An X-ray Diffraction Study of Magnetostriction in \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) (0.2 \( \leq x \leq 1.0 \))

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Abstract

The temperature dependence of the lattice parameter \( a \) of the powder samples of the mixed spinels \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) was measured in the temperature range 100--570 K by the X-ray powder diffraction technique. The temperature dependence of the magnetostriction was observed from these results. For \( x = 1.0, 0.9, 0.8, 0.3 \) and 0.2 the spontaneous magnetostriction \( \omega \) turned out to be positive and dependent on temperature. Based on the molecular field approximation the pressure coefficients of the Curie temperature \( dT_c/dp \) were estimated.

Introduction

The spinel series under study has normal spinel structure with the space group \( Fd\bar{3}m \). The boundary compounds, i.e. \( \text{ZnCr}_2\text{Se}_4 \) and \( \text{CuCr}_2\text{Se}_4 \), are a semiconductor with simple spiral magnetic structure [spiral angle equal to \( 42(1)^\circ \), \( T_N = 20 \) K] and metallic ferromagnet \( (T_c = 460 \) K), respectively (Plumier, 1965; Yamishita, Yamaguchi, Nakatani, Watanabe & Masumoto, 1979). It follows from the neutron diffraction and magnetic measurements that:

1. The transition from helical structure to ferromagnetism is connected with a steep increase of the transition temperature. As a matter of fact the concentration range \( 0.1 < x < 0.2 \) defines the boundary area for this sudden increase. This means that the double exchange mechanism is effective for samples with higher concentration of \( \text{Cu} \) i.e. \( x \geq 0.2 \) (Krok, Spalek, Juszczyk & Warczewski, 1983).

2. In all the samples the long temperature range of the nonlinearity of the reciprocal molar susceptibility \( \chi_M^{-1} \) as a function of temperature was observed (Krok, Juszczyk, Warczewski, Mydlarz, Szamraj, Bombik & Byszewski, 1983; Krok, Juszczyk, Warczewski, Mydlarz, Szamraj, Bombik, Byszewski & Spalek, 1983). This means that the ferromagnetic interactions are so strong that they preserve the short-range interaction in a paramagnetic state. The existence of these interactions has been confirmed by the results of a high field susceptibility study (Juszczyk, Duda, Mydlarz & Krok, 1985).

Such a strong ferromagnetic interaction can cause a deformation of the elementary cell. Kanomata & Ido (1974) have shown that in \( \text{CuCr}_2\text{Se}_4 \) a volume spontaneous magnetostriction occurs and that the pressure coefficient of Curie temperature \( dT_c/dp \), calculated from the Bean & Rodbell (1962) model, is in good agreement with the value measured by the direct method (Kanomata & Ido, 1970). For this reason X-ray diffraction was used for the determination of \( dT_c/dp \) for the compounds under study. In this paper the temperature dependence of the lattice parameter \( a \) was determined with the use of the X-ray powder diffraction method in order to study the influence of the copper concentration on spontaneous magnetostriction for \( 0.2 \leq x \leq 1.0 \).

Based on the molecular field theory proposed by Bean & Rodbell (1962), the pressure coefficients \( dT_c/dp \) were calculated.

Experimental

Powder samples of spinels \( \text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4 \) with \( x = 1.0, 0.9, 0.8, 0.3 \) and 0.2 were prepared using the method described by Okońska-Kozłowska & Krok (1978).

The X-ray measurements of the temperature dependence of the lattice parameter for these samples were carried out in the temperature range 100--570 K with a step of 10 K using the HZG-4/A (German Democratic Republic) powder vertical diffractometer with Cu K\( \alpha \) radiation. To avoid systematic errors the powder samples were mixed with an internal standard of corundum. The measured value of the position of the corundum reflection (lying in the proximity of the sample reflection) at a chosen temperature was compared with the corresponding value calculated on the basis of the thermal expansion of corundum (Touloukian, 1977). In order to minimize statistical errors the powder samples were mixed with an internal standard of corundum. The measured value of the position of the corundum reflection (lying in the proximity of the sample reflection) at a chosen temperature was compared with the corresponding value calculated on the basis of the thermal expansion of corundum (Touloukian, 1977). In order to minimize statistical errors the K\( \alpha \) lines of the high-angle reflections have been used for the lattice parameter measurements. The angle \( 2\theta \) was changed with a step of 0.005\( \circ \) and the computing time was equal to 8 s. Because the reflection profile turned out to be symmetrical in the maximum area its shape was approximated by a curve \( I = 1/k_0 + k_12\theta + k_2(\theta)^2 \) \( (k_0, k_1, k_2 = \) parameters to be refined), taking the maximum of this curve as a position of the reflection. All statistical errors obtained by the repeated measurements are smaller than 0.002\( \circ \) \( \theta \).
Table 1. The values of the linear thermal expansion coefficient at high temperature

<table>
<thead>
<tr>
<th>x</th>
<th>$\alpha \times 10^{-6}$ K$^{-1}$</th>
<th>$\omega \times 10^{-4}$</th>
<th>$S$</th>
<th>$M$</th>
<th>$-dT_c/d\rho$ (10$^{-8}$ K Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>11.1(2)</td>
<td>15.2(9)</td>
<td>1.26(2)</td>
<td>0.98(1)</td>
<td>0.94(9)</td>
</tr>
<tr>
<td>0.9</td>
<td>9.4(1)</td>
<td>4.6(9)</td>
<td>1.20(2)</td>
<td>0.96(1)</td>
<td>0.30(6)</td>
</tr>
<tr>
<td>0.8</td>
<td>9.5(1)</td>
<td>11.3(9)</td>
<td>1.19(2)</td>
<td>0.94(1)</td>
<td>0.78(8)</td>
</tr>
<tr>
<td>0.3</td>
<td>9.6(1)</td>
<td>24.9(9)</td>
<td>1.35(2)</td>
<td>0.60(1)</td>
<td>3.79(30)</td>
</tr>
<tr>
<td>0.2</td>
<td>9.4(1)</td>
<td>20.0(9)</td>
<td>1.41(2)</td>
<td>0.46(1)</td>
<td>5.38(30)</td>
</tr>
</tbody>
</table>

Results and discussion

The temperature dependence of the lattice parameter for the concentrations $x = 1.0, 0.9, 0.8, 0.3$ and 0.2 is presented in Fig. 1 (errors are smaller than the sizes of the experimental points).

The solid curves present the hypothetical nonmagnetic behaviour calculated from the Grüneisen-Debye theory (Kittel, 1966). The validity of this procedure is shown among others for the nonmagnetic spinel CdIn$_2$S$_4$ by Bindloss (1971).

The Grüneisen–Debye formula for the thermal expansion is expressed by

$$\alpha(T) = \frac{\Gamma C_V(\theta_D/T)}{B3V_{\text{mol}}}$$

where $\Gamma$ is the Grüneisen constant, $B$ is the bulk modulus, $\alpha(T)$ is the thermal expansion coefficient, $C_V(\theta_D/T)$ is temperature-dependent specific heat, and $\theta_D$ is the Debye temperature. The experimental values of the Debye temperature $\theta_D$ are taken from Tarnawski, Kusz & Krok (1988) (who determined inter alia the temperature dependence of specific heat). It turned out that $\theta_D$ for $T > 50$ K is constant and equal to 325(5) K in the entire concentration range ($0.0 \leq x \leq 1$).

To obtain the temperature dependence of the thermal expansion coefficient $\alpha(T)$ the specific heat $C_V(\theta_D/T)$ was calculated from the formula

$$C_V(\frac{\theta_D}{T}) = 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D} \frac{x^4e^x}{(e^{x} - 1)^2} \, dx,$$

where $k_B$ is Boltzmann’s constant and $x_D = \theta_D/T$.

The ratio $\Gamma/B$ was determined by fitting relation (1) to the experimental points at high temperature, where magnetostriction effects do not exist. Values of the high-temperature thermal expansion coefficient $\alpha$ are presented in Table 1.

One can see in Fig. 1 that in the temperature region $T < T_c$ discrepancy between the experimental and hypothetical nonmagnetic curves appears. The $T_c$ values indicated by the arrows are taken from the paper by Krok, Spatek, Juszczyk & Warczewski (1983). This discrepancy indicates that spontaneous positive and temperature-dependent magnetostriction takes place.

The spontaneous volume magnetostriction is equal to the volume difference between the state in which the atomic moments are ordered (ferromagnetic or antiferromagnetic) and the state in which they are disordered (paramagnetic). It is equal to

$$\omega = \frac{(V_{\text{exp}} - V_0)}{V_0}$$

where $V_{\text{exp}}$ and $V_0$ are the observed and hypothetical nonmagnetic volume of the elementary cell, respectively. The values of $\omega$ at 100 K (i.e. the lowest temperature attained in these experiments) are presented in Table 1. One can see that for all the copper concentrations $x$ magnetostriction is positive and its value for small $x$ increases slightly with respect to the value of CuCr$_2$Se$_2$, with a minimum at $x = 0.9$. 

![Fig. 1. Temperature dependence of the lattice parameter for $x = 1.0, 0.9, 0.8, 0.3, 0.2$ (closed circles) and the normal thermal expansion curves deduced from the Grüneisen–Debye theory (solid lines).](image-url)
On the basis of the molecular field theory of ferromagnetism, the magnetovolume effect can be interpreted in terms of the volume dependence of the effective exchange integral. The volume change due to the ferromagnetic ordering \( \omega \) is given by (Shiga & Nakamura, 1969)

\[
\omega = K M \frac{2}{2} \frac{d\eta}{d\omega}
\]

where \( K \) is the compressibility, \( M \) the magnetization, \( \beta \) a positive constant and \( J \) the effective exchange constant. In this spinel series Cr is the only magnetic atom and superexchange interactions between \( \text{Cr}^{n+} \) \((n=3, 4)\) ions take place. All the solid solutions under study are ferromagnets with a metallic type of conductivity. According to the Bethe–Slater curve, \( dJ/d\omega \) has a positive sign for ferromagnetic metals and alloys. It may explain the positive sign of \( \omega \) in the spinels presented here at \( T = 0 \text{K} \), because the effective exchange interaction of the localized model is temperature dependent owing to the thermal expansion. A positive sign of the magnetovolume effect may be explained also in the framework of the Stoner–Edwards–Wohlfarth (SEW) theory of itinerant electron ferromagnets (Wohlfarth, 1977, 1980; Edwards & Macdonald, 1983). According to this theory the thermally excited electrons and holes are assumed to move independently in the common mean field, but their collective nature is totally neglected.

The physical origin of the magnetostriiction caused by the \( s-d \) coupling to band electrons may be explained as follows. In the paramagnetic state, where the \( 3d \) band of Cr is not polarized, the \( 3d \) holes (the carriers of magnetism in the spinels under study) occupy the lower parts of both up and down spin sub-bands which have mainly bonding character, \( i.e. \) less kinetic energy. If the \( 3d \) band is polarized perfectly below the Curie temperature, the up spin band is fully occupied by holes and the number of holes with bonding character decreases. The density of states near the Fermi level increases, resulting in a decrease in the bandwidth. This decrease in the bandwidth can be accomplished by an expansion of the lattice. The free energy associated with ordering is therefore minimized by allowing a volume expansion, which suggests a positive contribution to volume striction. The details are probably more complex, since additional contributions to this striction are to be expected from the volume dependence of the Coulomb forces (exchange) and of the number of \( d \) holes, but the bandwidth effect appears to be dominant in most cases (Lines, 1979). Analytically the magnetovolume change may be expressed by

\[
\omega = C K M \frac{2}{2} \eta_{\text{M}}(T)
\]

where \( M_0 \) is the local moment at \( 0 \text{K} \), \( C \) the compressibility, \( K \) the magnetoelastic coupling constant defined in terms of the Landau theory of phase transitions, and

\[
\eta_{\text{M}}(T) = 1 - \frac{(T/T_c)^2}{1 + \frac{2}{3} \frac{N k_B M^2}{\Delta}}
\]

A magnetovolume effect may be explained also by Moriya’s (1981) unified theory of magnetism. With the use of the average squared amplitude of the local spin density fluctuations Moriya describes the magnetovolume effect in the whole temperature range of interest and above \( T_c \) as well. But in the spinels under study we do not observe a magnetic contribution to the relative thermal change in volume in the paramagnetic state. Therefore the SEW theory describes best of all this interesting phenomenon in the compounds under study.

According to (5) we may explain that in the compounds with \( x = 0.2 \) and \( 0.3 \) \( \omega \) has a higher value at \( T = 100 \text{K} \) than in the case of \( x = 0.8 \) and \( 0.9 \), because \( M_0^2 \) for the latter compositions is smaller (Krok, Spalek, Juszczyk & Warczewski, 1983).

According to the model proposed by Bean & Rodbell (1962) in the molecular field approximation one obtains the pressure coefficient of the Curie temperature

\[
\frac{dT_c}{dp} = -\frac{\omega}{N k_B M^2} \left( \frac{3}{2} \frac{\Delta}{\Delta + 1} \right)
\]

where \( \omega \) is the spontaneous magnetostriction, \( N \) the number of magnetic ions (\( \text{Cr}^{3+} \) and \( \text{Cr}^{4+} \)) per unit volume, \( k_B \) is Boltzmann’s constant, \( M = M_{\text{sat}}(T)/M_{\text{sat}}(0) \) \( [M_{\text{sat}}(T) = \text{saturation magnetization at temperature } T, M_{\text{sat}}(0) = \text{saturation magnetization at } 0 \text{ K}] \). \( \Delta \) is the effective spin per site (\( \Delta = S_3 x_3 + S_4 x_4 \), where the corresponding spins of \( \text{Cr}^{3+} \) and \( \text{Cr}^{4+} \) are \( S_3 = 1.5 \) and \( S_4 = 1 \), respectively, and \( x_3 + x_4 = 1 \) are the values of the concentrations of \( \text{Cr}^{3+} \) and \( \text{Cr}^{4+} \) ions, respectively), deduced from the value of the magnetic moment per formula (Krok, Spalek, Juszczyk & Warczewski, 1983).

The values of \( dT_c/dp \) at \( T = 100 \text{K} \) are given in Table 1. They are of the order of \( 10^{-6} \text{ Pa K}^{-1} \) and are in good agreement with the values for such spinel compounds as \( \text{CuCr}_2X_4 \) where \( X = \text{S, Se and Te} \) (Kanomata & Ido, 1974), \( \text{CdCr}_2X_4 \) where \( X = \text{S, Se} \) (Martin, Kellog, White & White, 1965) and \( \text{Co}_{0.55} \text{Cu}_{0.45} \text{Cr}_2S_4-Y \text{Se}_y \) where \( 0 \leq Y \leq 1.5 \) (Gogółowiec, Kusz, Warczewski & Juszczyk, 1986).

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References


