

Cation distribution and magnetic properties of ternary $Zn_{2.33-x}Co_xSb_{0.67}O_4$ spinels

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 2317

(<http://iopscience.iop.org/0953-8984/8/14/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:28

Please note that [terms and conditions apply](#).

Cation distribution and magnetic properties of ternary $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ spinels

A Ilic†, B Antic‡, D Poleti†, D Rodic‡, I Petrović-Prelević§ and Lj Karanović§

† Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, PO Box 494, 11001 Belgrade, Yugoslavia

‡ Institute of Nuclear Sciences 'Vinca', Laboratory of Solid State Physics, PO Box 522, 11001 Belgrade, Yugoslavia

§ Crystallographic Laboratory, Faculty of Mining and Geology, University of Belgrade, PO Box 162, 11001 Belgrade, Yugoslavia

Received 24 October 1995

Abstract. The series of spinels $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ ($0.23 \leq x \leq 2.33$) was prepared by ceramic technology. The crystal structures were refined from the x-ray diffraction data using the Rietveld profile method. The high-temperature magnetic susceptibility was measured by the Faraday method in the temperature range 290–600 K and the data were fitted to the Curie–Weiss law. The cation distribution in these diluted magnetics is obtained from x-ray diffraction and high-temperature magnetic susceptibility measurements. It was found that, for $x \leq 0.93$ Co^{2+} ions occupy exclusively the octahedral position in the spinel type of structure. In the low-concentration region a strong clustering of magnetic ions is observed. In the range $1.33 \leq x \leq 2.33$, Co^{2+} ions are distributed in both tetrahedral and octahedral cationic sites. The Curie–Weiss paramagnetic temperature Θ is negative in the whole range of concentrations, as the consequence of a predominant antiferromagnetic interaction. The appearance of the Co^{2+} ions in tetrahedral sites (around $x = 1.33$) leads to a drop in the absolute Θ -value. The effective magnetic moments of Co^{2+} ions are about $4.60\mu_B$ for $x \leq 1.33$ and depend on the Co^{2+} concentration for $x > 1.33$.

1. Introduction

Because of the extraordinary usefulness of the compounds with spinel(Sp)-type structure, they have been intensively studied in the last two decades [1–3]. Very much attention has been paid to magnetic semiconductors with the Sp structure [3]. On the other hand, among diluted magnetic semiconductors (DMSs) [4], DMSs of Sp type have not been extensively investigated. The magnetic properties of some DMS spinel sulphides, selenides and tellurides have been described in the literature [5, 6], but the lack of data on oxides is obvious.

The $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ ($0.23 \leq x \leq 2.33$) Sp compounds are DMSs and have been chosen for this study for the following reasons. The concentration of magnetic ions can be easily controlled, thus allowing their properties and related phenomena in the wide range of concentrations to be studied. Variation in magnetic ion concentration can change the structural, magnetic and other physical properties which could be important for possible applications.

The parent compound for the system examined is diamagnetic $\text{Zn}_{2.33}\text{Sb}_{0.67}\text{O}_4$ which has already been described by Kasper [7]. The magnetic properties of $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$

Sp compounds arise because of the replacement of diamagnetic Zn^{2+} by magnetic Co^{2+} ions, which possess both spin and orbital moments ($S = 3/2$ and $L = 3$, for free Co^{2+}). Co_3O_4 (which is used as the starting compound both in synthesis and for comparison) is an antiferromagnetic with a Néel temperature of 40 K and a Curie–Weiss paramagnetic temperature of -53 K [8].

The aim of this work is manifold: first, to show that synthesis of $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ Sp compounds is possible with a wide range of concentrations; second, to establish the structural parameters of Sp compounds, especially the magnetic Co^{2+} ion distribution in two non-equivalent crystallographic sites. This distribution may be affected by the presence of high-valence Sb(V) species [9]. The determination of quantities such as the Curie constant, the magnetic moment, the Curie–Weiss paramagnetic temperature and their concentration dependences gave further insight in the magnetic ion distribution, including their clustering around cationic sites. The final goal is to attempt to find the relationships between the structure and the magnetic properties.

2. Experimental details

2.1. Sample preparation

The $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ samples ($0.23 \leq x \leq 2.33$) were prepared by the ceramic method, using reagent-grade ZnO , Sb_2O_3 and Co_3O_4 as starting materials. The oxides were homogenized in an agate mortar and then pre-sintered in air at a temperature of 1370 K for 3 h. The final sintering was done at 1470 K for 5 h. The presence of a single Sp phase was confirmed by the x-ray powder diffraction technique in all samples.

2.2. X-ray data collection and structure refinement

The x-ray powder diffraction data for $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ ($x = 0.23, 0.47, 0.93$ and 1.33) were collected at room temperature using a Rigaku diffractometer with a Rigaku rotating anode and a Philips goniometer. The data were collected in the 2θ range 10.00 – 120.00° , with a step length of 0.05° and a counting time of 10 s per step. The data for samples with $x = 1.73$ and 2.33 were collected at room temperature on a Philips PW 1710 diffractometer. The 2θ range was 10.00 – 120.00° with a step length of 0.02° and a counting time of 10 s per step.

The structures were refined in the Sp space group $Fd\bar{3}m$ (No. 227; origin at centre $\bar{3}m$). The structure of Co_3O_4 [10] was taken as a starting model: tetrahedral A cations are in the special 8a position ($1/8, 1/8, 1/8$); octahedral B cations are in the special 16d position ($1/2, 1/2, 1/2$); oxygen ions are in the special 32e position (u, u, u). The starting u -value was 0.25 (the value for the ideal Sp structure). The refinements were done by the Rietveld method using the software package FULLPROF [11].

Peaks below 40° (2θ) were corrected for asymmetry. The atomic scattering curves and pseudo-Voigt profile functions were used in the refinements. The background profiles were determined manually.

Several attempts were made in order to check the Co^{2+} and Zn^{2+} distributions among the A and B sites.

(a) Cation occupation numbers were coupled to keep the stoichiometry and varied. For example, in the formula $(\text{Zn}_{1-\delta}\text{Co}_\delta)_A(\text{Zn}_{1.33-x+\delta}\text{Co}_{x-\delta}\text{Sb}_{0.67})_B\text{O}_4$ valid for $x \leq 1.33$, the occupation numbers δ of Co^{2+} at the tetrahedral site were zero within the standard deviation $\sigma(\delta)$. Similarly, for $x = 1.73$ the occupancy of Zn^{2+} at B sites was zero within the standard

deviation which indicated that Zn^{2+} fills only A sites. However, the significance of these results was low, since the standard deviations of occupation numbers were large. As could be expected, the correlation between occupation numbers and temperature factors was also large.

(b) The occupation numbers N were varied manually in steps of 0.05 and, with all parameters fixed, the R -values are calculated. This approach yielded the lowest R_B and R_F when the occupation of tetrahedral sites by Zn^{2+} is as large as possible, i.e. $N_A(\text{Zn}) = 1$ for $x \leq 1.33$ and $N_A(\text{Zn}) = 0.60$ for $x = 1.73$.

The results in (a) and (b) are in agreement and show that, for $x \leq 1.33$, Co^{2+} ions occupy only octahedral sites and, above $x = 1.33$, Zn^{2+} ions occupy exclusively tetrahedral sites. Accordingly, the occupation numbers were fixed during the last stages of refinement.

In the last cycle of refinements, 13 (or 14 with sample displacement) parameters were varied: oxygen position parameter u , lattice parameter a and three thermal isotropic parameters B_A , B_B and B_O (for three different crystallographic positions). The remaining parameters were the scale factor, the zero point, five parameters of profile function and one asymmetry parameter. The refined crystal data, bond distances and agreement parameters R_p , R_{wp} , R_B , R_F and R_e are listed in table 1.

Structural data for $\text{Zn}_{1.63}\text{Co}_{0.70}\text{Sb}_{0.67}\text{O}_4$ are taken from [12].

Table 1. Crystal data for $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ spinels.

	Value for the following x -values						
	0.23	0.47	0.70	0.93	1.33	1.73	2.33
d_{A-O} (Å)	2.069(5)	2.009(5)	1.992(3)	2.007(5)	1.986(8)	2.018(3)	1.942(3)
d_{B-O} (Å)	2.035(5)	2.065(5)	2.071(3)	2.063(5)	2.070(8)	2.051(3)	2.090(3)
B_A (Å ²)	0.31(9)	0.70(9)	0.69(4)	0.8(1)	1.0(2)	0.12(4)	0.17(5)
B_B (Å ²)	0.41(6)	0.63(6)	0.68(3)	0.68(9)	0.2(1)	0.12(3)	0.64(3)
B_O (Å ²)	2.6(3)	0.9(2)	0.74(9)	0.6(2)	1.7(3)	0.54(9)	0.3(1)
R_p	6.76	4.47	11.17	2.79	2.78	9.07	10.08
R_{wp}	8.96	5.94	11.94	3.68	3.64	11.80	14.40
R_B	9.76	6.27	4.15	6.80	7.46	4.59	8.41
R_F	9.26	5.84	3.22	6.92	9.14	4.13	7.82
R_e	4.91	3.94	9.17	2.58	2.88	8.42	9.88

2.3. High-temperature susceptibility measurement

The magnetic susceptibility of the samples was measured by the Faraday method in the temperature interval 290–600 K. The applied field was 0.6 T. The temperature stability was ± 1 K or better.

The susceptibility data were corrected for the diamagnetic contribution using ionic diamagnetic values [13]. It was found that the molar paramagnetic susceptibilities of $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ ($x = 0.23, 0.47, 0.70, 0.93, 1.33, 1.73$ and 2.33) obey the Curie–Weiss law (figure 1):

$$\chi_M = \frac{C_M(x)}{T - \Theta(x)} \quad (1)$$

where C_M and Θ are the Curie constant and the Curie–Weiss paramagnetic temperature, respectively. Note that the susceptibility of the ferrimagnetic phase far above the Néel

temperature asymptotically approaches the Curie–Weiss law (equation (1)). The results are used to calculate C_M and Θ , from the least-squares fit of the linear function $1/\chi$ versus T .

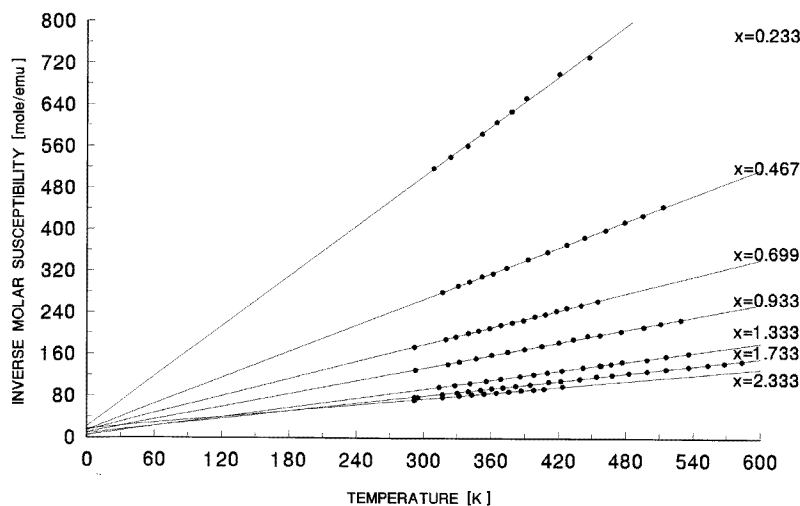


Figure 1. The inverse susceptibilities versus temperature for $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ spinels.

The effective magnetic moments are calculated from $C_M(x)$ and the equation [14]:

$$\mu_{eff} = \left(\frac{8C_M(x)}{x} \right)^{1/2}. \quad (2)$$

3. Results and discussion

3.1. Crystal structures

The lattice parameter value a depends linearly on the Co^{2+} ion concentration (figure 2). The Vegard rule is obeyed: $a(x) = bx + a_0$, where $b = -0.017(1)$ and $a_0 = 8.598(2)$ (correlation coefficient $r = 0.980$). The oxygen position parameters u lie in the usual range between 0.25 and 0.27 [2] but show an irregular concentration dependence (figure 2). As expected, for $0.47 \leq x \leq 1.73$, the u -values (and strongly correlated cation–oxygen distances) are similar. There is no appropriate explanation for the discrepancy of the end members.

The fact that the a -values become smaller with increase in the Co^{2+} content is surprising if Shannon's [15] ionic radii for Zn^{2+} and Co^{2+} ions in octahedral coordination are considered. However, it has already been shown that the radius of $(\text{Co}^{2+})^{\text{VI}}$ should be smaller than the radius of $(\text{Zn}^{2+})^{\text{VI}}$ in Sp structures. In our opinion the best set of cation–anion distances valid for this case are the data listed by Poix [16]: $d_A(\text{Zn–O}) = 1.97 \text{ \AA}$, $d_A(\text{Co–O}) = 1.967 \text{ \AA}$, $d_B(\text{Zn–O}) = 2.141 \text{ \AA}$ and $d_B(\text{Co–O}) = 2.126 \text{ \AA}$. The exception is the Sb–O distance which should be 1.980 \AA [12] instead of the value of 1.895 \AA given by Poix. Using these data, or appropriate mean values if two or more ions occupy the same position, the cationic distribution given in section 2 and the equation

$$a_{calc} = \frac{8d_A}{3\sqrt{3}} + \frac{8d_B}{3} \quad (1)$$

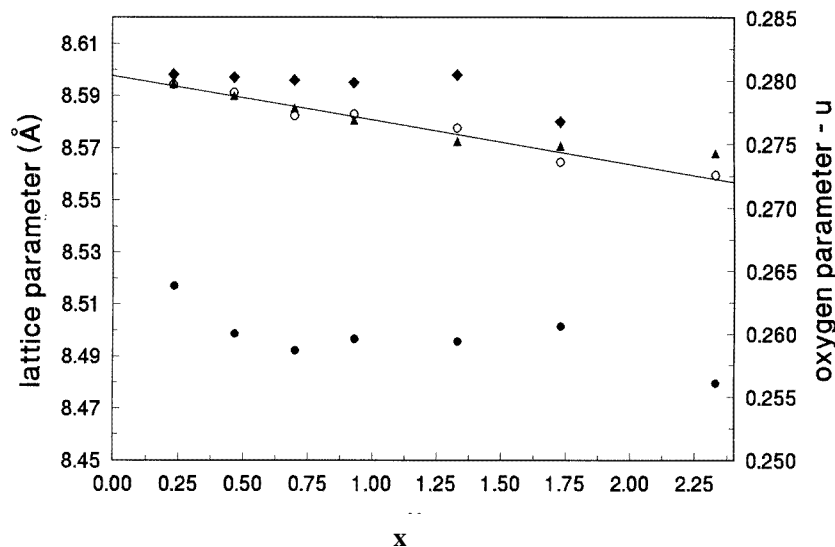


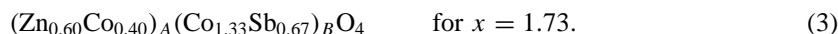
Figure 2. The concentration dependence of the lattice parameter (left-hand axis) (○, experimental values (line regression); ▲, a_{calc1} ; ◆, a_{calc2}) (for explanation see the text) and the concentration dependence of the oxygen parameter $-u$ (right-hand axis) (●).

proposed in [2] it is possible to predict the Sp lattice parameters. A comparison of the calculated lattice parameters a_{calc1} and the experimental a -values (figure 2) shows that the maximal deviation is less than 0.0082 Å. Such agreement is satisfactory for most crystallographic purposes.

The results of crystal structure refinements (see section 2) indicate that the cation distribution for different x -values can be described by the formulae



and



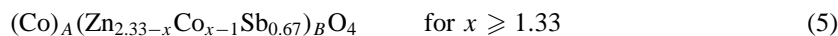
Such a distribution is expected for the following reasons:

- (i) In all known compounds, Sb(V) has been found to be octahedrally coordinated [17].
- (ii) Zn^{2+} ions have the largest preference for tetrahedral sites in Sp structures [18], while Co^{2+} ions have only a small preference for tetrahedral [19] or even for octahedral sites [18].

Equation (1) can also be used to check the cation distribution in the samples examined. When the distribution was opposite to those in equations (2) and (3), i.e. in accordance with the formulae



and



the new set of calculated lattice parameters a_{calc2} , also shown in figure 2, was obtained. It is obvious that the agreement between these and the experimental values is much worse than between a_{calc1} and a . These results also support cation distributions obtained by crystal structure refinements.

3.2. Magnetic properties

The gram-ion susceptibilities of $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ at room temperature are shown in figure 3. The effective magnetic moments of Co^{2+} ions are listed in table 2.

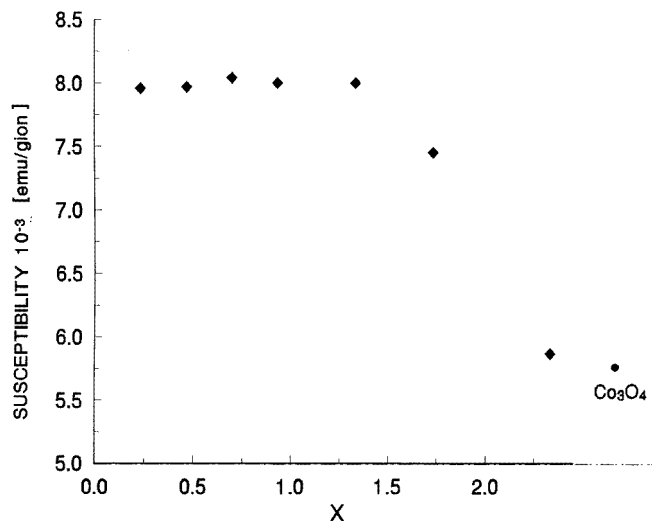


Figure 3. The gram-ion magnetic susceptibility of Co^{2+} ions in $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ at room temperature.

Table 2. Effective magnetic moments of Co^{2+} ions for $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ spinels.

x -value	0.23	0.47	0.70	0.93	1.33	1.73	2.33	Co_3O_4
$\mu_{eff}(\mu_B)$	4.63	4.54	4.56	4.57	4.55	4.40	4.25	4.14 ^a

^a Taken from [8].

The gram-ion susceptibilities χ_A calculated from room-temperature (293 K) measurements are almost independent of concentration for $x \leq 1.33$, which means that Co^{2+} ions occupy only one (B) position. Above $x = 1.33$ (the magnetic ions occupy both A and B sites), χ_A is a combination of octahedral and tetrahedral values and is nonlinear versus concentration because of the octahedral–tetrahedral interaction. The decrease in χ_A shows that tetrahedral χ_A -values are smaller than octahedral χ_A -values, which is obvious from comparison with the Co_3O_4 value (figure 3), where only tetrahedral sites have magnetic moments [8].

The dependence of the molar Curie constants versus Co^{2+} content is given in figure 4. A change in slope is visible in the vicinity of $x = 1.33$. In the first region the molar Curie constants follow the linear law $C_M(x) = C_{MO}x$, where the value of $C_{MO} = g_{eff}^2 J_{eff}(J_{eff} + 1)/3k_B$ was found to be $2.61 \text{ emu K mol}^{-1}$. For $x > 1.33$, Co^{2+} ions start to fill tetrahedral sites and $C_M(x)$ deviates from the above-mentioned linearity (figure 4). The decrease in slope can be explained by the influence of a smaller ‘tetrahedral’ Curie constant, also visible in the case of Co_3O_4 , studied earlier [8].

For samples with $x \leq 1.33$ the effective magnetic moment of Co^{2+} ions is about $4.60\mu_B$ (table 2). The small differences in μ_{eff} can be attributed to the different cation–anion bond

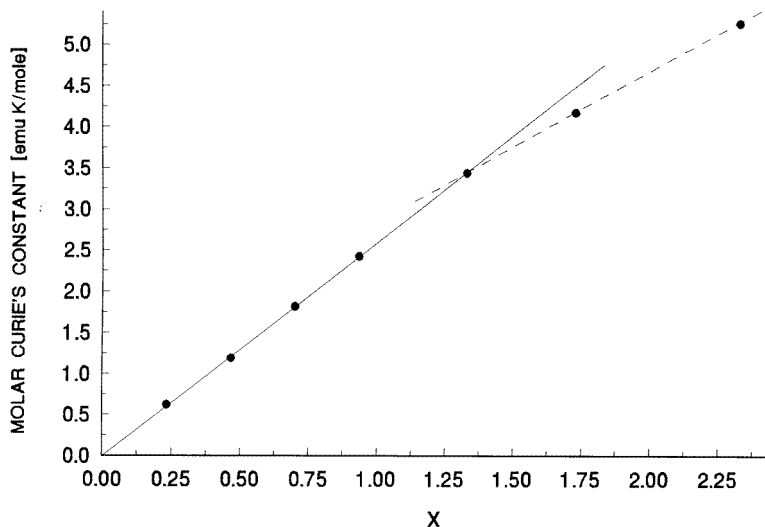


Figure 4. The molar Curie constant of $\text{Zn}_{2.33-x}\text{Co}_x\text{Sb}_{0.67}\text{O}_4$ spinels: ---, guide for the eye.

lengths and to the influence of the second coordination spheres. The magnetic moment of Co^{2+} in the tetrahedral site is smaller than that of Co^{2+} in the octahedral site, which also agrees with the findings for other Co^{2+} compounds [3]. For that reason, μ_{eff} decreases for $x > 1.33$.

The deduced Curie–Weiss paramagnetic temperatures Θ are negative, and hence the antiferromagnetic interaction dominates in all samples. The change in Θ with magnetic ion concentration is complex (figure 5). In the low-concentration region where $|\Theta(x)|$ increases, its value depends on the B–B interaction. The occurrence of non-linearity (upward curvature) can be understood as the consequence of clustering in B sites [20]. Namely, Θ is proportional to the number of first magnetic neighbours, which linearly increases with increasing x only in the case of a random (homogeneous) distribution of Co^{2+} ions in B positions. An inhomogeneous distribution of magnetic ions, i.e. clustering, increases the number of magnetic neighbours and consequently influences the $|\Theta|$ -values.

The appearance of new (A–B and A–A) interactions leads to a drop in $|\Theta|$ at $x = 1.33$. To explain this effect we keep in mind the following.

(i) At $x = 0.93$ the $|\Theta|$ -value is the same as at $x = 0.70$, which suggests that the gradual $|\Theta|$ decrease arises before the concentration $x = 1.33$ is reached.

(ii) The B–B interaction is antiferromagnetic (according to the sign of Θ in the low-concentration region).

(iii) The A–A interaction is antiferromagnetic (according to the sign of Θ for $\text{Co}^{2+}\text{Co}_2^{3+}\text{O}_4$).

If the third interaction A–B is also negative, then the sum of the three interactions should give a monotonically increasing function $|\Theta(x)|$ in the whole concentration range up to $x = 2.33$. Therefore the obtained $|\Theta(x)|$ dependence indicates that the A–B interaction is positive, but a further explanation of the $|\Theta(x)|$ behaviour is necessary. Assume that a small number of Co^{2+} ions, invisible to x-ray diffraction, appears at about $x = 0.93$ in tetrahedral sites. In the concentration region immediately above $x = 0.93$ the octahedra–tetrahedra exchange interaction prevails over the tetrahedra–tetrahedra interaction. Namely, very

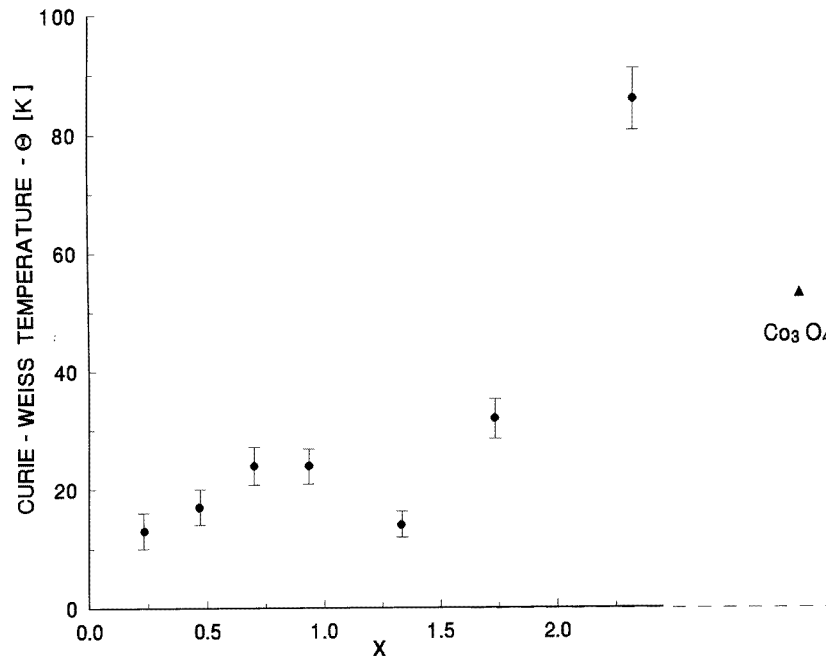


Figure 5. The Curie–Weiss temperatures versus magnetic ion concentration. The value for Co_3O_4 [8] is given for comparison.

diluted Co^{2+} in tetrahedra sites cannot undergo a strong tetrahedra–tetrahedra interaction but can interact with concentrated Co^{2+} in octahedra sites. The $|\Theta|$ decrease in the region $0.93 \leq x \leq 1.33$ shows that the octahedra–tetrahedra interaction is of the opposite sign to the tetrahedra–tetrahedra interaction, i.e. the octahedra–tetrahedra interaction is a ferromagnetic.

In the region $1.33 \leq x \leq 2.33$, all three interactions B–B, B–A and A–A contribute to the Θ -values. The increase in $|\Theta(x)|$ shows that the tetrahedra–tetrahedra contribution to $\Theta(x)$ dominates the octahedra–octahedra contribution.

3.3. Comparison of magnetic and structural data

The magnetic properties should correlate with the cation type present, its ground (high- and low-spin) state and cation distribution. The effective magnetic moments for $x \leq 1.33$ (table 2) confirm the presence of high-spin Co^{2+} ions in octahedral B sites. Also, several magnetic variables (χ_A , C_M and μ_{eff}) indicate the value $x = 1.33$ as the strongest division point and, hence, support the cation distribution presented by equations (2) and (3), which follows from crystal structure refinements.

On the other hand, it is well known that the x-ray diffraction method is not sensitive to small changes in atomic number (i.e. the number of electrons). In such cases it is necessary to use the neutron diffraction technique in order to obtain precise data on the cation distribution. When the series of $\text{Zn}_x(\text{Co}^{2+}\text{Co}^{3+})_{3-x}\text{O}_4$ ($0.5 < x < 1.0$) Sp compounds was studied by neutron powder diffraction, a small but significant amount of Zn^{2+} ions was found in octahedral sites in spite of the large tetrahedral preference of Zn^{2+} ions [21]. For example, the formula found for $x = 0.99$ was $(\text{Zn}_{0.79}\text{Co}_{0.01}^{2+}\text{Co}_{0.20}^{3+})_A(\text{Zn}_{0.20}\text{Co}_{1.80}^{3+})_B\text{O}_4$ [21].

Consequently, some $\text{Zn}^{2+} \leftrightarrow \text{Co}^{2+}$ exchange among A and B sites in the Sp examined

could not be excluded. It seems that such exchange for $x < 1.33$ is negligible. Even at $x = 1.33$, χ_A , C_M and μ_{eff} do not deviate from the observed trends. However, the value of Θ indicates the change in the cation distribution. This allows us to establish the Curie–Weiss temperature as the criterion for small changes in cation distribution, when the x-ray technique is not appropriate.

4. Conclusions

Single-phase polycrystalline samples of $Zn_{2.33-x}Co_xSb_{0.67}O_4$ ($0.23 \leq x \leq 2.33$) were obtained by the solid state reaction. The high-valence Sb(V) species allows a large number of magnetic Co^{2+} ions to enter the Sp structure up to the electroneutrality limit $x = 2.33$. In the whole range of concentrations, Sb(V) occupies only B positions and only in that way influences the distribution of other cations. For $x \leq 0.93$, Co^{2+} ions occupy exclusively B positions; for $x \geq 1.33$ these ions occupy both cationic positions. The refinements of the occupancies, the gram-ion susceptibilities, the Curie constants and the effective magnetic moments do not give a clear answer about the Co^{2+} ion distribution around the critical concentration $x = 1.33$. These quantities are not sufficiently sensitive to the small amount of Co^{2+} ions which may appear in the 8a position around this point. The A–A and B–B interactions are antiferromagnetic; the A–B interaction is of ferromagnetic type. The three above-mentioned interactions cause the $\Theta(x)$ dependence. The difference between the interactions allows identification of a small number of Co^{2+} ions in the 8a position around $x = 1.33$. Clustering of magnetic ions, in B sites, at low concentrations affects the Θ -values.

References

- [1] Grimes N W 1975 *Phys. Tech.* 22
- [2] Hill R J, Craig J R and Gibbs G V 1979 *Phys. Chem. Miner.* **4** 317
- [3] Krupicka S and Novák P 1982 *Ferromagnetic Materials* vol 3, ed E P Wohlfarth (Amsterdam: North-Holland) p 189
- [4] Kossut J and Dobrowolski W 1993 *Handbook of Magnetic Materials* vol 7, ed K H J Bushow (Amsterdam: North-Holland) p 231
- [5] Palacio F, Campo J, Sagredo V, Attolini G and Pelosi C 1995 *J. Magn. Magn. Mater.* **140–144** 2023
- [6] Baran M, Szymczak R, Szymczak H and Tsurkan V 1995 *J. Magn. Magn. Mater.* **140–144** 2043
- [7] Kasper H 1967 *Monatsh. Chem.* **98** 1207
- [8] Roth W L 1964 *J. Phys. Chem. Solids* **25** 1
- [9] Tarte P and Rulmont A 1988 *J. Mater. Sci. Lett.* **7** 551
- [10] Knop O, Reid K I G, Saturano and Nakagawa Y 1968 *Can. J. Chem.* **46** 3463
- [11] Rodríguez-Carvajal J 1990 *Abstracts of the Satellite Meet. on Powder Diffraction of the 15th Congr. of the International Union of Crystallography (Toulouse, 1990)* p 127
- [12] Poleti D, Vasović D, Karanović Lj and Branković Z 1994 *J. Solid State Chem.* **111** 39
- [13] Selwood P C 1956 *Magnetochemistry* (New York: Interscience) p 78
- [14] Shaked H, Aldred A T and Dwight A E 1979 *J. Magn. Magn. Mater.* **10** 38
- [15] Shannon R D 1976 *Acta Crystallogr. A* **32** 751
- [16] Poix P 1965 *Bull. Soc. Chim. Fr.* **5** 1085; 1969 *C. R. Acad. Sci., Paris C* **268** 1139
- [17] Cotton F A and Wilkinson G 1988 *Advanced Inorganic Chemistry* 5th edn (New York: Wiley) p 430
- [18] Navrotsky A and Kleppa O J 1967 *J. Inorg. Nucl. Chem.* **29** 2701
- [19] O'Neill H St C and Navrotsky A 1984 *Am. Miner.* **69** 733
- [20] Antic B, Mitric M and Rodic D 1995 *J. Magn. Magn. Mater.* **145** 349
- [21] Krezhov K and Konstantinov P 1993 *J. Phys.: Condens. Matter* **5** 9287