ, Θ_{CW}, and χ_{hf} on composition parameter y.

For larger concentrations of selenium ($y > 1.0$), the overlap of orbitals and the interaction between them become smaller and μ, Θ_{CW}, and χ_{hf} increase.

V. CONCLUDING REMARKS

In this paper the magnetic properties of the new ferrimagnetic spinel series with mixed anions have been described. From the interpretation scheme the effective exchange integrals between and inside the sublattices of Co and Cr ions for the nearest neighbors and the degree of mixing x_3:x_4 in the mixed-valent configuration $Cu^{+}_{0.45}Co^{2+}_{0.55}(Cr^{3+}_{x_3}Cr^{4+}_{x_4})_2S^{2-}_{4-y}Se^{2-}_{y}$ have been determined. In order to confirm this valence configuration, the low-temperature neutron diffraction experiment is being carried out. It will be subject of a separate publication. The studies of the transport properties are necessary to clarify the situation in the critical concentration range of y. They are under way and will be published later.

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