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Neutron diffraction study of the structure of chalcogen spinels $Cu_{1+y}Cr_2X_4$ (X ≡ Se, Te)

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Abstract

The structure of the copper excess chromium spinels $Cu_2Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$ was determined by neutron diffraction at 300 K and at 4 K. The structure refinement reveals a simultaneous occupation of tetrahedral as well as of pseudo-octahedral sites by the excess y copper ions in $Cu_{1+y}Cr_2X_4$. The relatively high temperature factors are discussed in terms of a specific local disorder model within the spinel space group $Fd\bar{3}m$. From these results and the change in the lattice parameter a_0 with y a model was derived that is able to describe the sequence of occupation of tetrahedral and pseudo-octahedral lattice sites in the course of copper intercalation.

1. Introduction

Recently, we reported on the electrochemical intercalation at 300 K of additional copper into the chromium chalcogen spinels $CuCr_2X_4$ yielding non-stoichiometric or line phases $Cu_{1+y}Cr_2X_4$ (X ≡ S, $y=1$; X ≡ Se, Te, $0 \leqslant y \leqslant 1$) [1]. In addition to the physical properties, especially the strong influence of the intercalation process on the strength of the ferromagnetic coupling, the structural aspects of these intercalation compounds are of particular interest for an understanding of the correlation between structure, bonding and reactivity of these phases.

$Cu_{1+y}Cr_2Se_4$ and $Cu_{1+y}Cr_2Te_4$ exhibit ferromagnetic behaviour with an unusually high Curie temperature $T_c = 432$ K and $T_c = 364$ K respectively for $y=0$ [2]. Increasing the copper stoichiometry via electrochemical intercalation reaction leads to a continuous decrease in T_c for both phases. Since X-ray photoelectron spectroscopy studies have shown chromium to be in the oxidation state Cr^{3+} for $0 \leqslant y \leqslant 1$, the ferromagnetic coupling mechanism has been suggested by us to proceed via holes in the anion valence band [3]. As a consequence of the electron transfer to the valence band during the intercalation process, the hole concentration decreases continuously according to the following equation with increasing copper stoichiometry y:

$$Cu^+(Cr^{3+})_2(X_4)^{7-} + yCu^+ + ye^- \rightleftharpoons (Cu^+)_{1+y}(Cr^{3+})_2(X_4)^{(7+y)-} \quad (1)$$

The structures for $Cu_{1+y}Cr_2X_4$ (X ≡ Se, Te) have not been known in detail until now. Lotgering and van der Steen [4], who investigated the structure of the thermal phase $Cu_2Cr_2Te_4$ by X-ray diffraction, suggested a statistical distribution of the excess copper on the 48 f tetrahedral positions (space group, $Fd\bar{3}m$). Because of the dominating scattering power of the tellurium anions, they were not able to determine the x parameter of this position exactly as well as the distortion of the $Cu(48f)X_4$ tetrahedron, resulting from $x \neq 3/8$. In order to correlate the changes in the physical properties with changes in the lattice more detailed studies on the structural level are obviously required. We report here on the results of neutron diffraction studies of the chalcogen spinel phases $Cu_2Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$.

2. Experimental details

The chalcogen spinels $CuCr_2Se_4$ and $Cu_{1+y}Cr_2Te_4$ were prepared by annealing stoichiometric mixtures of the elements in evacuated silica ampoules at 950 K for two weeks and subsequent slow cooling.

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The sample of the copper intercalation compound $Cu_2Cr_2Se_4$, which cannot be obtained by thermal preparation, consisted of a series of smaller batches prepared electrochemically by cathodic reduction of $CuCr_2Se_4$ in aprotic CuCl–CH_3CN electrolytes [1]. Every batch was checked separately for stoichiometry and lattice parameters (X-ray Guinier technique).

The products of the thermal and electrochemical reactions were analysed chemically by atomic absorption spectroscopy. For the present investigation samples with the stoichiometry $Cu_{2.0}Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$ were selected.

Neutron diffraction studies were carried out at room temperature and at 4 K on the D2B diffractometer at the Institute Laue–Langevin in Grenoble, France. The wavelength used was 1.59 Å with a scattering angle between 10° and 150° (2θ) corresponding to d values between 9.1 and 0.82 Å. Neutron scattering factors were taken from ref. 5; the angle-dependent magnetic scattering amplitude for the Cr^{3+} ions is reported in ref. 6.

3. Results and discussion

The neutron diffraction patterns as well as the X-ray diagrams (higher resolution) of $Cu_2Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$ did not exhibit any additional peaks or peak broadening (which would be expected in the case of a loss in symmetry) as compared with the parent $CuCr_2X_4$ structure. The profile refinement using the Rietveld method [7] was consequently carried out in the space group $Fd\bar{3}m$.

3.1. $Cu_2Cr_2Se_4$

Figure 1 shows part of the spinel-type structure of $CuCr_2X_4$ with the chromium ions occupying the 16 d or B sites and the copper ions the 8 a or A sites. Indicated as well are three types of interstitial sites provided by the parent structure: the tetrahedral 8 b site within the Cr_4X_4 unit, the tetrahedral 48 f position lying between the Cr_4X_4 and the CuX_4 units and the octahedral 16 c site situated halfway between two 8 a sites on the threefold symmetry axis. Of these three proposed interstitial sites, additional copper was solely located on the tetrahedral 48 f positions suggested already by Lotgering and van der Steen [4]. The site occupation was refined to a value equivalent to a copper excess stoichiometry $y = 0.55$, which was found, however, to be too low to account for all intercalated ions. As in the case of $Cu_{1.5}Cr_2Se_3Br$ [8] the y and z parameters of the 16 c site were therefore released, converting 16 c thereby to the 96 h position. An additional amount of 0.41 Cu (formula unit)$^{-1}$ is found to be located on this pseudo-octahedral site, the shift from the centre being relatively small with $y = -z = 0.018$. The total stoichiometry of copper on interstitial sites therefore amounts to $n = 0.96 \pm 0.06$, which is in good agreement with the value determined by chemical analysis ($y = 0.99 \pm 0.01$).

Table 1 presents the result of the final fit, and Fig. 2 the plots of the measured, the calculated and the difference diffraction pattern.

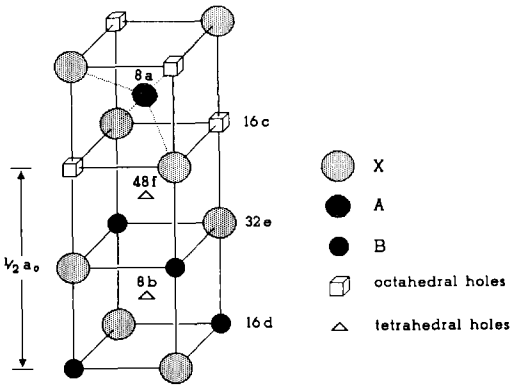

Fig. 1. Section of the cubic unit cell of the normal AB_2X_4 spinel lattice demonstrating the three types of interstitial sites in $CuCr_2X_4$: octahedral 16 c, tetrahedral 8 b and 48 f sites.

TABLE 1. Structural parameters of $Cu_2Cr_2Se_4$ at 295 K ($Fd\bar{3}m$, International Tables No. 227, origin in $\bar{3}m$)

Atom	Site	x	y	z	N	B
Se	32 e	0.2582(1)	0.2582(1)	0.2582(1)	4.00	1.20(4)
Cr	16 d	1/2	1/2	1/2	2.00	0.8(1)
Cu(1)	8 a	1/8	1/8	1/8	1.00	2.2(1)
Cu(2)	48 f	0.370(5)	1/8	1/8	0.55(4)	5.9(8)
Cu(3)	96 h	0	0.018(7)	−0.018(7)	0.41(2)	5(2)

N (atoms (formula unit)$^{-1}$), occupation factor; $a_0 = 1056.50(5)$ pm; B, isotropic temperature factor; $R_F = 5.20\%$.

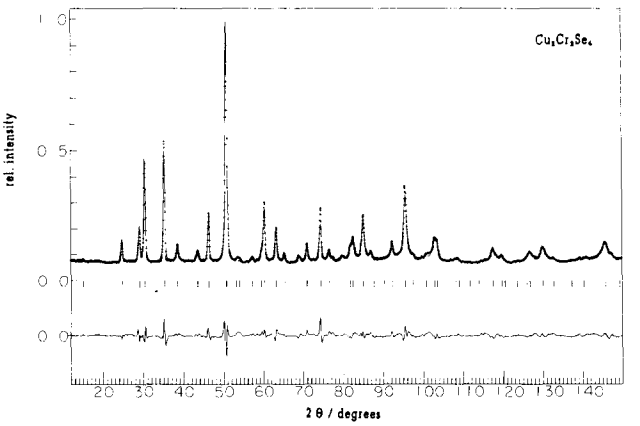

Fig. 2. Rietveld profile refinement for the neutron diffractogram of $Cu_2Cr_2Se_4$ at 295 K: —— calculated curve; +, data points. At the bottom the peak positions and the difference plot are indicated.

At first sight the occupation of the pseudo-octahedral 96 h position is surprising. All the electrons entering the host lattice during the reduction can be accepted by the valence band. Copper is present as Cu^+ and there is no reason to assume a metal cluster formation as found in $Cu_{1.5}Cr_2Se_3Br$ [8]. Instead of electronic reasons we have obviously to assume steric arguments to explain the occupation of this site: if all Cu^+ ions were located on the small tetrahedral 48 f site the spinel lattice would have to respond with a rather large volume increase leading to an energetically unfavourable situation. A partial occupation of the 48 f tetrahedral and of the larger 96 h pseudo-octahedral site can be considered as a compromise between the attempt to limit the lattice expansion while keeping a maximum number of copper ions on sites tetrahedrally surrounded by chalcogen atoms. In this context we may interpret the shift from the centered 16 c position to the 96 h site as a tendency of copper to achieve a distorted tetrahedral coordination within the octahedral void. The slightly increased value of the anion parameter u can be understood in terms of an additional effort by the lattice to minimize the volume expansion.

The small distortion $\delta = u - \frac{1}{4}$ of the anion sublattice, where $u = 0.25$ for the undistorted case, can be directly correlated with the x parameter of the 48 f site: $x = \frac{3}{8} - \Delta x$. If Δx is equivalent to δ the 48 f site then represents a distorted tetrahedron with four equal copper–anion distances. This situation is nearly achieved in $Cu_2Cr_2Se_4$ where we find $\delta = 0.008$, $\Delta x = 0.005$ and Cu(2)–Se distances of 228 pm and 231 pm.

Table 2 shows important bond distances and bond angles of $Cu_2Cr_2Se_4$. The Cu(2)–Se distances are relatively small as compared with the Cu(1)–Se separation of 243.7 pm, which underlines the arguments given above on the limitation of the occupation of the 48 f site for steric reasons. The symmetrical distortion of the tetrahedra leads to Se–Cu(2)–Se bond angles slightly different from the ideal value of 109.5°; the angle facing Cu(1) is enlarged to 120° while that facing the Cr_4Se_4 unit decreases to 99°.

The splitting of the 16 c site into the sixfold 96 h site allows a relaxation of the Cu(1)–Cu(3) distance, which remains, however, quite small at 230 pm as compared with 255 pm found in copper metal. The site symmetry is still mainly octahedral with Se–Cu(3)–Se angles of 95°, 170° and 90°. The Cu(3)–Se distances are, however, already asymmetric with two chalcogen neighbours at 254 pm, two at 274 pm and two at 293 pm. Every 96 h position has 2×3 tetrahedral 48 f positions in direct neighbourhood. Out of the three resulting distances only that at 248 pm appears to be large enough to allow a simultaneous occupation of both sites. The diffusion from the pseudo-octahedral site to the 48 f positions and vice versa should be facilitated by the other two relatively short distances of 215 pm and 205 pm. Figure 3 shows that this diffusion could take place via a face shared by two different neighbouring coordination polyhedra.

TABLE 2. Interatomic distances in picometres and bond angles γ for $Cu_2Cr_2Se_4$ compared with those of $CuCr_2S_4$

	$CuCr_2Se_4$[a]	$Cu_2Cr_2Se_4$	
		295 K	4 K
Cu(1)–Cu(1)	447.5	457.5	457.0
Cu(1)–Cu(2)		259(5)	267.0(1)
Cu(1)–Cu(3)		230(6)	232(2)
Cu(2)–Cu(3)		2×205(6)	196(1)
		2×215(7)	234(2)
		2×248(7)	267(2)
Cu(3)–Cu(3)		27(7)	43(3)
Cu(1)–Se	237.4	243.7(1)	243.3(1)
Cu(2)–Se		2×231(3)[b]	235.4(1)[c]
		2×228(3)[b]	222.0(1)[c]
Cu(3)–Se		2×254(7)[d]	243(2)[e]
		2×274(1)[d]	276.0(3)[e]
		2×293(7)	305(2)
Cu(2)–Cr		232(3)	226.6(1)
Cr–Se	250.8	255.8(1)	255.5(1)
Se–Se	343.2	349.0(1)	348.6(1)
	373.9	373.6(2)	373.1(1)
	387.6	398.0(1)	397.5(1)

[a] $u = 0.2576$, $a_0 = 1033.4$ pm (295 K).
[b] $\gamma_1 = 119°$, $\gamma_2 = 100°$, $\gamma_3 = 109°$.
[c] $\gamma_1 = 115.2°$, $\gamma_2 = 103.5°$, $\gamma_3 = 109.3°$.
[d] $\gamma_1 = 95°$, $\gamma_2 = 170°$, $\gamma_3 = 90°$.
[e] $\gamma_1 = 100°$, $\gamma_2 = 162°$, $\gamma_3 = 92°$.

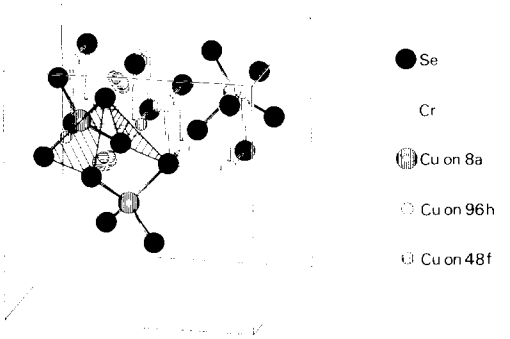

Fig. 3. Structure of $Cu_2Cr_2Se_4$: indicated are faces shared by the coordination polyhedra of 48 f and 96 h sites.

Table 3 lists the results of the refinement of the diffraction pattern measured at 4 K; bond distances and angles are included in Table 2. No significant changes take place on lowering the temperature. The x parameter of the 48 f site increases from 0.37 to 0.378, reducing thereby the Cu(2)–Cr distance but increasing the distance to the Cu(1) position. The Cu(2)–Se bonds become more asymmetric in length while the corresponding Se–Cu(2)–Se bond angles approach values of ideal tetrahedral surroundings.

TABLE 3. Structural parameters of $Cu_2Cr_2Se_4$ at 4 K ($Fd\bar{3}m$. International Tables No. 227, origin in $\bar{3}m$)

Atom	Site	x	y	z	N	B
Se	32 e	0.2581(1)	0.2581(1)	0.2581(1)	4.00	0.85(2)
Cr[a]	16 d	1/2	1/2	1/2	2.00	0.19(6)
Cu(1)	8 a	1/8	1/8	1/8	1.00	1.76(7)
Cu(2)	48 f	0.3781(1)	1/8	1/8	0.52(2)	2.7(3)
Cu(3)	96 h	0	0.029(2)	−0.029(2)	0.44(1)	2.3(3)

N (atoms (formula unit)$^{-1}$), occupation factor; $a_0 = 1055.15(1)$ pm; B, isotropic temperature factor; $R_N = 5.32\%$, $R_M = 7.19\%$. [a]Magnetic moment: $\mu_{Cr} = (2.36 \pm 0.04)\ \mu_B$.

TABLE 4. Structural parameters of $Cu_{1.81}Cr_2Te_4$ at 295 K ($Fd\bar{3}m$, International Tables No. 227, origin in $\bar{3}m$)

Atom	Site	x	y	z	N	B
Te	32 e	0.2569(1)	0.2569(1)	0.2569(1)	4.00	1.28(2)
Cr	16 d	1/2	1/2	1/2	2.00	1.52(3)
Cu(1)	8 a	1/8	1/8	1/8	1.00	1.70(3)
Cu(2)	48 f	0.3778(7)	1/8	1/8	0.56(1)	2.9(1)
Cu(3)	96 h	0	0.097(3)	−0.097(3)	0.28(2)	21(3)

N (atoms (formula unit)$^{-1}$), occupation factor; $a_0 = 1126.01(2)$ pm; B, isotropic temperature factor; $R_F = 5.75\%$, $R = 4.21\%$.

The splitting of the 16 c site into the sixfold ring of 96 h sites is more pronounced at low temperatures and has to be interpreted as an attempt to improve the tetrahedral character of the Cu(3) coordination and to increase the small Cu(1)–Cu(3) bond length.

The high temperature factors found for the copper atoms occupying the 8 a, 48 f and 96 h sites are a result of the large static disorder present in this compound. The Cu(2) and the Cu(3) positions are statistically occupied: 1/11 of the 48 f sites and only 1/35 of the 96 h sites are filled. The local distortion resulting from the small Cu(2)–Se distances cannot be described adequately by the macroscopic anion parameter u. Furthermore, the repulsion between Cu(1) and Cu(3) locally distorts the cubic symmetry of the 8 a site and the implied small value of 230 pm for the Cu(1)–Cu(3) distance appears not to be realistic. Because of these local distortions the Cu(1)–Cu(3) distance is not well defined within this macroscopic structure model based on the space group $Fd\bar{3}m$; this disorder is compensated on refining by an increase in the temperature factors for both copper positions.

The small value of the magnetic moment found for $Cu_2Cr_2Se_4$ at 4 K is quite remarkable: $\mu_{Cr} = 2.36\ \mu_B$ has to be compared with the expected free ion value of 3 μ_B for Cr^{3+}. Direct magnetic measurements on a series of $Cu_{1+y}Cr_2Se_4$ compounds are planned to elucidate this unusual result.

3.2. $Cu_{1.81}Cr_2Te_4$

Table 4 presents the result of the Rietveld refinement of the neutron data for $Cu_{1.81}Cr_2Te_4$ at room temperature, and Fig. 4 shows the plots of the measured, the calculated and the difference pattern. The excess copper is located as in $Cu_2Cr_2Se_4$ on the 48 f ($n = 0.56 \pm 0.01$) and the 96 h ($n = 0.28 \pm 0.02$) positions. The resulting stoichiometry is in agreement with the chemical analysis ($y = 0.81 \pm 0.01$). The relative occupancies are, as compared with $Cu_2Cr_2Se_4$ slightly changed in favour of the 48 f site supporting the idea that this site is first occupied for the tellurium compound in the course of the intercalation process until steric reasons enforce

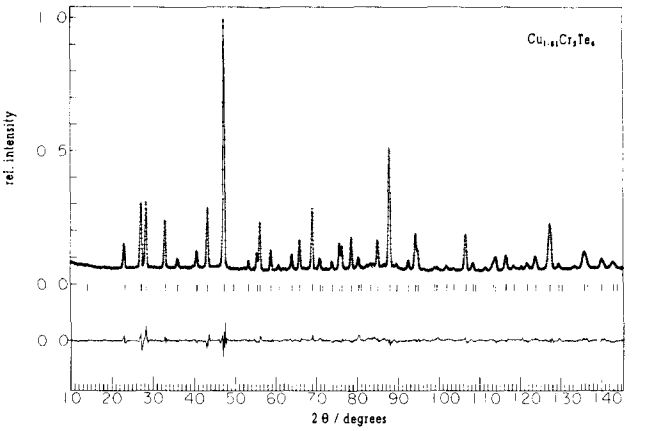

Fig. 4. Rietveld profile refinement for the neutron diffractogram of $Cu_{1.81}Cr_2Te_4$ at 295 K: —, calculated curve is presented by a solid line; +, data points. At the bottom the peak positions and the difference plot are indicated.

the additional use of the larger 16 c–96 h vacancy. The x parameter of the 48 f site is relatively large ($x = 0.378$) and leads to strongly differing Cu(2)–Te bond lengths (Table 5) while the corresponding Te–Cu(2)–Te angles approach values of the perfect tetrahedron: $\gamma_1 = 114.1°$, $\gamma_2 = 104.6°$ and $\gamma_3 = 109.3°$. Comparing the size of the 48 f site with that of the tetrahedral 8 a site ($d_{Cu(1)-Te} = 257$ pm) we see once more that steric reasons are obviously responsible for the additional occupation of a larger interstitial site with increasing copper concentration.

The main difference between the lattice structures of the two chromium chalcogenides $Cu_2Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$ is the large displacement of Cu(3) from the centre of the octahedral site found for the latter compound. Figure 5 illustrates this situation where the 96 h positions lying on a strongly extended sixfold ring approach tetrahedral symmetry with four shortened Cu(3)–Te distances of 2×207 pm and 2×328 pm. The Te–Cu(3)–Te angles are 148°, 124° and 93° as compared with 95°, 170° and 90° for nearly octahedrally surrounded Cu(3) in $Cu_2Cr_2Se_4$. As a second consequence the Cu(1)–Cu(3) separation, which is very short in $Cu_2Cr_2Se_4$ at 230 pm, increases significantly to 289 pm. Four out of six Cu(2)–Cu(3) distances are large enough to allow

TABLE 5. Interatomic distances in picometres and bond angles γ for $Cu_{1.81}Cr_2Te_4$ compared with those of $CuCr_2Te_4$

	$CuCr_2Te_4$[a]	$Cu_{1.81}Cr_2Te_4$	
		295 K	4 K
Cu(1)–Cu(1)	481.7	487.6	487.0
Cu(1)–Cu(2)		284.7(8)	286.0(9)
Cu(1)–Cu(3)		289(3)	295(6)
Cu(2)–Cu(3)		2×148(1)	145(6)
		2×290(3)	298(5)
		2×383(2)	395(4)
Cu(3)–Cu(3)		154(3)	167(6)
Cu(1)–Te	252.6	257.2(1)	257.3(1)
Cu(2)–Te		2×237.7(5)[b]	236.3(5)[c]
		2×250.3(5)[b]	251.1(5)[c]
Cu(3)–Te		2×207(3)[d]	204(3)[e]
		2×328(2)[d]	334(3)[e]
		2×416(3)	426(6)
Cu(2)–Cr		242.0(4)	240.7(5)
Cr–Te	271.5	274.0(2)	273.4(1)
Te–Te	374.1	376.1(2)	375.0(2)
	393.4	398.2(2)	397.9(2)
	412.5	420.1(2)	420.2(2)

[a] $u = 0.2561$, $a_0 = 1112.5$ pm (295 K).
[b] $\gamma_1 = 114.1°$, $\gamma_2 = 104.6°$, $\gamma_3 = 109.3°$.
[c] $\gamma_1 = 113.6°$, $\gamma_2 = 105.6°$, $\gamma_3 = 109.5°$.
[d] $\gamma_1 = 148°$, $\gamma_2 = 124°$, $\gamma_3 = 93°$.
[e] $\gamma_1 = 156°$, $\gamma_2 = 120°$, $\gamma_3 = 92°$.

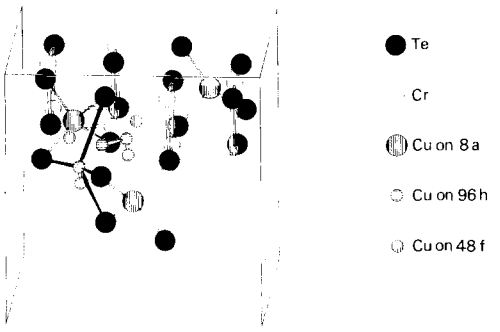

Fig. 5. Structure of $Cu_{1.8}Cr_2Te_4$: indicated is one sixfold ring of 96 h positions and two neighbouring 48 f sites. The distorted tetrahedral surrounding of the 96 h site is clearly demonstrated.

a simultaneous occupation of the two sites. The site changes (diffusion) between Cu(3) positions should be favoured by the small and similar distances between Cu(3) positions within one sixfold ring ($d_{Cu(3)-Cu(3)}$ = 154 pm) and the nearest-neighbour Cu(2)–Cu(3) distance of 148 pm.

At low temperatures again no significant changes are found: using the information obtained from the high temperature fit and chemical analysis values the total copper content n on interstitial sites was constrained to be equal to 0.81. Table 6 shows the results of the final fit, and Table 5 bond distances and angles. The shift of the Cu(3) position from the centre of the octahedral site is slightly enlarged at 4 K; the x parameter of the 48 f site increases to 0.379. The occupation of the two interstitial sites is independent of temperature.

A reasonable temperature factor is observed now for Cu(1), presumably a consequence of the relaxed Cu(1)–Cu(3) distance. Unrealistically high Debye–Waller factors at 300 K and at 4 K are found for Cu(3). Once more we have to assume that the local disorder introduced into the system by excess copper ions is responsible for this result. One-tenth of the 48 f positions and only one out of fifty 96 h positions are occupied by copper in $Cu_{1.81}Cr_2Te_4$. Average Cu(3)–Te distances as low as 204 pm (Table 5) are certainly unlikely and indicate the existence of strong local distortions in the sixfold ring of 96 h positions.

The value of the magnetic moment of the chromium with $\mu_{Cr} = 2.86\ \mu_B$ is close to the expected spin-only value for Cr^{3+} ($3d^3$).

From the neutron diffraction studies we can recognize that the occupation factor of the tetrahedral 48 f site in $Cu_{2.0}Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$ is nearly the same although the copper stoichiometries of both samples are different. This leads us to the assumption that the occupation ratio between the two sites taking up the intercalated copper is probably equal at the maximum stoichiometry $Cu_2Cr_2X_4$ (48 f:96 h ≈ 4:3). On the contrary, the change in the cubic lattice parameters a_0 of the non-stoichiometric series $Cu_{1+y}Cr_2X_4$ with increasing y value is different; we conclude therefore that the intercalation mechanisms for the three chalcogenides are different. From Fig. 6(a) we can derive an almost linear increase in the lattice parameter a_0 for $Cu_{1+y}Cr_2Te_4$ over the whole intercalation range, whereas a_0 for $Cu_{1+y}Cr_2Se_4$ (Fig. 6(b)) remains constant in the region $0 \leqslant y \leqslant 0.3$. For the copper intercalation in the sulphide $CuCr_2S_4$ even the existence of a two-phase region ($CuCr_2S_4$–$Cu_2Cr_2S_4$) can be observed [1].

Since the tetrahedral sites in the telluride lattice are rather large as a consequence of the Te^{2-} anion radius, the intercalated copper ions are located on the tetrahedral 48 f sites at low copper excess concentrations. Steric arguments require, however, the use of the larger

TABLE 6. Structural parameters of $Cu_{1.81}Cr_2Te_4$ at 4 K ($Fd\bar{3}m$, International Tables No. 227, origin in $\bar{3}m$)

Atom	Site	x	y	z	N	B
Te	32 e	0.2571(1)	0.2571(1)	0.2571(1)	4.00	0.61(2)
Cr[a]	16 d	1/2	1/2	1/2	2.00	0.70(4)
Cu(1)	8 a	1/8	1/8	1/8	1.00	0.74(3)
Cu(2)	48 f	0.3793(8)	1/8	1/8	0.57(1)	1.4(2)
Cu(3)	96 h	0	0.105(5)	−0.105(5)	0.24(1)	15(3)

N (atoms (formula unit)$^{-1}$), occupation factor; $a_0 = 1124.63(3)$ pm; B, isotropic temperature factor; $R_M = 5.82\%$, $R_N = 5.85\%$.
[a] Magnetic moment: $\mu_{Cr} = (2.86 \pm 0.03)\ \mu_B$.

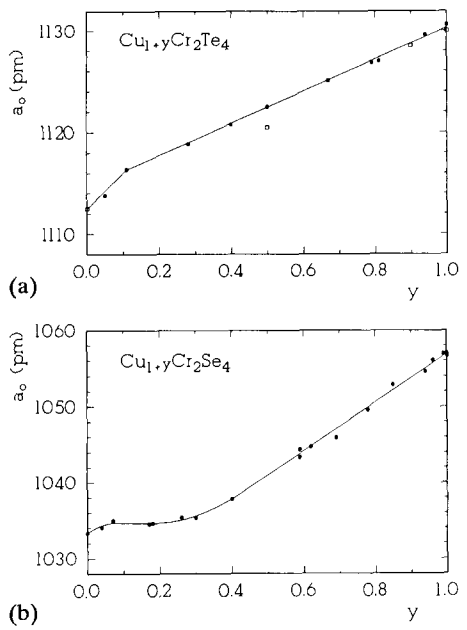

Fig. 6. Cubic lattice parameter a_0 of (a) $Cu_{1+y}Cr_2Te_4$ and (b) $Cu_{1+y}Cr_2Se_4$ as a function of the stoichiometric index y.

pseudo-octahedral 96 h positions after the uptake of a critical amount of excess copper ions in order to reduce the lattice expansion as compared with the exclusive occupation of tetrahedral sites. This model for the intercalation mechanism is in good agreement with the observed continuous change in lattice parameters over the total intercalation range $0 \leqslant y \leqslant 1$. In $CuCr_2Se_4$ the tetrahedral vacancies are obviously too small for the uptake of the relatively large copper ions. The lack of change in the lattice parameter a_0 for the range $0 \leqslant y \leqslant 0.3$ implies that the Cu^+ ions occupy positions within the larger octahedral void in this region, although Cu^+ tends normally to prefer tetrahedral anion coordination. For a copper threshold stoichiometry $y = 0.3$ the copper ions start to occupy the tetrahedral 48 f sites, which results in a continuous increase in the unit cell volume. For $CuCr_2S_4$ the interatomic distances between the intercalated copper and the sulphide anions are rather small for tetrahedral as well as for octahedral positions. At low intercalation values the lattice matrix cannot respond with a homogeneous structure (*i.e.* variable stoichiometry) but favours a two-phase system between starting phase $CuCr_2S_4$ and the compound with the maximum stoichiometry $Cu_2Cr_2S_4$ and significantly higher lattice volume. In order to verify these models concerning the intercalation mechanism and the occupation ratio of the two copper sites for $Cu_{1+y}Cr_2X_4$ further neutron diffraction studies at different intercalation values y will be necessary.

4. Conclusions

For the structurally related copper chromium spinel $Cu_{1.5}Cr_2Se_3Br$ it was pointed out that electronic reasons (chromium–anion band unable to accept additional electrons) enforce the formation of $(Cu_3)^{2+}$ clusters under exclusive use of the pseudo-octahedral 96 h site for the intercalated excess Cu^+ ions [8]. The valence band of $CuCr_2X_4$ phases ($X \equiv S$, Se, Te) is able, however, to accept one additional electron per formula unit [3]. Steric reasons are responsible for the partial occupation of the larger 96 h site in $Cu_2Cr_2Se_4$ and $Cu_{1.81}Cr_2Te_4$. With neutron diffraction we were able to show that the relatively small 48 f site becomes occupied by 0.55 Cu (formula unit)$^{-1}$ in $Cu_2Cr_2Se_4$ and 0.56 Cu (formula unit)$^{-1}$ in $Cu_{1.81}Cr_2Te_4$ while the remaining part of the excess copper is located in the acentric octahedral positions. The repulsive interaction with neighbouring copper ions on the 8 a site leads here to the splitting of the 16 c site into the sixfold ring of 96 h sites. This provides not only a more tetrahedral coordination for the strongly chalcophilic copper ions but may favour also Cu^+ ionic transport within the three-dimensional network of face-sharing interstitial polyhedra.

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