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Distribution of Metal Ions and Magnetic Properties in Spinel System $Zn_{(1-x)}Ga_{2x/3}Cr_2Se_4$

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A system of zinc-chromium selenides with Ga^{3+} substitution have been prepared by the chemical transport method. The X-ray structure of the single crystals and their magnetic properties have been studied to determine the cation distribution in the fcc cubic spinel. The magnetic properties of the system appeared to be strongly dependent on a location of the Ga admixture on the tetrahedral or the octahedral positions of the spinel sublattice. Three crystals with different stoichiometry revealed distinct values of the saturation magnetic moment, μ_{sat}, i.e., 5.2, 3.8, and $< 0.1\mu_B$. The Zn^{2+} ion deficiency forced Ga^{3+} to occupy the tetrahedral sites and left all the Cr^{3+} ions on the octahedral sites in $(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$, for which a slightly lowered value of magnetic moments have been observed. In $(Zn_{0.95}\square_{0.05})[Ga_{0.03}Cr_{1.93}\square_{0.04}]Se_4$, a lack of stoichiometry caused the Ga ions to locate on the octahedral sites. The small number of Ga^{3+} at these sites was able to considerably affect the magnetic exchange interactions. At high Ga^{3+} concentration in $(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$, it turned out that the saturation magnetic moment's value was below the limit of observations. © 1999 **Academic Press**

INTRODUCTION

$ZnCr_2Se_4$ belongs to the group of cubic normal spinels showing both semiconducting and magnetic properties below $T_N = 20$ K (1–4). A general feature of the chromium chalcogenide spinels reported in the literature (e.g., (5, 6)) is that the measured magnetic saturation moments are significantly smaller than the theoretical value $6\mu_B$/formula unit. Since Cr^{3+} with electronic structure $3d^3$ on the octahedral site was the only magnetic ion in this compound, it appeared that interpretation of the magnetic properties could not be based on a model of spins with the collinear orientation. To explain the magnetic interactions between the Cr^{3+} ion pairs, a helical spin ordering has been assumed (7, 8). Below T_N the spins of the ions in the layers perpendicular to the pseudotetragonal c axis are parallel, but turned by the angle $\varphi = 42°$ against adjacent (001) planes. The exchange interactions between the layers form a helix propagating along the c axis (1, 4, 9). The magnetic and electronic transport properties can appreciably be altered by a cationic admixture both of magnetic and of nonmagnetic type. The influence of Ga ions on the properties of the single crystals of $Zn_{(1-x)}Ga_{2x/3}Cr_2Se_4$ ($x = 0.0$, 0.05, and 0.4) has been described in Refs. (10–13). Also, the polycrystalline materials of this system for $x = 0.1$–0.5 have been reported (14–16). From the measurements based on EPR (15), neutron diffraction (16), electrical conductivity, and Seebeck effect (13) it resulted that the chromium cations take the Cr^{3+} valence (15), the gallium ions are located only on the tetrahedral positions (17), and the electrical conductivity of the p-type decreases, while the Seebeck coefficient increases with the increase of gallium concentration (13). Magnetic measurements proved that the compounds of $Zn_{(1-x)}Ga_{2x/3}Cr_2Se_4$ are antiferromagnetics. The magnetic order in the chalcogenide spinels is connected with the superexchange interactions, which are positive between the nearest-neighbors and negative between the next-nearest-neighbors (11, 18–20). Since there are controversial

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hypotheses as to the cation distribution and because there is still a lack of data from the single crystals, we found it interesting to study how in the substituted spinels the different amounts and the different cation distribution influence the magnetic properties of this class of the single crystals. We report here a family of three quarternary chromium selenides, with different concentrations of Ga^{3+} substituent. A complete description of the single crystal syntheses, the X-ray crystal structures with the cation distribution over the spinel tetrahedral (A) and octahedral [B] sites together with the magnetic characterization, is given.

EXPERIMENTAL

1. Sample Preparation

Single crystals of the $Zn_{(1-x)}Ga_{2x/3}Cr_2Se_4$ system were grown by the method of chemical vapor transport with $CrCl_3$ as a transport agent and with selenides (ZnSe, Ga_2Se_3). Starting materials for the selenides' syntheses were high-purity elements: zinc (99.999%), gallium (99.999%), selenium (99.999%). The selenides were synthesized by heating in evacuated quartz ampoules at 1073 K for six days, then ground in an agate mortar and heated once more for six days at the same temperature as before. Phase analysis of the metal selenides was done by X-ray powder diffraction.

The crystal growth was carried out with stoichiometric amounts of selenides and $CrCl_3$ as a transport agent in quartz ampoules evacuated to about 10^{-3} Pa. The temperature of the crystallization zone was limited from 955 to 1116 K. The temperature of the solution zone was between 1073 and 1195 K. The monocrystals of regular octahedral shape and the edges of about 0.5 to 5 mm with metallic luster were obtained. For further studies three single crystals, denoted I–III, with different Ga^{3+} concentrations have been selected.

2. Single Crystal Structure Determination

The samples with a mean edge length between 0.12 and 0.15 mm were chosen for measurements on a Kuma KM-4 diffractometer (Mo*Kα* radiation, graphite monochromator). For each compound a set of 30 to 35 reflections from $14^\circ \leq 2\theta \leq 32^\circ$ range, and centered at their setting angles, were used for least-squares calculations of the unit cell parameters without symmetry constraints. Within the limits of two standard deviations the unit cell of the three crystals remained cubic. The other details of the crystal data, a summary of the intensity data collection, and structure calculations are given in Table 1. For each sample empirical absorption correction was applied based on the azimuthal ψ scans of several symmetry equivalent reflections and using a procedure given in the SHELXTL-Plus90 program package (21). The structures were refined by the full-matrix least-squares method using the SHELXL93 program system (22). The origin of the unit cell was taken at the point $\bar{3}m$ of the space group $Fd\bar{3}m$ (No. 227 in the International Tables for X-ray Crystallography), the tetrahedral, octahedral and anion sites being in the positions $8a, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}$; $16d, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; and $32e$, x, x, x; respectively. The Zn, Ga, and Cr atoms were refined with coupled site occupation factors (SOF) and isotropic displacement parameters. The results of the structure refinement and the selected bond distances and angles are collected in Tables 2 and 3, respectively.

3. Magnetic Measurements

The magnetic properties were investigated in high magnetic stationary fields up to 140 kOe. Complete cooling and heating cycles were carried out in the temperature range 4.2–200 K using an induction magnetometer. Molecular magnetic moments as a function of the magnetic field applied at 4.2 K are shown in Fig. 1. The saturation moments per formula unit for the crystals under study are given in Table 2. For the crystal III, which in the structure refinement was identified as $(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$, a ratio of the signal to the background was too low to give a measurable μ_{sat} value. We have thus concluded that in this crystal $\mu_{sat} < 0.1\mu_B$/f.u., which is the value corresponding to the standard deviation of the measurement of the saturation magnetic moment.

RESULTS AND DISCUSSION

The X-ray scattering factors for Zn and Ga are nearly the same; therefore the cation distribution resulting from the refinement of X-ray diffraction powder data is often ambiguous. Although modern single crystal refinement techniques allow the successful refinement of the site occupation factors, in the absence of neutron diffraction studies, the most chemically reasonable cation distribution had to be related to the crystal-chemical arguments and to the results of other types of experiments.

Accordingly, the structure calculations for crystal I were initiated with the model of a mixed distribution of Zn, Ga, and Cr cations over (A) and [B] sites. In Fig. 2 the idealized cubic spinel structure with the tetrahedral and octahedral coordination of the cations is shown. After completion of the refinement with the mixed occupancies ($R_1 = 0.051$, $wR_2 = 0.112$) it appeared that Zn, Ga, and Cr shared the tetrahedral sites in proportions 0.60, 0.37, and 0.03, respectively, while the octahedral sites were in proportions 0.01, 0.02, and 0.98, respectively. However, 0.03 of the site occupation is an amount corresponding to about twice the estimated standard deviation (e.s.d.) for the site occupation factor. The refinement did not truly converge as the maximum shift/e.s.d. was 0.41. Besides, the apparent deficit of

TABLE 1
The Details of Crystal Data, X-Ray Data Collection, and Structure Refinement

	I	II	III
	Crystal data		
Chemical formula	$(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$	$(Zn_{0.95}\square_{0.05})[Ga_{0.03}\ Cr_{1.93}\square_{0.04}]Se_4$	$(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$
Crystal system	cubic	cubic	cubic
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$
a (Å)	10.465(1)	10.474(1)	10.482(1)
V (Å^3)	1146.1(3)	1149.1(3)	1151.7(3)
Z	8	8	8
Density calc. (Mg/m$_3$)	5.664	5.710	5.801
Absorption coeff. μ (mm^{-1})	33.3	33.6	34.8
	Data collection		
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073	Mo$K\alpha$, 0.71073
Monochromator	graphite	graphite	graphite
2θ range (°)	91.5	74.5	103.8
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan speed (°/s)	0.010 to 0.04	0.010 to 0.06	0.015 to 0.05
Scan width (°)	$1.1 + 0.25\tan\theta$	$1.25 + 0.25\tan\theta$	$1.2 + 0.25\tan\theta$
Index range: h	− 12, 0	− 17,12	0, − 23
k	− 20, 20	− 17,17	0, 23
l	− 20, 20	− 17,12	0, 23
No. reflections collected	3652	2501	3967
No. independent reflections	257	160	359
No. observed reflections	223	151	206
Standard reflections/ measurements:	2/50	2/50	2/50
Decay of standards	negligible	negligible	negligible
	Refinement		
Refinement on	F^2	F^2	F^2
F_o criterium	$\lvert F_o\rvert \geq 2\sigma(F_o)$	$\lvert F_o\rvert \geq 2\sigma(F_o)$	$\lvert F_o\rvert \geq 2\sigma(F_o)$
Corrections:			
Lorentz-polarization			
Absorption (numerical), T_{min} and T_{max}	0.02 and 0.66	0.05 and 0.68	0.01 and 0.65
Extinction (empirical as in SHELXL93)	$x = 0.0015(1)$,	$x = 0.0055(4)$	$x = 0.0012(1)$
R_{int} (before; after absorption)	0.09; 0.056	0.14, 0.07	0.11, 0.068
Number of varied parameters	10	10	10
Final R_1	0.034	0.042	0.040
Final wR_2	0.104	0.086	0.092
Goodness of fit	0.92	1.83	0.91
Min.; max. residual (eÅ^{-3})	− 1.8, 1.6	− 2.1, 1.78	− 1.6, 1.8

Zn^{2+} on the tetrahedral positions suggests that all Cr^{3+} are located on the octahedral 16*d* sites, as Cr^{3+} is known to show a greater site preference than any other 3*d* ion to occupy octahedral sites (23). In subsequent calculations all the Cr^{3+} ions were situated on the [B] sites, while Zn^{2+} and Ga^{3+} were mixed on the (A) sites. Although the site prefer-

TABLE 2
Structural and Magnetic Characteristics of the Spinel System $Zn_{(1-x)}Ga_{2x/3}Cr_2Se_4$

Compound	$\mu_{sat.}$ at 4.2 K (μ_B/f.u)	T_N (K)	Anion parameter u	Site occupation		Thermal displacement amplitude U_{iso} 10^3 (Å^2)		
				(A)	[B]	(A) site	[B] site	Se
$(Zn)[Cr_2]Se_4$[a]	6.0	20	0.259	1.0	2.0			
I: $(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$	5.2(1)	21	0.25927(5)	0.63:37	2.0	17.4(2)	15.2(2)	14.56(1)
II: $(Zn_{0.95}\square_{0.05})[Ga_{0.03}\ Cr_{1.93}\square_{0.04}]Se_4$	3.8(1)	21	0.25929(8)	0.95	0.03:1.93	8.7(5)	7.8(4)	7.1(3)
III: $(Zn)[Ga_{0.4}\ Cr_{1.6}]Se_4$	≈ 0	23	0.25939(5)	1.0	0.40:1.60	8.6(4)	9.1(4)	8.9(2)

Note. The atom positions are: (A) site: 8*a*: ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$); [B] site:16*d*: ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$); Se site: 32*e*: *x*, *x*, *x*, (*u* parameter).

[a] Data from (3) (unit cell $a = 10.443$ Å).

TABLE 3
Selected Bond and Interatomic Distances (in Å) and Bond Angles (in °)

Distances and angles	$(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$	$(Zn_{0.95}\square_{0.05})[Ga_{0.03}Cr_{1.93}\square_{0.04}]Se_4$		$(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$	
Zn/Ga–Se	2.429(0.1)	Zn–Se	2.436(1)	Zn–Se	2.439(1)
Zn/Ga–Se	2.525(0.1)	Ga/Cr–Se	2.525(1)	Ga/Cr–Se	2.526(1)
Zn/Ga–Zn/Ga	4.531(1)	Zn–Zn	4.535(2)	Zn–Zn	4.538(3)
Cr–Cr	3.700(1)	Ga/Cr–Ga/Cr	3.701(2)	Ga/Cr–Ga/Cr	3.706(2)
Zn/Ga–Cr	4.338(1)	Zn–Ga/Cr	4.342(2)	Zn–Ga/Cr	4.345(3)
Se_A–Se_A	3.974(1)	Se_A–SeA	3.978(2)	Se_A–SeA	3.984(3)
Se_B–Se_B	3.425(1)	Se_B–Se_B	3.427(2)	Se_B–Se_B	3.427(3)
Se_B–Se_B	3.705(1)	Se_B–Se_B	3.708(2)	Se_B–Se_B	3.711(2)
Se–Zn/Ga–e	109.47(0)	Se–Zn–Se	109.47(0)	Se–Zn–Se	109.47(0)
Se–Cr–Se	94.37(1)	Se–Ga/Cr–Se	94.49(1)	Se–Ga/Cr–Se	94.52(2)
Se–Cr–Se	85.63(1)	Se–Ga/Cr–Se	85.51(3)	Se–Ga/Cr–Se	85.48(2)
Se–Cr–Se	180.0(0)	Se–Ga/Cr–Se	180.0(0)	Se–Ga/Cr–Se	180.0(0)

ence energy of Zn is twice as high as Ga, the latter model converged with $R_1 = 0.034$ and $wR_2 = 0.104$, maximum shift/e.s.d. = 0.006. The resulting occupancies on the tetrahedral site were (0.63 Zn + 0.37 Ga) ± 0.03 (Table 2). We conclude, therefore, that the second approach with all the Cr^{3+} ions on the octahedral sites and mixed $(Zn^{2+} + Ga^{3+})$ occupation on the tetrahedral sites is more justified than the first one. The formula describing the cation distribution in the crystal I is $(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$. This choice gives not only a better statistical convergence (*R* factors), but is also consistent with the results of magnetic measurements. The saturation magnetic moment 5.2 μ_B/f.u. is characteristic of zinc-chromium selenides with high Cr^{3+} concentration (Fig. 1). The atomic coordinates and the thermal displacement amplitudes for the second refinement are given in Table 2; the bond lengths and bond angles are given in Table 3. As noted before, a small amount of nonmagnetic Ga ions on the [B] sites may considerably affect the Cr–Se–Cr and Cr–Se–Se–Cr magnetic superexchange interactions. Based on the present result we cannot exclude a hypothesis that the saturation moment, smaller than the theoretical 6μ_B/f.u., is a consequence of migration of some Ga^{3+} to the octahedral sites in this crystal.

The structure refinement of crystal II, modeled as a random distribution of Zn, Ga, and Cr over both the (A) and [B] sites, showed the amount of Zn^{2+} ions (0.95) much higher than was observed in crystal I. The tetrahedral sites are now almost fully occupied by Zn^{2+} ions. Small deficiency of Cr^{3+} allowed Ga^{3+} to be located on the octahedral sites. The site occupation refinement led thus to the formula $(Zn_{0.95})[Ga_{0.03}Cr_{1.93}]Se_4$. This result points to the cation deficiency, which is known to occur not only for

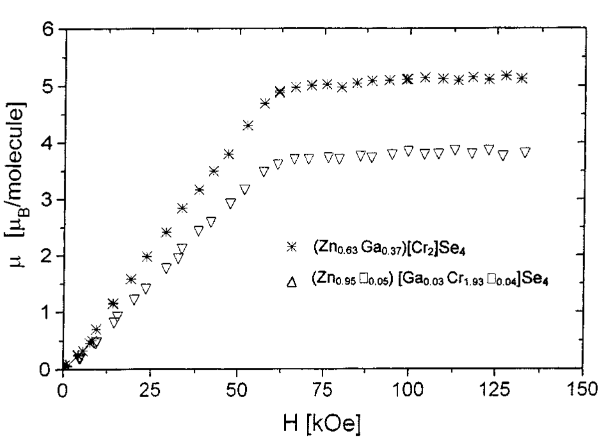

FIG. 1. The magnetic moments measured at the temperature 4.2 K versus the external magnetic field.

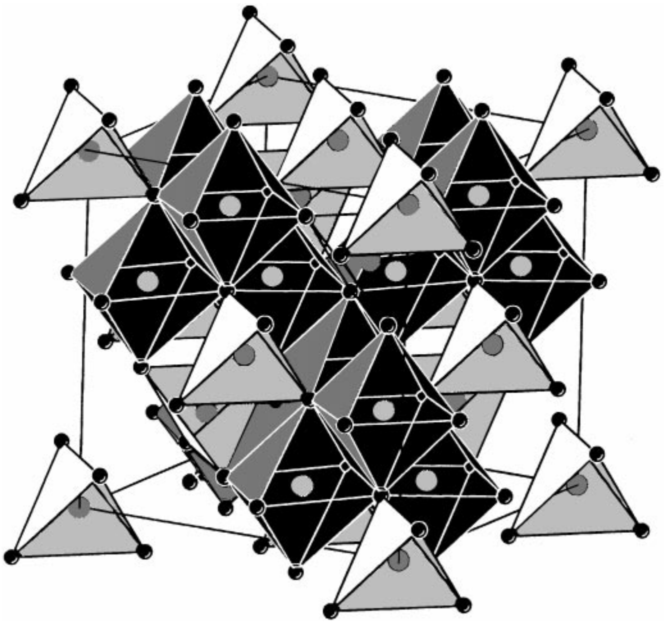

FIG. 2. The tetrahedral and octahedral coordination of Zn^{2+} and Cr^{3+} ions in the cubic spinel structure. The origin of the unit cell is at the point $\bar{4}3m$, at $-\frac{1}{8}$, $-\frac{1}{8}$, $-\frac{1}{8}$ from the center $\bar{3}m$.

crystals from different preparations, but occasionally for crystals within the same growth batch (6). The neutron diffraction studies evidenced the existence of a few percent of vacancy concentration in the series of $Zn_{(1-x)}Ga_xCr_2Se_4$ spinels (16). Also the *p*-type electrical conductivity in the $ZnCr_2Se_4$ semiconductor was explained in connection with the Zn^{2+} vacancies playing the role of doubly charged acceptors (24). Therefore, crystal II should be described as $(Zn_{0.95}\square_{0.05})[Ga_{0.03}Cr_{1.93}\square_{0.04}]Se_4$, where $\square$ denotes cation vacancies. Such a cation distribution caused a perturbation in the periodicity of the crystal lattice. In the octahedral sublattice, a substitution of nonmagnetic Ga^{3+} for Cr^{3+} affected some of the paths of spin exchange between the Cr^{3+} pairs, causing the saturation magnetic moments to be reduced to the value $3.8\mu_B$ (Table 2). This result clearly demonstrates the essential role of Cr^{3+} ions in the magnetic exchange interactions.

High deficiency in the Cr^{3+} concentration in the last crystal caused the unusually large number of Ga^{3+} to be accommodated on the octahedral sites. Moreover, there were no other cations competing with Zn^{2+} for the tetrahedral site; therefore, the cation distribution, resulting from the structure refinement of crystal III, has been assigned as $(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$. The magnetic measurements showed that 0.40 of Ga^{3+} ions at the octahedral sites were sufficient to suppress the magnetic exchange interactions.

CONCLUSIONS

In the single crystals of $Zn_{(1-x)}Ga_yCr_{(2-y)}Se_4$, various magnetic structures have been identified. Depending on the stoichiometry of the other cations, the Ga^{3+} ion can accommodate both the tetrahedral and the octahedral sites. The pronounced deficit of Zn^{2+} forces Ga^{3+} to occupy the tetrahedral (A) sites, while the deficiency of Cr^{3+} causes the Ga^{3+} ions to be moved to the octahedral [B] sites. The small number of nonmagnetic Ga^{3+} ions substituted for Cr^{3+} at the [B] sites is able to considerably reduce the magnetic exchange interactions. There exists some critical number of the Cr^{3+} ions on the [B] sites, below which the magnetic properties of the system become unobservable. The saturation magnetic moments strongly depend on the cation vacancies but are less dependent on the number of Ga^{3+} at the tetrahedral sites.

With increasing lattice constants the magnetic interactions in these materials appear to be weaker and the transition temperatures T_N are shifted to the slightly higher temperatures. The mean Cr–Se–Cr distance between the ions involved the superexchange interactions increases from 3.700(1) Å in $(Zn_{0.63}Ga_{0.37})[Cr_2]Se_4$ with $\mu_{sat} = 5.2(4)\mu_B$/f.u., to 3.706(2) Å in $(Zn)[Ga_{0.4}Cr_{1.6}]Se_4$ with $\mu_{sat} < 0.1\mu_B$/f.u.

REFERENCES

1. F. K. Lotgering, *Solid State Commun.* **3,** 347 (1965).
2. P. K. Baltzer, H. W. Lehman, and M. Robbins, *Phys. Rev. Lett.* **15,** 493 (1965).
3. R. Plumier, *Compt. Rend. Acad. Sci.* (*France*) **260,** 3348 (1965).
4. R. Plumier, M. Lecomte, A. Miedan-Gros, and M. Sougi, *Phys. Lett. A* **55,** 239 (1975).
5. P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.* **151,** 367 (1966).
6. H. L. Pinch and S. B. Berger, *J. Phys. Chem. Solids* **29,** 2091 (1968).
7. A. Herpin, P. Mérier, and J. Villain, *J. Phys. Radium* **21,** 67 (1960).
8. R. Plumier, *J. Phys.* **27,** 213 (1967).
9. J. Akimitsu, K. Siratori, G. Shirane, M. Iizumi, and T. Watanabe, *J. Phys. Soc. Japan* **44,** 172 (1978).
10. I. Okońska-Kozłowska, H. D. Lutz, T. Groń, J. Krok, and T. Mydlarz, *Matter. Res. Bull.* **19,** 1 (1984).
11. S. Juszczyk, J. Krok, I. Okońska-Kozłowska, T. Mydlarz, and A. Gilewski, *J. Magn. Magn. Mater.* **46,** 105 (1984).
12. T. Groń, H. Duda, and J. Warczewski, *J. Magn. Magn. Mater.* **83,** 487 (1990).
13. T. Groń, H. Duda, and J. Warczewski, *Phys. Rev. B* **41,** 12424 (1990).
14. I. Okońska-Kozłowska, V. Koch, W. Schmidt, and H. D. Lutz, *Z. Anorg. Allg. Chem.* **510,** 88 (1984).
15. A. A. Zhukov, Ya. A. Kesler, V. F. Meshcheriakov, and A. V. Rozancev, *Solid State Phys.* **26,** 1 (1984).
16. J. Kusz, J. Warczewski, A. Bombik, and A. Oleś, *Z. Kristallogr.* **185,** 682 (1988).
17. H. Rej, A. Bombik, J. Kusz, A. Oleś, M. Pinot, and J. Warczewski, *J. Magn. Magn. Mater.* **111,** 47 (1992).
18. S. Juszczyk, *J. Magn. Magn. Mater.* **73,** 27 (1988).
19. S. Juszczyk, *J. Magn. Magn. Mater.* **75,** 285 (1988).
20. S. Juszczyk, *J. Magn. Magn. Mater.* **83,** 473 (1990).
21. G. M. Scheldrick, "SHELXTL-Plus," Siemens Analytical Instruments, Madison, WI, 1990.
22. G. M. Scheldrick, "SHELXL93, Program System for Crystal Structure Refinement," 1993.
23. A. Weiss and H. Witte, "Kristallstruktur und chemische Bindung," Verlag Chemie, Weinheim, 1983.
24. T. Watanabe, *J. Phys. Soc. Japan* **37,** 140 (1974).