JOURNAL OF SOLID STATE CHEMISTRY 35, 50–58 (1980)

Crystallographic and Magnetic Studies of Cation-Deficient Spinels $M_{2/3+x}Cr_{2-x}S_4$ (M = Al; Ga; In)

I. NAKATANI

National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153, Japan

Received October 15, 1979

Crystallographic studies are carried out on the cation-deficient spinel compounds $Ga_{2/3}Cr_2S_4$ and $Al_{2/3+x}Cr_{2-x}S_4$ ($\frac{1}{3} \leq x \leq \frac{2}{3}$). X-Ray analysis of both compounds indicates that there exist $\frac{1}{3}$ vacancy per formula unit in 8*a* positions and all chromium atoms in 16*d* positions, with the rest of the metal positions occupied by gallium or aluminum atoms. Aluminum atoms give a wide range of substitution for chromium atoms, but gallium atoms do not. It is found by electron diffraction that vacancy ordering occurs in $Ga_{2/3}Cr_2S_4$ below about 1100°C, as well as in $InCr_{5/3}S_4$. The magnetic properties of these compounds are investigated. Both $InCr_{5/3}S_4$ and the disordered form of $Ga_{2/3}Cr_2S_4$ exhibit weak ferromagnetism at low temperatures. The facts are explained in terms of the vacancy distribution in the 8*a* positions.

I. Introduction

The chalcogenide spinels of type MCr_2X_4, where M is a divalent metal ion (such as Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+}, Co^{2+}, or Mn^{2+}) and X is a chalcogen ion (S^{2-} or Se^{2-}), have been extensively studied with respect to their magnetic and electrical properties (*1–3*). These compounds are all semiconducting and ferromagnetic except $ZnCr_2S_4$ and $ZnCr_2Se_4$ which are antiferromagnetic. They have a cubic unit cell containing eight molecules and a space group $Fd3m$. The chalcogen ions are in 32*e* positions which make nearly cubic close-packing (it would be perfect for the coordinate u = 0.375 of the chalcogen ion). Each M^{2+} ion in the 8*a* positions is surrounded tetrahedrally by four chalcogen ions (tetrahedral site), and each Cr^{3+} ion in the 16*d* posisions is surrounded octahedrally by six chalcogen ions (octahedral site). The cation can be substituted extensively by other metal ions while the chalcogen ions retain their character as cubic close-packing. A number of new spinel compounds have been derived so far. It was recently found (*4*) that a cation-deficient spinel-type compound is formed in the chromium chalcogenide $Ga_{2/3}Cr_2S_4$ which is substituted by trivalent gallium ion for the divalent metal ion M^{2+}. This spinel was reported to be ferromagnetic with positive asymptotic Curie temperature and to have a high anisotropy. Lotgering and van der Steen also stated the existence of cation-deficient spinel compounds $Cr_{8/9}Al_{16/9}\square_{1/3}S_4$ (*5, 6*) and $Cr_{8(1-x)/3}In_{8x/3}\square_{1/3}S_4$ ($\frac{3}{8} \leq x \leq 1$) (*6, 7*). On the latter materials they made a detailed investigation. They suggested from X-ray powder diffraction analysis that the vacancies and In^{3+} ions together occupy the 8*a* positions

0022-4596/80/130050-09$02.00/0

and are ordered in the 8a positions at the composition $x = \frac{3}{8}$. These defect spinel compounds belong to the sesquisulfide category of sesquioxide spinels with the general formula A_2X_3, like β-In_2S_3, γ-Al_2O_3, and γ-Fe_2O_3.

In the present paper, further investigation was made on the crystallographic studies of the defect spinels on the systems $M_{2/3+x}Cr_{2-x}S_4$ (M = Al, Ga, or In). In the system of M = Al or Ga, site occupations of each metal ion and of vacancy were determined by X-ray analysis. The vacancy ordering was also investigated by means of the single-crystal electron diffraction method. The magnetic properties of these materials were examined and were explained in terms of the vacancy distribution.

II. Experimental

II.1. Preparation

All of the samples on the system $M_{2/3+x}Cr_{2-x}S_4$ (M = Al, Ga, or In) were prepared by firing stoichiometric mixtures of the elements, which were in a powder of Cr (99.9%); grains of Ga (99.999%) or In (99.999%) or ribbons of Al (99.99%); and grains of S (99.999%). The firing procedure was repeated four times as described below. At first, the mixture was sealed in an evacuated quartz tube whose inner wall was coated with pyrolytic graphite, then heated at 750°C for 20 hr and furnace cooled to room temperature. These products were then ground into a fine powder and were reheated in a way similar to that described above. The third heating was needed to achieve a higher degree of homogeneity. In the third heating, the materials of the systems containing Al and Ga were heated at 1000 and 1150°C, respectively, for 20 hr in alumina crucibles sealed in evacuated quartz tubes. The alumina crucibles were needed in order to prevent direct reaction between the materials and the quartz tubes at high temperature. The quartz tubes were then quenched in water. The third heat treatments for the materials containing In were made at 750°C in evacuated quartz tubes for 20 hr, followed by quenching in water. Samples, obtained in powder form, were identified by the X-ray diffraction method using Cu$K\alpha$ radiation. The lattice constants were determined from the high-angle diffraction lines by extrapolating the values to the Bragg angle of 90° using the Nelson–Riley function.

In the system $Al_{2/3+x}Cr_{2-x}S_4$, X-ray powder diffraction patterns showed no trace of other phases for the samples of composition ranging from $x = \frac{1}{3}$ to $\frac{5}{3}$. Compositions were $x < \frac{1}{3}$ did not yield the single phase of the spinel, but did yield two phases of spinel and Cr_2S_3. When the composition is limited at $x = 2$, Al_2S_3 is formed. The variation of the lattice constants for the spinel obeys Vegard's law within the range of $\frac{1}{3} \leq x \leq \frac{5}{3}$ as shown in Fig. 1. In the system containing Ga, the pure spinel phase was obtained only at the composition $x = 0$, i.e., $Ga_{2/3}Cr_2S_4$. Samples of other compositions contained Ga_2S_3 or Cr_2S_3 in addition to the spinel.

In the fourth heat treatment, the spinel $Ga_{2/3}Cr_2S_4$ was subject to annealing at temperatures from 670 to 1170°C for 20 hr, and quenching. X-Ray powder patterns of the samples quenched from higher than 1150°C can be indexed solely by the spinel struc-

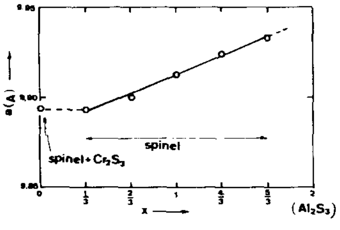

FIG. 1. Variation of lattice constant of the system $Al_{2/3+x}Cr_{2-x}S_4$.

ture with cell size 9.895 Å. On the samples quenched from 1100°C or lower temperatures, however, diffraction patterns revealed reflections other than spinel type. These extra reflections could be indexed as 200, 420, and 640 with a cubic unit cell very nearly the same (9.888 Å) as that of the high-temperature form of $Ga_{2/3}Cr_2S_4$. The intensity distribution shows almost no difference from that of the high-temperature form except for the presence of the extra reflections. In the spinel structure, which belongs to space group *Fd*3*m*, reflections whose indices $h + k \neq 4n$ for any *hk*0 are not possible. This low-temperature phase is transformed to the high-temperature phase by heat treating above 1150°C. In the spinel $AlCr_{5/3}S_4$ no phase transition had taken place by the fourth heat treatment at temperatures between 600 and 1100°C.

In the system containing In, all of the compounds except $x = \frac{1}{3}$, i.e., $InCr_{5/3}S_4$, did not yield single-phase materials. The compound $InCr_{5/3}S_4$ gave a powder diffraction pattern identical to that of the low-temperature phase of $Ga_{2/3}Cr_2S_4$. The compound $InCr_{5/3}S_4$, however, undergoes no phase transition on annealing at temperatures from 600 up to 1100°C, at which temperature the sample decomposes to In_2S_3 and Cr_2S_3.

The compositions of the samples were checked by chemical analysis (Table I).

TABLE I

RESULTS OF CHEMICAL ANALYSIS

Compound	Composition (atomic ratio)	
	Charged	Chemically analyzed
$AlCr_{5/3}S_4$		
Al	1.00	0.98
Cr	1.67	1.70
S	4.00	4.00
$Ga_{2/3}Cr_2S_4$		
Ga	0.67	0.64
Cr	2.00	1.98
S	4.00	4.00
$InCr_{5/3}S_4$		
In	1.00	1.01
Cr	1.67	1.66
S	4.00	4.00

II.2. X-Ray and Electron Diffraction Measurements and Results

II.2.1. Measurements. As mentioned above, all X-ray diffraction patterns of $Al_{2/3+x}Cr_{2-x}S_4$ ($\frac{1}{3} \leq x \leq \frac{5}{3}$) and the high-temperature form of $Ga_{2/3}Cr_2S_4$ satisfy the extinction rule for the spinel. In order to determine the site occupancy of each ion, measurements of integrated intensities were carried out using a Rigakudenki diffractometer with a proportional counter installed on a high-power X-ray generator using Cu*K*α radiation. Powder samples were bonded with acryl resin, and were shaped into disks with flat surfaces. A flat specimen is desirable to minimize the error due to the absorption of the sample. Diffraction profiles of $AlCr_{5/3}S_4$ and $Ga_{2/3}Cr_2S_4$ for 2θ between 14° and 160° were taken in stepwise scanning at intervals of 2/100°, and they were corrected for background. On the samples of $x = \frac{2}{3}, 1, \frac{4}{3}$, and $\frac{5}{3}$ in the system of $Al_{2/3+x}Cr_{2-x}S_4$, only the diffraction peaks of 222 and 220 were measured, whose intensities are sensitive for the occupation in 8*a* and 16*d* positions.[1] Observed intensity ratios of I_{222}/I_{220} were compared to the calculated ones. For $InCr_{5/3}S_4$ and the low-temperature form of $Ga_{2/3}Cr_2S_4$, which show extra reflections on the X-ray powder diffraction, single-crystal patterns were obtained by means of selected-area electron diffraction with a JEOL JM-150 electron microscope.

II.2.2. Calculations and results. If the ionic arrangements are assumed to be char-

---

[1] The structure factor F for the reflections of 222 and 220 is written as: $F_{222} = 16f_d + 8f_e(\cos 12\pi u + 3\cos 4\pi u)$; $F_{220} = 8f_a - 16f_e(\cos 8\pi u - 1)$, where f_a, f_d, and f_e are atomic scattering factors of ions occupying 8*a*, 16*d*, and 32*e* positions, respectively.

acteristic of spinel on both materials (the high-temperature form of $Ga_{2/3}Cr_2S_4$ and the $Al_{2/3+x}Cr_{2-x}S_4$ system), the sulfur ions are in the 32*e* positions with cubic close-packing, and metal ions, i.e., aluminum, gallium, and chromium ions, occupy the 8*a* and 16*d* positions.

It can be said from the chemical analysis that there exist $\frac{1}{3}$ vacancy per molecule in the metal positions, though the density was not measured. Thus, when site mixing by each metal ion is considered, diffracted intensities are calculated for the four different models listed in Table II on $AlCr_{5/3}S_4$ and $Ga_{2/3}Cr_2S_4$. In both Models I and III, vacancies exist at the 8*a* positions, and the 16*d* positions are fully occupied. All the chromium ions exist at the 16*d* positions in Model I, while all the aluminum ions or gallium ions exist at the 16*d* positions in Model III. On the other hand, in both Models II and IV the 16*d* positions are unfilled, but the 8*a* positions are filled. All the aluminum or gallium ions occupy 8*a* positions in Model II, whereas they occupy 16*d* positions in Model IV. For every observable reflection, diffracted intensities were calculated considering the *u* parameter and the overall temperature factor *B* as the variables and they were corrected for multiplicity and the Lorentz-polarization factor. The calculated and observed intensities of the *i*th reflection $I^i_{(\text{calc})}$ and $I^i_{(\text{obs})}$ were normalized by proportional factors as follows:

$$i_{\text{calc}} = \frac{I^i_{(\text{calc})}}{\sum_n I^n_{(\text{calc})}},$$

$$I^n_{(\text{obs})} = \frac{I^i_{(\text{obs})}}{\sum_n I^n_{(\text{obs})}}.$$

The denominators in the above equations represent the sums of the calculated and of the observed intensities, respectively. The agreement factor *R* is

$$R = \frac{\sum_i \left| I^i_{\text{calc}} - I^i_{\text{obs}} \right|}{\sum_i I^i_{\text{obs}}}.$$

These calculations were made with the NEAC 3100 computer at the National Research Institute for Metals.

For the above-described Models I–IV, the agreement factors were calculated as a function of *u* with various values of *B*. The variation of the agreement factor can be seen in Figs. 2a and b as a function of *u* with optimum *B* values of 0.80 and 0.85 for $AlCr_{5/3}S_4$ and $Ga_{2/3}Cr_2S_4$, respectively. The best agreement was obtained with Model I for both $AlCr_{5/3}S_4$ and $Ga_{2/3}Cr_2S_4$. The value $u = 0.3825 \pm 0.0005$ is accepted as the one which gives the minimum agreement factors for both compounds. Comparisons between the observed and calculated

TABLE II

FOUR DIFFERENT MODELS OF ATOMIC ARRANGEMENT OF THE SPINELS $AlCr_{5/3}S_4$ AND $Ga_{2/3}Cr_2S_4$

Model	$AlCr_{5/3}S_4$	$Ga_{2/3}Cr_2S_4$
I	$Al_{2/3}\square_{1/3}[Cr_{5/3}Al_{1/3}]S_4$	$Ga_{2/3}\square_{1/3}[Cr_2]S_4$
II	$Al[Cr_{5/3}\square_{1/3}]S_4$	$Ga_{2/3}Cr_{1/3}[Cr_{5/3}\square_{1/3}]S_4$
III	$Cr_{2/3}\square_{1/3}[CrAl]S_4$	$Cr_{2/3}\square_{1/3}[Cr_{4/3}Ga_{2/3}]S_4$
IV	$Cr[Cr_{2/3}Al\square_{1/3}]S_4$	$Cr[CrGa_{2/3}\square_{1/3}]S_4$

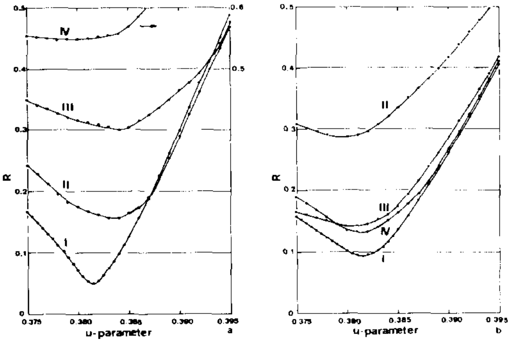

FIG. 2. Agreement factor *R* as a function of *u* with respect to four different models: (a) $AlCr_{5/3}S_4$; (b) $Ga_{2/3}Cr_2S_4$.

intensities based on these parameters are given in Table III.

For $Al_{2/3+x}Cr_{2-x}S_4$, intensity ratio I_{222}/I_{220} was calculated as a function of x on the basis of the above-described Models I–IV. Figure 3 shows the observed I_{222}/I_{220} compared with the calculated ratio based on Model I, i.e., $Al_{2/3}\square_{1/3}[Al_xCr_{2-x}]S_4$. One can see that Model I is preferable regardless of x. Therefore it is concluded that there always exist vacancies in the 8*a* positions and chromium ions exclusively in the 16*d* positions, and that the aluminum or the gallium ions occupy the 8*a* positions. Furthermore, the aluminum ions in the $Al_{2/3+x}Cr_{2-x}S_4$ system give a wide range of substitution for chromium ions in the 16*d* positions, but the gallium ions do not.

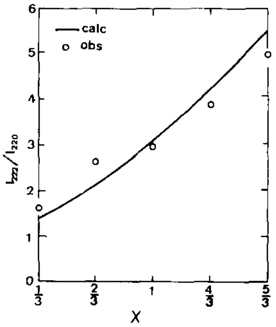

FIG. 3. Comparison between observed and calculated intensity ratio I_{222}/I_{220} as a function of x. Calculation is based on Model I, i.e., $Al_{2/3}\square_{1/3}[Cr_{2-x}Al_x]S_4$.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES (u = 0.3825)

	$AlCr_{5/3}S_4$		$Ga_{2/3}Cr_2S_4$	
hkl	I_{obs}	I_{calc}	I_{obs}	I_{calc}
111	1022	1034	409	330
220	96	77	378	440
311	949	1011	1512	1703
222	156	107	61	48
400	1819	1824	1338	1151
331	46	72	0	3
422	18	28	138	176
511–333	482	501	720	745
440	1543	1498	1651	1633
531	137	167	44	41
442	10	1	0	0
620	50	10	38	67
533	98	112	146	176
622	35	16	17	7
444	325	324	228	197
711–551	122	96	58	33
642	41	17	75	83
731–553	133	149	219	252
800	200	200	189	214
733	0	0	2	4
644	0	0	0	0
822	0	4	40	24
751–555	104	103	148	159
840	393	387	261	234
931	101	97	124	135
844	425	423	471	446
951–773	117	136	188	173
880	196	192	214	199
1200–884	411	410	256	245
1153–975	150	149	223	227
1240	823	854	854	857

For the low-temperature phase of $Ga_{2/3}Cr_2S_4$, the single-crystal electron diffraction pattern showed the presence of extra reflections which violate extinction rule $h + k \neq 4n$ for any $hk0$ ($h;k$ even) or $h,k,0$, permuted. Of course, no reflection was observed that arose from a tetragonal unit cell of $c/a = 3$ as in γ-Fe_2O_3 (*8*). As an example, a pattern is reproduced in Fig. 4, where the incident beam is parallel to ⟨001⟩. These extra reflections cannot be caused by double diffraction for the spinel structure.

On the assumption that the structure is

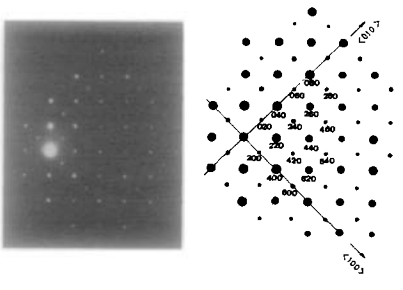

FIG. 4. Electron diffraction pattern of the ordered $Ga_{2/3}Cr_2S_4$ with beam parallel to ⟨001⟩.

based on the spinel structure with vacancies in the $8a$ positions, the presence of such extra reflections would lead to the ordered arrangement in the $8a$ position with a lower-symmetry space group, very probably $F\bar{4}3m$ which is a subgroup of $Fd3m$. The position $8a$, $(000;\ 0\frac{1}{2}\frac{1}{2};\ \frac{1}{2}0\frac{1}{2};\ \frac{1}{2}\frac{1}{2}0) + (000;\ \frac{1}{4}\frac{1}{4}\frac{1}{4})$, in the space group $Fd3m$ split into two fourfold positions $4a$, $000;\ 0\frac{1}{2}\frac{1}{2};\ \frac{1}{2}0\frac{1}{2};\ \frac{1}{2}\frac{1}{2}0$, and $4c$, $(4a) + \frac{1}{4}\frac{1}{4}\frac{1}{4}$, in the $F\bar{4}3m$. The most probable guess for the ordered structure of $Ga_{2/3}Cr_2S_4$ is that four of the gallium ions are in $4a$ and the $\frac{8}{3}$ vacancies together with the rest of the $\frac{4}{3}$ gallium ions are located at random over the $4c$ positions as $(Ga_{1/2})^{4a}(Ga_{1/6}\square_{1/3})^{4c}[Cr_2]S_4$. On the basis of this vacancy-ordered arrangement, preliminary calculation of the intensities was made with the same crystallographic parameters used for the disordered form. The agreement between observed and calculated intensities was fairly good for the X-ray powder diffraction pattern. In addition, the electron diffraction patterns of $InCr_{5/3}S_4$ had the same feature as the vacancy-ordered $Ga_{2/3}Cr_2S_4$. Consequently this vacancy-ordered $Ga_{2/3}Cr_2S_4$ is isostructural with $InCr_{5/3}S_4$, whose structure is suggested by Lotgering and van der Steen (*7*) as $(In_{1/2})^{4a}\ (In_{1/6}\square_{1/3})^{4c}[In_{1/3}Cr_{5/3}]S_4$.

II.3. Magnetic Measurements and Results

Magnetic properties were examined for the materials of $Al_{2/3+x}Cr_{2-x}S_4$ ($x = \frac{1}{3}$ and $\frac{5}{3}$), $Ga_{2/3}Cr_2S_4$, and $InCr_{5/3}S_4$. These samples were pressed and sintered under the same annealing conditions used for the syntheses, and then were shaped into spheres about 3 mm in diameter. Magnetization was measured by a vibrating sample magnetometer at temperatures between 5.1 and 300 K in a magnetic field up to 15 kOe. The Curie temperature T_c was obtained from the inflection point of the magnetization-vs-temperature curve in a constant field of 13 kOe.

Results of measurements for magnetization and susceptibility are shown in Figs. 5–7. The magnetic parameters are listed in Table IV.

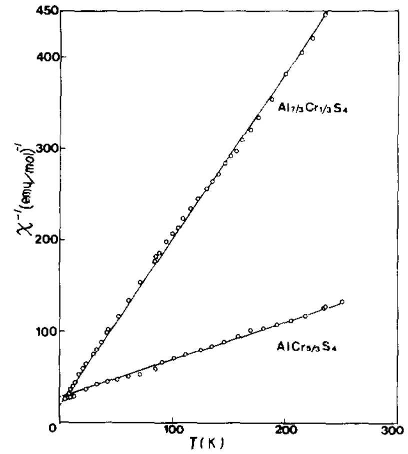

FIG. 5. Inverse susceptibilities as a function of temperature for $Al_{7/3}Cr_{1/3}S_4$ and $AlCr_{5/3}S_4$ in an applied field of 13 kOe.

The susceptibilities of the spinels $Al_{7/3}Cr_{1/3}S_4$ and $AlCr_{5/3}S_4$ follow the Curie–Weiss law in a constant field of 13 kOe, as shown in Fig. 5. Though the asymptotic Curie temperatures θ are negative, the Néel temperatures are not observed down to 5.1 K. The magnetizations at 5.1 K vary linearly with magnetic field, and do not show hysteresis.

As seen in Fig. 6a, the high-temperature phase of $Ga_{2/3}Cr_2S_4$ with the vacancy-disordered spinel structure is ferromagnetic with a T_c of about 30 K. The Curie–Weiss law is obeyed at high temperatures with θ of 20 K. The magnetization curve at 5.1 K shows a large hysteresis which is characteristic of ferromagnetism. The magnetization is, however, only slowly increasing with magnetic field, and is far from saturation even at 15 kOe (insertion on Fig. 6a). On the other hand, the low-temperature phase of $Ga_{2/3}Cr_2S_4$ with the vacancy-ordered spinel structure has a negative θ of −95 K and its inverse susceptibility-vs-temperature curve has a minimum at about 10 K like the Néel point, as shown in Fig. 6b. The magnetiza-

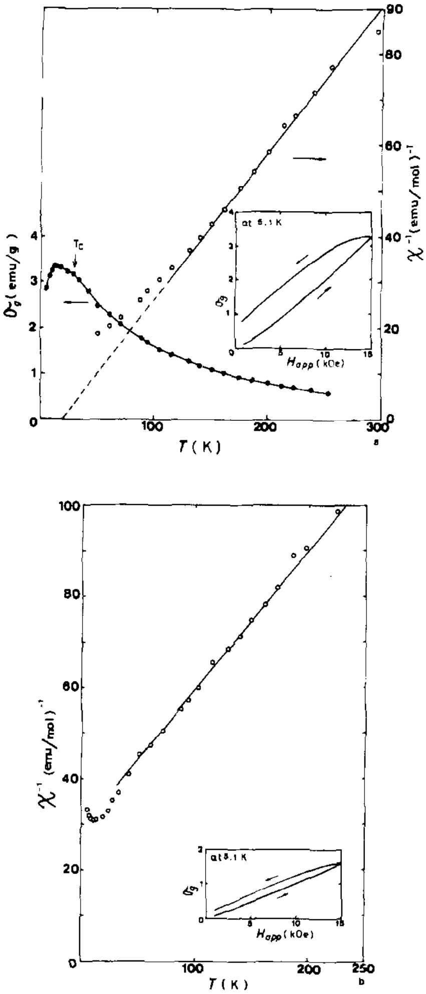

FIG. 6. Magnetic moments and inverse susceptibilities as a function of temperature in an applied field of 13 kOe: (a) high-temperature phase of $Ga_{2/3}Cr_2S_4$; (b) low-temperature phase of $Ga_{2/3}Cr_2S_4$. Insets: magnetization curves at 5.1 K.

tion at 5.1 K, however, shows a small hysteresis.

The vacancy-ordered spinel $InCr_{5/3}S_4$ is ferromagnetic below about 30 K and has θ of 42 K as indicated in Fig. 7. The magnetization curve at 5.1 K exhibits a large hysteresis, and also shows a feature similar to that of the high-temperature phase of $Ga_{2/3}Cr_2S_4$.

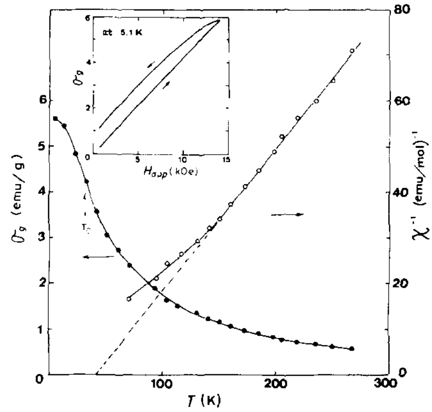

FIG. 7. Magnetic moment and inverse susceptibility as a function of temperature for $InCr_{5/3}S_4$ in an applied field of 13 kOe. Inset: magnetization curve at 5.1 K.

III. Discussion

It is well known as Verwey's rule that all of the chromium oxide and chalcogenide spinels have a normal spinel structure (*1*, *9–12*). The sesquisulfide spinels described are likely to obey that rule, because the vacancies are formed only on the tetrahedral sites which results in an average valence of 2, and the chromium ions occupy the octahedral sites exclusively. A (4*a*) and (4*c*) position ordering on the tetrahedral sites in $F\bar{4}3m$ occurs in the low-temperature phase of $Ga_{2/3}Cr_2S_4$, which is isostructural with $InCr_{5/3}S_4$ (*7*). The unit cells are the same for both the ordered and disordered structures. This type of (4*a*) and (4*c*) position ordering is well known to occur in such spinel-type compounds as $Fe_{1/2}Li_{1/2}Cr_2O_4$ (*13*), $Al_{1/2}Cu_{1/2}Cr_2S_4$ (*14*), and $Al_{1/2}Cu_{1/2}Cr_2Se_4$ (*14*). The vacancy-ordered spinel structure described is entirely different from the structures of other sesquisulfides and sesquioxides β-In_2S_3, γ-Al_2O_3, and γ-Fe_2O_3. β-In_2S_3 (*15*) is a vacancy-ordered superstructure of the spinel type with a large tetragonal unit cell $\frac{3}{2}$ times that of the spinel, in which the vacancies are located on the tetrahedral sites. γ-Al_2O_3 (*8*)

TABLE IV

STRUCTURAL AND MAGNETIC PARAMETERS OF THE SPINELS $M_{2/3+x}Cr_{2-x}S_4$

Compound	a (Å)	T_c (K)	θ (K)	n_{eff}/Cr	
$Al_{7/3}Cr_{1/3}S_4$	9.933	—	−6	3.59	Spinel structure
$AlCr_{5/3}S_4$	9.893 (u = 0.3825)	—	−66	3.39	
$Ga_{2/3}Cr_2S_4$	9.895 (u = 0.3825)	~30	20	3.53	
$Ga_{2/3}Cr_2S_4$	9.888	T_n ~ 10	−95	3.60	Vacancy-ordered spinel structure
$InCr_{5/3}S_4$	10.234	~30	42	3.92	

and γ-Fe_2O_3 (*8*) have a tetragonal superstructure consisting of three spinel cells stacked one by one in such a way that a complicated vacancy distribution on the octahedral sites has made a large unit cell of $c/a = 3$.

The Curie–Weiss law is obeyed at high temperature for all the materials examined. It seems that the chromium is in a trivalent state in these compounds, because the effective Bohr magneton number per chromium ion (n_{eff}/Cr shown in Table IV is close to the value (3.87) expected for the spin-only value of Cr^{3+}. The samples $Al_{2/3+x}Cr_{2-x}S_4$ have negative θ values and tend to become more negative with increasing chromium content. They are conceivably antiferromagnetic, though Néel temperatures are not observed down to 5.1 K. On the other hand, $InCr_{5/3}S_4$ and the high-temperature phase of $G_{2/3}Cr_2S_4$ have positive θ values. Their magnetizations do not show a sharp dependence on temperature, which makes the determination of T_c values impossible with sufficient accuracy; thus the values reported for these samples may have some error. The weak ferromagnetic moment observed in the low-temperature phase of $Ga_{2/3}Cr_2S_4$ can be explained by the presence of a small residual high-temperature phase.

In $InCr_{5/3}S_4$ and the high-temperature phase of $Ga_{2/3}Cr_2S_4$, the unusual feature on the magnetization curve which is hard to saturate cannot be explained by ionic anisotropy, which might be very small for the Cr^{3+} ion (*16*). The feature, however, may be associated with vacancies in the spinel structure. As can be seen in Fig. 8, each chromium ion at the 16*d* position is surrounded by six nearest-neighbor chromium ions at a distance of $\frac{1}{4}a2^{1/2}$ at about a 90° angle through an intervening anion. The chromium ion is also surrounded by six 8*a* site cations at a distance of $\frac{1}{8}a11^{1/2}$ through the anion. It is known that the ferromagnetism of the chromium chalco-

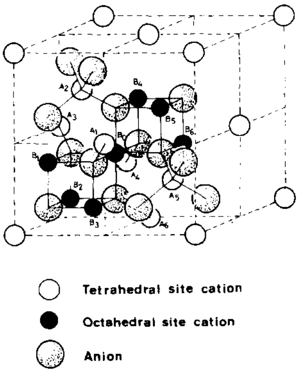

FIG. 8. Portion of spinel structure. It shows geometrical arrangement of first nearest octahedral site cations B_i (i = 1–6) and first nearest tetrahedral site cations A_i (i = 1–6) surrounding octahedral site cation B_0.

genide spinels comes mainly from the nearest-neighbor Cr–Cr interaction by superexchange through the anion. This superexchange interaction cannot be directly affected by the defect structure in $Ga_{2/3}Cr_2S_4$, since the formation of the vacancies is restricted only at the 8*a* positions. The local internal stress caused by the lattice defects, however, can give the local spin distortion field to ferromagnetic alignment of the moments of the chromium ions. Considering the statistical distribution of vacancies over the 8*a* positions, as much as 91%[2] of the chromium ions have one or more vacancies on the nearest-neighbor 8*a* positions. Thus, almost all of the moments of the chromium ions are locally distorted and fixed by the distortion field. It can be anticipated that the slope of the magnetization curve at 5.1 K arises from a lineup of the distorted spins in the external field against the distortion field. A quantitative analysis of such a local spin distortion may be very difficult, because it is necessary to take into account spin distortion at a greater distance from the center in a realistic model. In the case of $InCr_{5/3}S_4$ a more complicated problem is presented by partial substitution of indium ions for chromium ions at the 16*d* positions.

We have dealt with defect spinel compounds in which the divalent metal ions M^{2+} in the general formula MCr_2X_4 are substituted by trivalent metal ions such as Al^{3+}, Ga^{3+}, and In^{3+}. It seems likely that substitutions by other trivalent metal ions may be possible, which would lead to a class of new spinel compounds of semiconducting ferromagnets.

Acknowledgments

The author wishes to thank Dr. H. Nosé for his valuable suggestion and discussion. Thanks are also due to Dr. K. Masumoto for his stimulation and encouragement during the course of this study. The author expresses his appreciation to Professor Y. Komura of Hiroshima University for his beneficial advice and discussion on this study.

References

1. P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.* **151,** 367 (1966).
2. H. W. Lehman, *Phys. Rev.* **163,** 488 (1967).
3. P. J. Wojtowitcz, *IEEE Trans. Magn.* **5,** 840 (1969).
4. D. Brasen, J. M. Vandenberg, M. Robbins, R. H. Willens, W. A. Reed, R. C. Scherwood, and X. T. Pinder, *J. Solid State Chem.* **13,** 298 (1975).
5. F. K. Lotgering and G. H. A. M. van der Steen, *J. Solid State Commun.* **7,** 1827 (1969).
6. F. K. Lotgering and G. H. A. M. van der Steen, *J. Solid State Chem.* **3,** 574 (1971).
7. F. K. Lotgering and G. H. A. M. van der Steen, *J. Inorg. Nucl. Chem.* **33,** 673 (1971).
8. G. W. van Oosterhout and C. J. M. Rooymans, *Nature (London)* **181,** 44 (1958).
9. E. J. W. Verwey and E. L. Heilman, *J. Chem. Phys.* **15,** 174 (1947).
10. G. E. Bacon, *Acta Crystallogr.* **6,** 57 (1953).
11. S. Miyahara and H. Ohnishi, *J. Phys. Soc. Japan* **11,** 1296 (1956).
12. A. Miller, *J. Appl. Phys.* **30,** 24S (1959).
13. E. W. Gorter, *Philips Res. Rep.* **9,** 295 (1954).
14. H. L. Pinch, M. J. Woods, and E. Lopatin, *Mater. Res. Bull.* **5,** 425 (1970).
15. C. J. M. Rooymans, *J. Inorg. Nucl. Chem.* **11,** 78 (1959).
16. R. C. LeCraw, H. Van Philipsborn, and M. D. Sturge, *J. Appl. Phys.* **38,** 965 (1967).

---

[2] The probability $f(n)$ that n sites out of six 8*a* positions are vacant can be written as

$$f(n) = \frac{6!}{n!(6-n)!} p^n(1-p)^{6-n},$$

where p is the average fraction of vacancies on the 8*a* positions; then

$$p = \frac{1}{3}.$$

The fraction of the chromium ions that have one or more vacancies in the nearest-neighbor 8*a* positions is given as

$$\sum_{n=1}^{6} f(n) = 0.91.$$