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Effect of double exchange on magnetic properties of $Cu_xZn_{1-x}Cr_2Se_4$

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The results of extensive studies of magnetic properties for the spinels $Cu_xZn_{1-x}Cr_2Se_4$ are summarized. They concern the isotherms of static magnetization in applied induction up to 14 T, the Néel temperature T_N (for $x \leq 0.1$) and the Curie temperature T_C (for $x \geq 0.2$), and the high-temperature susceptibility, all in the full concentration range $0 \leq x \leq 1$. We determine first the concentration ratio $[Cr^{4+}]$:$[Cr^{3+}]$ from the concentration (x) dependence of the saturation magnetization at low temperatures and show that each Cu atom introduced to the system produces on average one Cr^{4+} ion. This means that Cu is mainly monovalent and the double exchange between Cr^{3+}-Cr^{4+} pairs takes place. This prediction has been tested further by calculating the ground-state spin configuration characterized by conical $\theta(x)$ and spiral $\Phi(x)$ angles, as well as the high-temperature susceptibility with both double exchange and superexchange taken into account, and by comparing them subsequently with the experimental data. The biquadratic exchange contribution was also included and proved to be essential in bringing to close numerical agreement the theory and the experimental data. From this comparison we have determined the width of the $3d$ band due to Cr ions, which is $W_d = 0.63 \pm 0.05$ eV, and the biquadratic exchange constant $p = 0.41$ K. Additionally, we have determined the partial contributions to the $3d$-band width coming from the first three coordination spheres. Our analysis shows quantitatively that the double exchange depending strongly on Cu concentration drives the transition from helimagnetism at $x = 0$ through a conical structure to ferromagnetism at $x \geq 0.8$.

I. INTRODUCTION

The mixed spinels $Cu_xZn_{1-x}Cr_2Se_4$ are normal spinels with a strong preference of Cr ions to locate in the octahedral (B) positions. The stoichiometric compounds $ZnCr_2Se_4$ and $CuCr_2Se_4$ are, respectively, a semiconductor with magnetic spiral structure[1,2] (with spiral angle $\Phi = 42° \pm 1°$) and a metallic ferromagnet.[2] The Néel temperature of the former is $T_N = 20$ K while the Curie temperature of the latter is much higher and equal to $T_C = 460$ K. Therefore, the synthesis of mixed spinels $Cu_xZn_{1-x}Cr_2Se_4$ carried out before[3] has given us an opportunity to study the problem how the relatively strong ferromagnetic interactions set in as the copper concentration x increases.

Besides, there is a long-standing discussion in the literature concerning the valence states of Cu and Cr ions in $CuCr_2Se_4$. There are two principal models: the Goodenough model,[4] which assumes that those states are Cu^{2+} and Cr^{3+}, and the Lotgering model,[2,5] which assumes that the valencies are Cu^{+} and Cr^{4+} mixed with Cr^{3+}.

The various models are schematically represented in Fig. 1, where a scheme of electronic band structure determining the valency is given. More recent data,[6,7] particularly those concerning the direct spin polarization measurements by polarized neutrons[7] show that the Lotgering model is closer to reality, though a small negative contribution of Cu and Se to the polarization is observed.

In this paper we show that the studies of the mixed spinels $Cu_xZn_{1-x}Cr_2Se_4$ as a function of x provide an unambiguous distinction between various models presented in Fig. 1. In particular, it turns out that the magnetic properties of $Cu_xZn_{1-x}Cr_2Se_4$ can be explained consistently only if we assume that the average ratio $[Cu^{+}]$:$[Cr^{4+}]$ is about 1:1 when the data are fitted systematically in the full concentration range (cf. Fig. 4). There are significant fluctuations around this ratio for some samples because the compounds $Cu_xZn_{1-x}Cr_2Se_4$ for $0.1 \leq x \leq 0.9$ can be obtained only by a rapid quenching

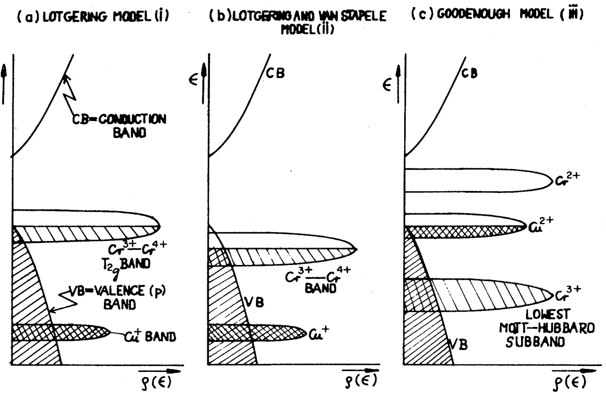

FIG. 1. Schematic representation of the electronic structure of $Cu_xZn_{1-x}Cr_2Se_4$ spinels. In the Lotgering model (i) Cu ions are monovalent and Cr^{3+}-Cr^{4+} configurations form a narrow band. In the Lotgering—Van Stapele model (ii) the anion band and 3*d* band overlap slightly due to Cr. In the Goodenough model (iii) Cu ions are divalent while Cr^3 ions fill the lowest Mott-Hubbard subband of 3*d* t_{2g} band.

of the freshly synthesized specimens.[3] For this purpose we have checked with the aid of the x-ray diffraction technique (Guinier camera and powder diffractometer) that the compounds were single phase [cf. Okońska-Kozłowska and Krok in Refs. 3 and 8(c)]. Additionally, we have measured the lattice constant of all compounds studied and showed that they obey the Vegard's law [cf. Fig. 1 in Ref. 8(c)]. Therefore, we believe that the data give a systematic trend that each Cu atom introduced to the compound creates, on average, one Cr^{4+} ion out of each Cr^{3+}. This result is in disagreement with our previous suggestion[8(a)] that chromium ions are in a 3 + state. The previous suggestion, however, was not a unique one, since the neutron diffraction was made on powder samples and therefore the information one gets is averaged and corresponds to the Cr^{3+}-Cr^{4+} mixture. To distinguish between Cr^{3+} and Cr^{4+} states, one needs to make measurements on monocrystalline samples with the use of the polarized neutron beam, as was done for $CuCr_2Se_4$ by Yamashita *et al.*,[7] whose results are in accord with our present analysis.

The purpose of this paper is twofold: firstly, to determine the valence of Cr ions from our studies of magnetic properties,[8] and secondly, to give a full quantitative account of the influence of the double exchange on a transition from helimagnetism in $ZnCr_2Se_4$ to ferromagnetism in $Cu_xZn_{1-x}Cr_2Se_4$ with $x \geq 0.8$, through a conical intermediate phase for $0.05 \leq x \leq 0.7$. In particular, we determine the bandwidth of the 3*d* band due to Cr ions and the double-exchange constants associated with them. Here we give only those results of our extensive experimental studies of the $Cu_xZn_{1-x}Cr_2Se_4$ systems[8] which are necessary to determine the fundamental characteristics of these compounds based on a theory presented below.

The main emphasis is placed on showing the full complexity (and attainability) of analysis of magnetic systems which exhibit both a transition from a noncollinear magnetic structure to a ferromagnetic one and, at the same time, a transition from semiconducting to highly correlated metallic phase.

The paper is organized as follows. In Sec. II we formulate the theoretical model which will be used in subsequent sections to interpret the data concerning $Cu_xZn_{1-x}Cr_2Se_4$ in the full concentration range. In Sec. III we give a short summary of the relevant experimental data and determine the ratio of mixing, $[Cr^{3+}]:[Cr^{4+}]$. In Sec. IV we determine the spiral $\Phi(x)$ and the conical $\Theta(x)$ angles as a function of x based on the minimization procedure for the ground-state energy. The biquadratic-exchange constant p and two of the first three spheres of coordinations contributions to the 3*d*-band width are obtained there from the comparison of the theory with experiment. In Sec. V we determine the contribution to the Curie-Weiss temperature coming from the superexchange and the double exchange, based on the data of high-temperature susceptibility. This allows for a calculation of the 3*d*-band width. Section VI contains a discussion and some specific questions still to be answered.

II. QUALITATIVE FEATURES OF THE THEORETICAL MODEL

The mixed spinels $Cu_xZn_{1-x}Cr_2Se_4$ offer a unique opportunity of studying the interrelation between the semiconductor-to-metal and the helimagnetism-to-ferromagnetism transitions. The situation is complex, however, because there exist various possibilities of interpretation of the electronic structure and the corresponding valencies of Cu and Cr cations. There are three main possibilities in explaining the properties of the systems $Cu_xZn_{1-x}Cr_2Se_4$ based on the proposals[2,4,5] made for $CuCr_2Se_4$, as is shown schematically in Fig. 1. They are the following ones:

(i) The Cu atoms introduced are monovalent. This means that each Cu^+ ion causes a change of valence $Cr^{3+} \rightarrow Cr^{4+}$ of one Cr^{3+} cation to attain the overall neutrality in the compound

$$Cu_x^{+}Zn_{1-x}^{2+}Cr_{2-x}^{3+}Cr_x^{4+}Se_4^{2-} .$$

In this case if the anion p band is full, then the interaction between Cr^{3+} and Cr^{4+} must be ferromagnetic and grow strongly with the concentration x as the Curie temperature T_C and the Curie-Weiss temperature Θ_{CW} do. This is the so-called Lotgering model.[2]

(ii) Each Cu atom is monovalent but there are a number of holes in the anion band of selenium. They introduce *p*-type carriers and besides, mediate the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions between the Cr ions. In addition to that, a number of Cr^{2+} ions or vacancies must also appear to fulfill the charge neutrality. This is the so-called Lotgering and Van Stapele model.[5]

(iii) The divalent Cu atoms and the holes coming from the 3*d* (Ref. 9) configuration of Cu^{2+} are coupled antiparallel to the remaining Cr^{3+} ions. In addition, it introduces an RKKY-type interaction between the Cr^{3+} ions which should be ferromagnetic and give a contribution to T_C and Θ_{CW} of the order of 300 K for higher x. This is the so-called Goodenough model.[4]

Our data for $Cu_xZn_{1-x}Cr_2Se_4$ allow for an evaluation of each of these proposals in the following way. Firstly, the compounds for $x \leq 0.2$ exhibit a semiconducting behavior even though the conductivity, which is p type, drops 3—4 orders of magnitude.[9] This means that the models (ii) and (iii) cannot be entirely correct since they would lead to a metallic behavior above a relatively low concentration of Cu. Conversely, the conductivity introduced by the holes corresponding to Cr^{4+} [model (i)] configuration may appear above the percolation threshold $x_c \simeq 0.15$—0.2 since the lowest Mott-Hubbard subband of the t_{2g} band due to Cr^{3+} ions can be quite narrow and therefore described by the overlap of the wave functions between the nearest neighbors. However, this concept needs further testing through conductivity measurements in the low-temperature regime, for which the hopping of the Cr^{4+} holes may be predicted.

Secondly, both models (ii) and (iii) yield an indirect exchange between Cr^{n+} ions via the conduction electrons. Although the indirect exchange may not be simply a RKKY type of interaction in the case of model (iii)—since the holes are in $3d$ band—we expect that it should lead to an oscillating behavior[10] of $\Theta_{\rm CW}$ vs x. Instead, a steady growth of both T_C and $\Theta_{\rm CW}$ is observed. The growth with x is approximately parabolic and may be related to the concentration dependence of the $3d$ t_{2g} band energy which is $\sim x_4(1-x_4)$, with x_4 being the atomic concentration of Cr^{4+} ions.

Thirdly, it is observed (cf. Fig. 2) that the values T_C and $\Theta_{\rm CW}$ are close for $x \geq 0.2$. Hence the contributions to all exchange integrals must act the same way, i.e., increase a tendency towards ferromagnetism. This again cannot be accounted for within the RKKY type of interaction.

Finally, direct support for the presence of Cr^{4+} ions in $CuCr_2Se_4$ comes from the measurements of partial polarizations of the ions involved done with the help of the polarized neutron scattering technique[7] as well as from the observation of Cr lines with the help of NMR technique.[11] However, a certain amount[12] of polarization coming from Cu^{2+} (Refs. 7 and 11) and from anions[7] is observed.

We conclude from the foregoing discussion that the main contribution to steady growth of T_C and $\Theta_{\rm CW}$ with x cannot be attributed to the RKKY interactions. The key suggestion of this work is as follows: the double-exchange interaction between Cr^{3+} and Cr^{4+} is responsible for the strong ferromagnetic interaction setting in the system with increasing copper concentration. This suggestion has been made before by Lotgering.[2,4] However, in what follows we build a theory which can be tested quantitatively. Additionally, from the comparison with the experiment we determine the microscopic parameters for those systems such as the bandwidth of the $3d$ Cr band and exchange constants of interactions between the first three coordination spheres.

The total exchange Hamiltonian can be broken down as follows:

$$H = H_{\rm sex} + H_{\rm dex} + H_{\rm bex} + H_R + H_{\rm anis} + H_{s\text{-}d} , \tag{2.1}$$

where the terms are given by Eqs. (2.2)—(2.7):

$$H_{\rm sex} = -\sum_{\substack{i,j \\ i\neq j}} J_{ij}^{\rm sex} \vec{S}_i \cdot \vec{S}_j , \tag{2.2}$$

represents the superexchange Cr^{n+}-Se-Cr^{m+} and Cr^{m+}-Se-Se-Cr^{n+} interactions,[13] with $z_{aa}=6$, $z_{ab}=12$, and $z_{ac}=12$ numbers of nearest neighbors in the first, second, and third Cr-Cr coordination spheres. The values of the first three integrals J_{ij} are taken from Ref. 8(a) as $J_{aa}z_{aa}=60$ K, $J_{ab}z_{ab}=175$ K, and $J_{ac}z_{ac}=-60$ K.

The double-exchange contribution[14] is

$$H_{\rm dex} = -\tfrac{1}{6} x_3(1-x_3) \sum_{\substack{i,j \\ i\neq j}} b_{ij} \vec{S}_i \cdot \vec{S}_j , \tag{2.3}$$

with x_3 being the concentration of Cr^{3+} ions (normalized in such way that $x_3+x_4=1$, where x_4 is the corresponding quantity for Cr^{4+} ions), and b_{ij} is the hopping integral ($b_{ij}=\langle i \mid V \mid j \rangle$) between the atomic t_{2g} states $\mid i \rangle$ and $\mid j \rangle$ for neighbors $\langle i,j \rangle$. However, our approach differs from that given in Ref. 14 in two respects. Namely, we take the band factor as $\sim x_3(1-x_3)$ corresponding to probability of finding one atom in the state Cr^{3+} and the neighboring one in the state Cr^{4+}. Additionally, we take the hopping electron between two Cr ions on the same footing as the remaining ones, i.e., we assume that the total spin per site $\bar{S}=\frac{3}{2}x_3+1x_4$, corresponding to spins $S_3=\frac{3}{2}$ and $S_4=1$ of Cr^{3+} and Cr^{4+}, respectively. This is because all t_{2g} electrons are indistinguishable quantum mechanically, and Cr cations supply both localized and itinerant $3d$ moments when Cr^{4+} cations are present. The condition of applicability of the double-exchange mechanism is $W_d > J_{d\text{-}d}$, where W_d is the bandwidth of the $3d$ t_{2g} band and $J_{d\text{-}d}$ is the value of the intra-atomic d-d exchange (the Hund's-rule coupling constant).

We have

$$H_{\rm bex} = \sum_{\substack{i,j \\ i\neq j}} p_{ij} (\vec{S}_i \cdot \vec{S}_j)^2 , \tag{2.4}$$

which describes the biquadratic-exchange contribution, containing both the double-exchange[14] and superexchange[15] parts. Next,

$$H_R = -\sum_{\substack{i,j \\ i\neq j}} J_{ij}^{R} \vec{S}_i \cdot \vec{S}_j , \tag{2.5}$$

represents the residual (e.g., RKKY) type of interaction due to a presence of holes in the $3d$ Cu^{2+} band and/or holes in the anion Se^{2-} p band, and caused by defects such as vacancies or overlap of the bands. We have

$$H_{\rm anis} = -D \sum_i (S_i^z)^2 , \tag{2.6}$$

which is the uniaxial anisotropy with easy axis $\langle 111 \rangle$ due to the small tetragonal distortion. It will be neglected in our analysis. Finally,

$$H_{s\text{-}d} = -J_{s\text{-}d} \sum_i \vec{S}_i \cdot \vec{s}_i , \tag{2.7}$$

represents the s-d interaction between the residual holes (Cu^{2+}) or of in the anion p band. The low value of the

Curie constant C_M observed (cf. Fig. 2) shows that $J_{s\text{-}d} < 0$. This interaction will be neglected in the following analysis but its effect will be estimated in Sec. VI.

Taking (2.1)–(2.7) we can calculate the ground-state and thermodynamical properties. This is what we are going to do next after reviewing briefly the experimental results.[8]

III. SUMMARY OF THE EXPERIMENTAL RESULTS AND DETERMINATION OF [Cr^{4+}]:[Cr^{3+}] RATIO

The brief summary of various magnetic properties as a function of the copper concentration x is given in Fig. 2. We plotted there the Néel temperature T_N (for $x < 0.2$) and the Curie temperature T_C (for $x \geq 0.2$), the Curie-Weiss temperature $\Theta_{\rm CW}$, the Curie constant C_M (both from the Curie-Weiss law in the high-temperature regime), and saturation magnetization M_s in the Bohr magnetons as determined at temperature $T=4.2$ K. We see that there is a steady increase of both T_C and $\Theta_{\rm CW}$ with growing x. Additionally, M_s decreases for $x \leq 0.8$ and C_M has a pronounced minimum at about $x=0.2$.

To show a gradual change of the transition from a spiral structure at $x=0$ to the ferromagnetic structure at $x \geq 0.8$ via a conical structure for $0.05 \lesssim x \leq 0.7$, we have plotted in Figs. 3(a)–3(d) the isotherms of magnetization in the static applied induction up to 14 T and for $x=0.01$, 0.05, 0.5, 0.7, and 0.8. We do not reproduce the $M(B)$ curves for other concentrations here but it turns out that for $x \geq 0.05$ there appears a substantial curvature in the medium-field range ($0.0 \lesssim B \lesssim 5T$). An extrapolation to $B=0$ of the curves for $x \geq 0.05$ gives a nonzero spontaneous magnetization, which means that above this concentration a ferromagnetic component appears in the system.

Next, we determine the [Cr^{4+}]:[Cr^{3+}] ratio. Namely, we assume that we have certain concentrations x_3 and x_4 of Cr^{3+} and Cr^{4+} ions, respectively. The magnetic moment per formula is given by $M=2(g_4x_4+\frac{3}{2}g_3x_3)$, where we assume that $x_3+x_4=1$, and $g_4=1.86$ and $g_3=2.0$ are the Landé factors for Cr^{4+} and Cr^{3+}, respectively. In Fig. 4 the open circles represent the values of x_4 vs x calculated this way. The straight line is the line $x_4=a_0x+b_0$ fitted through those points. From the fitting we get the values of parameters $a_0=0.51\pm0.05$, and $b_0=0.074\pm0.025$. The dashed lines represent the maximal estimated error of the fitting. From the value of the parameter a_0 we see that the dependence of $x_4(x)$ is on average such that the copper atom introduced to the system changes one Cr^{3+} ion into Cr^{4+}. In other words, the average formula is Cu$^+{}_x$Cr$^{3+}{}_{2-x}$Cr$^{4+}{}_x$Se$^{2-}{}_4$. Obviously, there is a substantial scattering of the points but the trend fits surprisingly well into the Lotgering suggestion[2,4] made for CuCr$_2$Se$_4$, and verified here in the full range of x. Additionally, there is $(7.4\pm2.5)\%$ of Cr^{4+} ions in polycrystalline ZnCr$_2$Se$_4$ samples synthesized and studied by us.

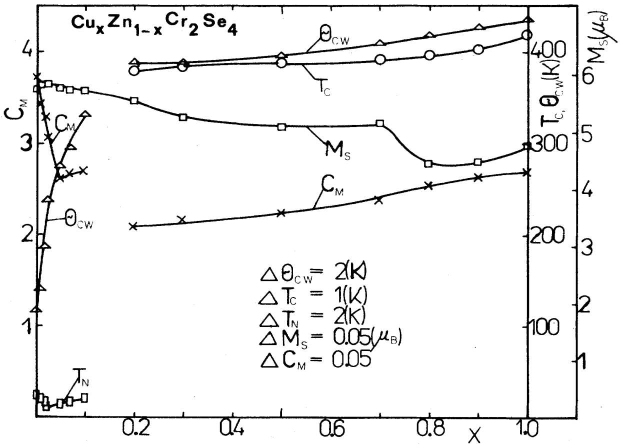

FIG. 2. Summary of experimental data for Cu$_x$Zn$_{1-x}$Cr$_2$Se$_4$ in the full concentration range x. The presented curves are the saturation magnetization M_s (□) at 4.2 K in the Bohr magnetons per formula, the transition temperatures T_N (▯) (for $x \leq 0.1$) and T_c (○) (for $x \geq 0.2$), the Curie-Weiss temperature $\Theta_{\rm CW}$ (△), and the molar Curie constant (×).

For the sake of completeness and reference in the detailed numerical analysis following, we have reproduced in Table I the values of the most important quantities concerning the samples studied by us. The quantity $S_{\rm eff}$ is the effective spin per Cr atom determined from the Curie constant. It will be discussed in Sec. V.

IV. SPIN CONFIGURATION IN THE GROUND STATE

For the quantitative formulation we begin with the classical expression for the ground-state energy (per spin), corresponding to the Hamiltonian (2.1). It is given by[15,8(a)]

$$\begin{aligned}E_G = & -MH - D\cos^2(\theta-\theta_0) \\ & -\frac{1}{2}\frac{M^2}{C_M}(\bar{J}_{aa}+\bar{J}_{ab}\cos\Phi+\bar{J}_{ac}\cos 2\Phi)\sin^2\theta \\ & +(\bar{J}_{aa}+\bar{J}_{ab}+\bar{J}_{ac})\cos^2\theta \\ & +\frac{M^2}{C_M}p\bar{S}^2\{1+2[1+2\sin^2\theta(\cos\phi-1)]^2\}\ , \qquad (4.1)\end{aligned}$$

where θ and Φ are the polar or conical (measured with respect to the applied direction which is along the z axis) and spiral angles, p is the amount of biquadratic exchange ($p=p_{aa}z_{aa}$), taken as nonzero only between the nearest neighbors and concentration independent. The effective exchange constants are

$$\bar{J}_{aa}=J_{aa}z_{aa}+\tfrac{1}{6}b_{aa}z_{aa}x_3(1-x_3)\ , \qquad (4.2)$$

$$\bar{J}_{ab}=J_{ab}z_{ab}+\tfrac{1}{6}b_{ab}z_{ab}x_3(1-x_3)\ , \qquad (4.3)$$

$$\bar{J}_{ac}=J_{ac}z_{ac}+\tfrac{1}{6}b_{ac}z_{ac}x_3(1-x_3)\ . \qquad (4.4)$$

In expression (4.1) we have neglected the terms (2.5) and (2.7). Additionally, in what follows we neglect the anisotropy term in (4.1) and set the applied field $H=0$.

Next we minimize (4.1) with respect to $\phi=\phi(x)$ and $\theta=\theta(x)$. From the equation $\partial E_G/\partial\phi=0$ we get either $\sin\theta=0$, or for $\theta\neq0$

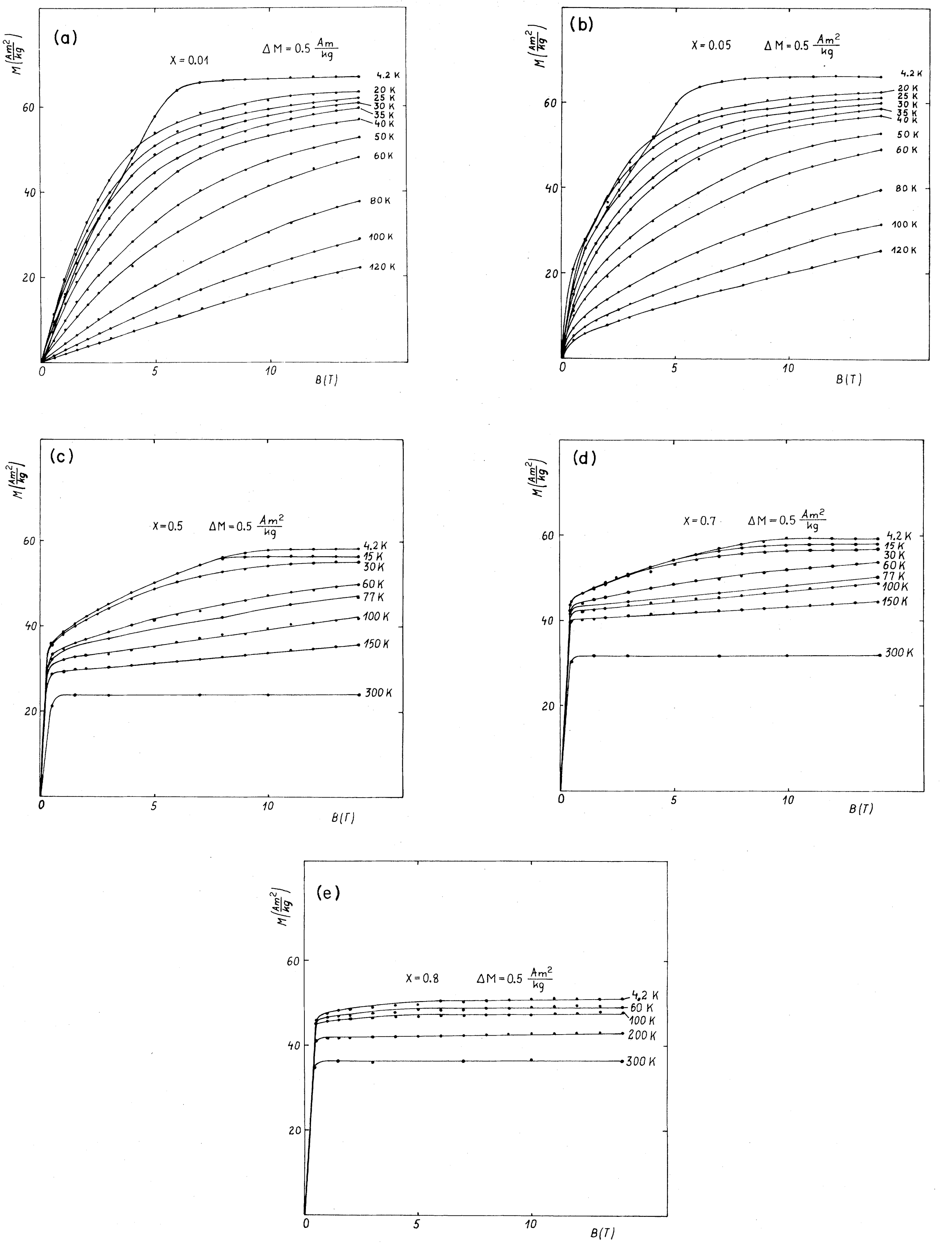

FIG. 3. Magnetization isotherms $M(B)$ for the samples chosen as representative: (a) $x=0.01$, (b) $x=0.05$, (c) $x=0.5$, (d) $x=0.7$, (e) $x=0.8$.

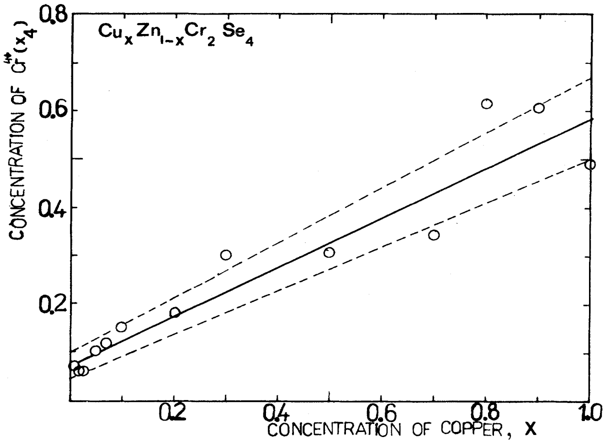

FIG. 4. Portion x_4 of Cr^{4+} ions as a function of copper concentration x. The solid line represents the one fitted through the points which were obtained from M_s data at $T=4.2$ K. The dashed line gives an estimate of the accuracy of fitting.

$$\tfrac{1}{2}(\bar{J}_{ab}\sin\phi+2\bar{J}_{ac}\sin 2\phi) -4p\bar{S}^2\sin\phi[1+\sin^2\theta(\cos\phi-1)]=0\,. \quad (4.5)$$

The analogical equation $\partial E/\partial\theta=0$ yields either $\cos\theta=0$, or for $\theta\neq\pi/2$

$$1+\sin^2\theta(\cos\Phi-1)=\frac{\bar{J}_{ab}(\cos\Phi-1)+\bar{J}_{ac}(\cos 2\Phi-1)}{8p\bar{S}^2}\,. \quad (4.6)$$

The spiral structure corresponds to solution $\theta=\pi/2$ and $0<\Phi<\pi$. For the conical structure both $0<\theta<\pi/2$ and $0<\Phi<\pi$.

For the conical structure we can substitute the quantity $1+\sin^2\theta(\cos\Phi-1)$ given by Eq. (4.6) into (4.5). We get then the equation for Φ

$$\tfrac{1}{2}\bar{J}_{ab}+2\bar{J}_{ac}\cos\Phi-\bar{J}_{ab}(\cos\Phi-1)-\bar{J}_{ac}(\cos 2\Phi-1)=0\,, \quad (4.7a)$$

which can be solved analytically for $\cos\phi$. The result is

$$\cos\Phi=\frac{1}{2}-\frac{\bar{J}_{ab}}{4\bar{J}_{ac}}+\left[\frac{5}{4}\left[\frac{\bar{J}_{ac}}{\bar{J}_{ab}}\right]^2+\frac{1}{2}\frac{\bar{J}_{ab}}{\bar{J}_{ac}}+\left[\frac{\bar{J}_{ab}}{4\bar{J}_{ac}}\right]^2\right]^{1/2}. \quad (4.7b)$$

We have chosen the root for which $\cos\Phi>0$ since $\Phi<\pi/2$. This result, when substituted to (4.6) gives

$$\sin\theta=\left[\frac{\bar{J}_{ab}(\cos\Phi-1)+\bar{J}_{ac}(\cos 2\Phi-1)-8p\bar{S}^2}{8p\bar{S}^2(\cos\Phi-1)}\right]^{1/2}. \quad (4.7c)$$

The procedure of determining $\theta(x)$ and $\Phi(x)$ is as follows. For $x=0$, i.e., for $ZnCr_2Se_4$, we take values[13] $\theta=90°$, $\phi=42°$, and the effective exchange integrals $\bar{J}_{aa}=60$ K, $\bar{J}_{ab}=175$ K, and $\bar{J}_{ac}=-60$ K as obtained previously.[8(a)] These values when substituted into (4.7c) give $p=0.41$ K. Additionally, the spiral angle for $x=0.025$ was found to be[8(b)] $39°\pm1°$. From this we get the ratio $\bar{J}_{ab}/\bar{J}_{ac}\,|_{x=0.025}=-3.13$. Finally, from the magnetization curves we draw the conclusion that for $x=0.80$ $\Phi=0$, which gives $\bar{J}_{ab}/\bar{J}_{ac}\,|_{x=0.8}=-4$. The known values of Φ in the three cases ($x=0$, 0.025, and 0.8) determine $\Phi(x)$ and $\theta(x)$ in the full concentration range. The corresponding curves are drawn in Fig. 5. Furthermore, the values of hopping integrals $B_{ab}=z_{ab}b_{ab}$ and $B_{ac}=b_{ac}z_{ac}$ are then

$$B_{ab}=673.2$$

and (4.8)

$$B_{ac}=226.2$$

(in units of K). These values do not permit us to draw a

TABLE I. Basic experimental data used in the following in order to determine the microscopic parameters (exchange integrals and the width of 3d band).

x	M_s (μ_B)	x_4	T_N (K)	T_c (K)	Θ_{CW} (K)	C_M (K mole^{-1})	S_{eff}	Angle of spiral Φ
0.0	5.74	0.074	22		118	3.74	1.500	42°±1°
0.01	5.82	0.071	20		142	3.43	1.454	
0.02	5.86	0.063	16		188	3.29	1.413	
0.025	5.85	0.063	10		240	3.03	1.342	39°±1°
0.05	5.74	0.102	14		276	2.60	1.237	
0.07	5.74	0.118	16		296	2.67	1.266	
0.1	5.74	0.126	20		332	2.70	1.279	
0.2	5.53	0.181		377	388	2.12	1.126	
0.3	5.25	0.299		382	391	2.17	1.203	
0.5	5.08	0.307		390	396	2.31	1.253	
0.7	5.14	0.339		395	411	2.41	1.303	
0.8	4.42	0.614		404	418	2.55	1.511	0°
0.9	4.44	0.606		408	427	2.63	1.527	
1.0	4.76	0.488		416	436	2.70	1.490	

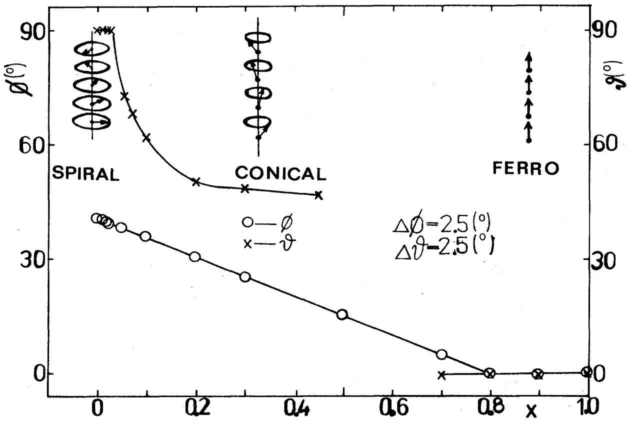

FIG. 5. Concentration x dependence of the spiral Φ and the conical Θ angles. Note the transitions from helical to conical phase at $x=0.05$, and from the conical to ferromagnetic phase for $x \simeq 0.8$. The function $\Phi(x)$ is nonlinear in x at the lowest concentrations.

conclusion about the bandwidth of the 3d Cr band because the dominant hopping integral B_{aa} is still unknown. This will be done in the next section.

The dependences $\theta(x)$ and $\Phi(x)$ drawn in Fig. 5 represent the spin configuration in the full concentration range. The spiral angle changes linearly with x, while there are two characteristic points for $\theta(x)$: The conical structure is predicted to play a role starting from $x=0.05$, in agreement with the change of character of the field dependence of the macroscopic magnetization (cf. Fig. 3). Furthermore, there should be a second singular point of $\theta(x)$ for $0.5<x<0.7$. Unfortunately, no experimental results are available in this concentration range. The ratios $x_4{:}x_3$ taken in order to draw the curves in Fig. 5 are those obtained from the fitted curve, i.e., $x_4=0.51x+0.074$ (cf. Fig. 4).

V. HIGH-TEMPERATURE SUSCEPTIBILITY

A. High-temperature expansion

Before analyzing the data of the high-temperature susceptibility, we derive the corresponding formula with the help of the high-temperature expansion. We start from the exact expression for the susceptibility

$$\chi=\frac{(g\mu_B)^2}{k_B T}\frac{1}{V}\sum_{i,j}\langle S_i^z S_j^z\rangle , \tag{5.1}$$

where V is the volume of the system. In the asymptotic region $\beta \equiv 1/k_B T \rightarrow 0$ we have

$$\langle S_i^z S_j^z\rangle=\frac{\langle S_i^z S_j^z\rangle_\infty-\beta\langle S_i^z S_j^z H\rangle_\infty}{1-\beta\langle H\rangle_\infty} , \tag{5.2}$$

where $\langle\ \rangle_\infty$ means the average taken at $\beta=0$ ($T=\infty$). Calculating the traces of the products of spin operators[16] we get

$$\langle S_i^z S_j^z\rangle_\infty=\delta_{ij}\tfrac{1}{3}X , \tag{5.3}$$

$$\langle S_i^z S_j^z(H-H_{\mathrm{b\,ex}})\rangle_\infty=-\tfrac{2}{9}X[J_{ij}^{\mathrm{s\,ex}}+\tfrac{1}{6}x_3(1-x_3)b_{ij}+J_{ij}^R] , \tag{5.4}$$

$$\langle S_i^z S_j^z H_{\mathrm{b\,ex}}\rangle_\infty=\delta_{ij}X^2\sum_{l(i)}p_{li}[\tfrac{2}{45}(8X-1)+\tfrac{1}{9}X(N-2)] , \tag{5.5}$$

and

$$\langle H\rangle_\infty=\langle H_{\mathrm{b\,ex}}\rangle_\infty=\tfrac{1}{3}NX^2\sum_{l(i)}p_{li} ,$$

where we have neglected again the anisotropy and s-d terms. Additionally, since in our case we have a mixture of spins due to the presence of both Cr^{4+} and Cr^{3+} we should set

$$X=2x_4+\tfrac{3}{2}(\tfrac{3}{2}+1)x_3 . \tag{5.6}$$

The expression for the susceptibility up to order $1/T$ can be written as

$$\chi=C_M\Bigg/\left[T-\frac{1}{k_B}\left[\langle H\rangle_\infty-\frac{\sum_{i,j}\langle S_i^z S_j^z H\rangle_\infty}{NX/3}\right]\right] , \tag{5.7}$$

where

$$C_M=\frac{1}{3}\frac{(g\mu_B)^2}{k_B}\frac{N}{V}X \tag{5.8}$$

is the Curie constant, and

$$\Theta_{\mathrm{CW}}=\frac{1}{k_B}\left[\langle H\rangle_\infty-\frac{\sum_{i,j}\langle S_i^z S_j^z H\rangle_\infty}{XN/3}\right] , \tag{5.9}$$

is the effective Curie-Weiss temperature. Substituting (5.3)–(5.5) into (5.2) we get

$$\Theta_{\mathrm{CW}}=\Theta_{\mathrm{s\,ex}}+\Theta_{\mathrm{d\,ex}}+\Theta_{\mathrm{b\,ex}}+\Theta_R , \tag{5.10}$$

where the contribution coming from the various exchange mechanisms are

$$\Theta_{\mathrm{s\,ex}}=\tfrac{2}{3}X\sum_p J_p^{\mathrm{s\,ex}}z_p , \tag{5.11}$$

$$\Theta_{\mathrm{d\,ex}}=\tfrac{1}{9}Xx_3(1-x_3)\sum_p b_p z_p \equiv \tfrac{1}{9}XBX_3(1-X_3) , \tag{5.12}$$

$$\Theta_{\mathrm{b\,ex}}=\tfrac{2}{5}X^2\sum_q p_q z_q\left[1-\frac{1}{3X}\right] , \tag{5.13}$$

and

$$\Theta_R=\tfrac{2}{3}X\sum_p J_p^R z_p . \tag{5.14}$$

The summations over p or q mean the summation over the consecutive coordination spheres, each of them containing z_p neighbors of a given central atom.

B. Comparison with experimental data

A method of the further analysis is as follows. Firstly, since the biquadratic exchange constant p is small, we assume it is constant in the whole concentration range. Secondly, we take p_q as nonzero only between the nearest neighbors ($z_{aa}=6$). Thirdly, to check whether the double-exchange mechanism gives consistent results we have used the experimentally determined values of Θ_{CW} as the input data in determining value of $B=\sum_p b_p z_p$ to see if it depends on concentration x of copper. In doing so we have neglected the contributions Θ_R and $\Theta_{\mathrm{b\,ex}}$. This oversimplification should give reasonable results for B at least for larger x when the strong and predominating ferromagnetic double exchange is taking place.

The results of such an analysis are presented in Table II. The value of Θ_{CW} was taken as

$$\Theta_{\mathrm{CW}}=\tfrac{4}{15}X\Theta_{\mathrm{Zn}}+\tfrac{1}{9}x_3(1-x_3)XB\ ,$$

where Θ_{Zn} was taken from (Ref. 13) and equal to 118 K. The consistent values of B are obtained for $x>0.2$. Therefore, we have taken as value of B the value averaged for the samples with $x>0.2$. We then get $B=4140\pm200$ K. This value was used in order to obtain the contribution to Θ_{CW} coming from the residual exchange (Θ_R). The value of $\Theta_{\mathrm{b\,ex}}$ was calculated taking the value of p determined previously. Both the fitted value (cf. Fig. 4) of $x_4=0.51x+0.074$ and the value of x_4 determined from M_s (cf. Table I) were taken for a comparison.

From the numbers presented in Table II we draw the following conclusion. The value of B for $x\le 0.2$ must be anomalously large in order to explain the trend of the data for Θ_{CW}. Besides, at the lowest concentrations of copper ($x\le 0.02$) the residual contribution Θ_R is also quite large and almost compensates the contribution $\Theta_{\mathrm{d\,ex}}$. This means that either the double-exchange mechanism is not effective at lowest concentrations, or there is an additional mechanism of interaction present which gives a contribution to Θ_{CW} comparable to or larger than $\Theta_{\mathrm{d\,ex}}$, or both. We are inclined to believe that both statements can be true. In other words, for low concentration $x\le 0.02$ a small number of holes in Cu^{2+} configuration and/or in the anion band can create a RKKY-type interaction which can produce a ferromagnetic contribution of the same order or even larger than that of the double exchange ($\Theta_{\mathrm{d\,ex}}$) if the value of $B=4140$ K is taken (cf. also the discussion in Sec. VI).

Additional evidence for the existence of holes with their spins antialigned with those of Cr^{n+} comes from the existence of localized-moment compensation which can be determined from the concentration dependence of the molar Curie constant C_M. This is shown in Fig. 6. In this figure we have drawn the experimentally determined data of C_M together with the theoretical prediction basing on our model, with Cr^{4+} concentration x_4 taken from the fitting the M_s data. One sees that there is a pronounced deep in the experimentally determined value of C_M which cannot be accounted for within the present model, neglecting the holes antialigned to Cr ions.

We should point out that if all Cr ions were Cr^{3+} then the Curie constant should have been equal to 3.75 K/mole. Conversely, if the ratio $[\mathrm{Cr}^{3+}]$:$[\mathrm{Cr}^{4+}]$ is 1:1 then $C_M=2.74$ K/mole. The latter value coincides with what we have found out experimentally for $\mathrm{CuCr_2Se_4}$. To estimate the deviation of the value of effective spin S_{eff} from that given by the one in our model ($S_{\mathrm{eff}}\rightarrow\frac{3}{2}x_3+x_4$), we have extracted the value of S_{eff} writing down the corresponding formula for C_M in terms of S_{eff}

$$C_M=\frac{\mu_B^2 N_{\mathrm{AV}}}{3k_B}\left[x_4\left(S_{\mathrm{eff}}-\tfrac{1}{2}\right)\left(S_{\mathrm{eff}}+\tfrac{1}{2}\right)g_4^2 + x_3 S_{\mathrm{eff}}(S_{\mathrm{eff}}+1)g_3^2\right]\ , \qquad (5.15)$$

where N_{AV} is Avogadro's number, and S_{eff} is the effective spin per Cr^{3+} ion. The value of $S_{\mathrm{eff}}(x)$ is given in Fig. 6. S_{eff} should be equal to $\frac{3}{2}$ if there were no compensation of

TABLE II. Contributions to the effective Curie-Weiss temperature Θ_{CW} coming from various exchange interactions [cf. Eq. (5.10)], and the value of B [cf. Eq. (5.12)].

		$x_4=0.51x+0.074$				x_4 from M_s data			
x	B (K)	$\Theta_{\mathrm{s\,ex}}$ (K)	$\Theta_{\mathrm{d\,ex}}$ (K)	$\Theta_{\mathrm{b\,ex}}$ (K)	Θ_R (K)	$\Theta_{\mathrm{s\,ex}}$ (K)	$\Theta_{\mathrm{d\,ex}}$ (K)	$\Theta_{\mathrm{b\,ex}}$ (K)	Θ_R (K)
0		113.9	114.1	11.71	−121.7	118.0		11.7	
0.01	12864	113.6	121.0	11.6	−104.2	114.2	116.0	11.6	−99.9
0.02	17558	113.4	125.8	11.6	−62.8	114.5	104.2	11.6	−42.3
0.025	24083	113.2	131.4	11.5	−16.2	114.5	104.2	11.55	+9.8
0.05	16500	112.5	146.8	11.4	+5.3	112.3	159.3	11.4	−7.0
0.07	12978	112.0	159.8	11.3	+13.0	111.4	178.6	11.3	−5.3
0.1	11162	111.1	177.7	11.1	+32.0	110.1	188.3	11.1	+22.5
0.2	7661	108.1	229.5	10.5	39.8	108.0	246.2	10.6	+23.5
0.3	5668	105.5	270.7	9.9	4.9	101.6	327.4	10.0	−48.0
0.5	4217	99.8	322.4	8.9	−35.1	101.0	331.6	8.9	−44.9
0.7	3953	94.3	337.9	7.8	−29.0	99.4	343.3	7.8	−39.5
0.8	3988	91.5	333.9	7.4	−14.7	84.3	308.0	7.4	+18.4
0.9	4141	88.7	322.6	6.9	+8.9	84.6	311.8	6.9	+23.7
1.0	4391	85.8	304.8	6.4	+38.9	90.0	339.8	6.4	−0.3

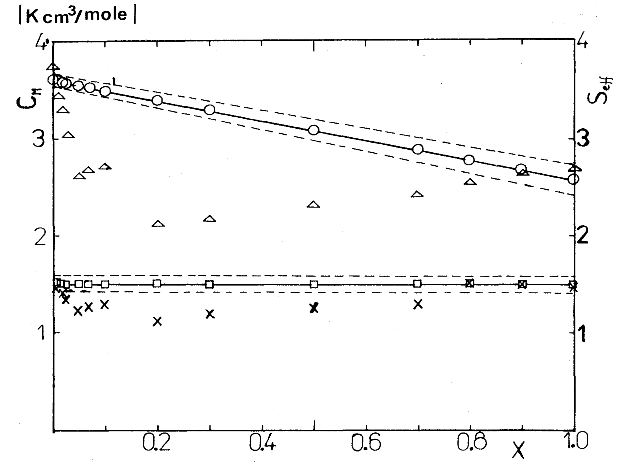

FIG. 6. Molar Curie constant vs x: experimental points (△) and the values determined theoretically based on the law $x_4=0.51x+0.074$ (○). The dashed lines give an estimate of error coming from the accuracy of fitting shown in Fig. 4. The lower curves represent the effective spin of Cr^{3+} as determined from Eq. (5.15) (×) and from our theory.

the Cr spins. Instead, the obtained values of $S_{\rm eff}$ fall below 1.2 for $x=0.2$, which gives about 25% less than expected. This shows that a certain number of compensating spins is present in $Cu_xZn_{1-x}Cr_2Se_4$ for $x\le 0.8$. The other possibility is that there is a degree of canting between the neighboring Cr^{3+}-Cr^{4+} ions due to the presence of the short-range order in the paramagnetic phase since the hopping of electrons in the d band correlates strongly with their spins. This effect has not been included in the model of the double exchange employed here.[14] The detailed discussion of the problem of the anomalous behavior of $C_M(x)$ is given in the next section.

Knowing the value of $B=B_{aa}+B_{ab}+B_{ac}=z_{aa}b_{aa}+z_{ab}b_{ab}+z_{ac}b_{ac}$, we can get B_{aa} since B_{ab} and B_{ac} have been found before [cf. Eq. (4.8)]. We get $B_{aa}=3240\pm200$ K. The bandwidth of the $3d$ t_{2g} band due to Cr ions is then $W_d=2B=8280\pm400$ K$\simeq$0.63$\pm$0.05 eV. This is a fundamental parameter of the electronic structure. It has been found from an interpretation scheme of our magnetic measurements. Furthermore, we have determined the hopping integrals b_{ij} between the pairs of sites from first, second, and third coordination spheres. They are $b_{aa}\simeq 540\pm35$ K, $b_{ab}\simeq 56$ K, and $b_{ac}=18.7$ K, respectively.

The values b_{ij} determined above give the values of effective exchange constants in the full concentration range. They are listed in Table III, where also partial contributions coming from double-exchange $[\tilde{B}_{ij}=\frac{1}{6}B_{ij}x_3(1-x_3)]$ and the total-exchange integrals $(\tilde{J}_{ij}=J_{ij}z_{ij}+\tilde{B}_{ij})$ are given. Hence we have determined the microscopic parameters of the systems $Cu_xZn_{1-x}Cr_2Se_4$ in the full concentration range. We estimate the accuracy of the values given in Table III to be about 10%.

VI. DISCUSSION AND CONCLUDING REMARKS

In this paper we have formulated a quantitative scheme of interpreting the data of saturation magnetization M_s, high-temperature susceptibility χ, and the configuration angles (Φ,θ) as a function of concentration x for the system $Cu_xZn_{1-x}Cr_2Se_4$. From the interpretation scheme we have determined the microscopic parameters of those systems such as the effective intersite exchange integrals for the first three neighbors, the bandwidth of the $3d$ band due to mixed Cr^{3+}-Cr^{4+} ions in the mixed-valence state, and the degree of mixing $x_3{:}x_4$ in the mixed-valent configuration $Cu^{+}{}_x(Cr^{3+}{}_{x_3}Cr^{4+}{}_{x_4})_2Se^{2-}{}_4$. This was only possible after taking into account superexchange and double exchange, as well as the biquadratic exchange.

The microscopic parameters determined here allow for a full quantitative description of thermodynamic properties and the phase transitions of the systems $Cu_xZn_{1-x}Cr_2Se_4$. In particular, the magnetization isotherms [cf. Figs. 3(a)—3(e)] can be calculated provided the anisotropy field measured previously[8(a),8(b)] is included at

TABLE III. Effective exchange integrals for the systems $Cu_xZn_{1-x}Cr_2Se_4$. The integrals for the first free coordination spheres are given.

x	$\tilde{B}_{aa}$ (K)	$\tilde{B}_{ab}$ (K)	$\tilde{B}_{ac}$ (K)	$\tilde{J}_{aa}$ (K)	$\tilde{J}_{ab}$ (K)	$\tilde{J}_{ac}$ (K)	$J_{aa}=\tilde{J}_{aa}/z_{aa}$ (K)	$J_{ab}=\tilde{J}_{ab}/z_{ab}$ (K)	$J_{ac}=\tilde{J}_{ac}/z_{ac}$ (K)
0.0	259.0	7.7	2.6	60.0	175.0	−60.0	63.8	14.5	−10.0
0.01	290.5	8.2	2.8	350.5	183.2	−57.2	58.4	15.3	−9.5
0.02	307.0	8.6	2.9	367.0	183.5	−57.0	61.2	15.3	−9.5
0.025	317.0	8.9	3.0	377.0	184.0	−57.0	62.8	15.3	−9.5
0.05	356.0	10.0	3.4	416.0	185.0	−56.7	69.3	15.4	−9.5
0.07	389.5	11.0	3.7	449.5	186.0	−56.3	74.8	15.5	−9.4
0.1	436.5	12.3	4.2	496.5	187.3	−55.8	82.8	15.6	−9.3
0.2	578.5	16.3	5.5	638.5	191.3	−54.5	106.4	15.9	−9.1
0.3	698.0	19.7	6.6	758.0	194.6	−53.4	126.3	16.2	−8.9
0.5	880.5	24.8	8.4	940.5	199.8	−51.6	156.8	16.7	−8.6
0.7	978.5	27.6	9.3	1038.5	202.5	−50.7	173.0	16.9	−8.5
0.8	996.5	28.0	9.5	1056.5	203.0	−50.6	176.0	18.9	−8.4
0.9	993.0	29.0	9.4	1053.0	203.0	−50.6	175.5	16.9	−8.4
1.0	969.0	27.3	9.2	1029.0	202.3	−50.8	171.5	16.9	−8.5

low temperature ($T \lesssim 30$ K). Even more interesting would be calculating the transition temperatures T_N (for $x \leq 0.1$) and T_c (for $x \geq 0.2$), and in particular, of the jump from $T_N = 20$ K at $x = 0.1$ to $T_c = 380$ K at $x = 0.2$. However, at present we have no satisfying method of calculating the transition temperature in the noncollinear phase with a reasonable accuracy. This is the reason why we have taken in our analysis the paramagnetic temperature Θ_{CW} which can be calculated precisely from the high-temperature expansion for χ (the mean-field approximation is not good even qualitatively since we have a biquadratic-exchange term).

The knowledge of $T_N(x)$ and $T_c(x)$ would be interesting also because of an additional reason. Namely, we are not entirely certain if we can apply the concept of double exchange for the samples with the lowest concentration ($x \lesssim 0.2$). This is because both Cu^{+} and Cr^{4+} ions introduce a certain degree of disorder which may trap effectively the holes in the narrow $3d$ band. The observed nonzero activation energy[9] for $x \leq 0.2$ may be due to an activation from the trapped state across the mobility edge or to a thermally activated hopping. In such a case the double exchange is triggered at $T = 0$ above a percolation threshold $x_c \sim 0.1$—0.2 for a transition to a state with metallic conductivity. This may be one of the reasons why we get consistent values for $B = \sum_{j(i)} b_{ij}$ only for the sample with higher concentration of Cu (i.e., $x > 0.3$). The other reason of this inconsistency is given in Sec. V A when discussing the results presented in Table II. Besides, the delocalization of the Cr^{4+} holes at $x = x_c$ would cause a steep increase of the transition temperature which is observed on increasing x from 0.1 to 0.2. Additionally, it should be noted that the conical angle decreases strongly in the concentration range $x \in [0.05, 0.2]$, so the trapped states may be caused by the exchange interactions themselves, as postulated by de Gennes a long time ago.[17] Clearly, further studies of the transport properties are necessary to clarify the situation in the low-concentration range. We hope to do such studies in the near future.[9]

The mixed-valent configuration $\mathrm{Cr^{3+}}_{x_3}\mathrm{Cr^{4+}}_{1-x_3}$ should give a substantial enhancement of the electronic specific heat in the metallic phase, particularly in the ferromagnetic phase, i.e., for $x \geq 0.8$. The enhancement factor should be of order 4—5 at least. Information from the field and concentration dependence of the electronic specific heat may throw some light onto an inter-relation between the mixed-valent dynamics (hopping of d electrons of Cr) and the double-exchange mechanism.

The analysis presented in Secs. III—V contains some simplifications. We list them briefly. Firstly, we have neglected the anisotropy which is weak only above $T \simeq 30$ K, as has been shown before.[8(a)—8(b)] This means that the configuration angles $\theta(x)$ and $\Phi(x)$ may be slightly different from those represented in Fig. 5. The inclusion of anisotropy does not introduce any essential complication in our analysis. In other words, we have presented the results in Sec. IV in the simplest possible form which is still realistic. Secondly, we have started from a model of the double exchange in which the hopping electrons between Cr ions contribute to the magnetic moment on the same footing as the remaining ones regarded as a skeleton of localized spins. The specific situation here is that the same ($3d$) electrons are responsible both for magnetic moment and a mediation of the double-exchange interaction between the neighboring Cr ions. The detailed quantum dynamics of the hopping electrons[18] has been neglected in the present approach.[14] It will be needed if we are interested in the contribution to the conductivity of those hopping electrons in a very narrow band. Thirdly, we have not discussed the influence of the residual itinerant holes p or d types onto a diminution of the Curie constant and the saturation magnetization.

Let us discuss the last point in more detail. The contribution of itinerant d or p holes due to the presence of Cu^{2+} and Se^{-} holes, respectively, as invoked by some authors[4,5] to the magnetic properties should not be a decisive one because the Curie-Weiss temperature Θ_{CW} does not show any sign of oscillations as a function x (cf. the values of Θ_R in Table II, where it is shown that Θ_R is small always except for the three lowest concentrations). On the other hand, the diminution of the Curie constant C_M can be estimated as follows. Assuming that the d-d (or p-d) coupling between the holes and Cr ions is antiferromagnetic, one gets the following formula for the high-temperature susceptibility[19]:

$$\chi = \chi_P + \frac{C_M[1 - |J_c| \chi_P/(g_\mu B)^2]}{1 + \Theta_{\mathrm{CW}} \left[1 + \dfrac{J_c^2 \chi_p/(g\mu_B)^2}{\bar{J}_{aa} + \bar{J}_{ab} + \bar{J}_{ac}} \right]} , \tag{6.1}$$

where χ_P is the Pauli susceptibility due to the holes, and J_c is the d-d (p-d) exchange coupling constant. Taking $J_c = -1$ eV, $\chi_P \simeq 5 \times 10^{-6}$ cm^3/g, one gets $\Delta C_M / C_M \sim 0.1$—$0.2$, i.e., the desired order of magnitude in order to explain the maximum deviation in Fig. 6 for $x = 0.2$. It should be noted that p-d exchange is expected to be negative[20] for small x while the d-d exchange between the hole in the Cu^{2+} band and the Cr ions should be rather positive since we expect that the Hund's rule holds in this case. Additionally, the formation of magnetic polarons[21] cannot explain both the C_M diminution and the tails observed in the temperature dependence of susceptibility when approaching T_N or T_c from above.

Apart from the fact that we used some simplifications in our analysis and that the situation is not entirely clear at the lowest concentrations studied, we think that the present approach provides for the first time a quantitative and consistent picture of magnetic properties of a system in which the double exchange is taking place. Moreover, using as an example $\mathrm{Cu}_x\mathrm{Zn}_{1-x}\mathrm{Cr}_2\mathrm{Se}_4$, we have shown how the transitions from helimagnetism to ferromagnetism and from a semiconductor to metal with a fluctuating valence are inter-related if a part of the localized moments present in the system delocalizes and forms a very narrow band with the carriers strongly coupled to the remaining localized spins via the Hund's rule.

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