In a similar manner the following results are obtained:

$$I_2=N^{-1}\Sigma_{\mathrm{k}}(J_0-J_{\mathrm{k}})\phi_{\mathrm{k}}=(\pi\nu\mathfrak{z}J)[Z_{5/2}\theta^{5/2}+(5/4)\pi\nu Z_{7/2}\theta^{7/2}+\cdots], \quad \text{(A9)}$$

$$I_3=N^{-1}\Sigma_{\mathrm{k}}\ln[1-\exp(-\beta\omega_{\mathrm{k}})]=-[Z_{5/2}\theta^{3/2}+\tfrac{3}{4}\pi\nu Z_{7/2}\theta^{5/2}+\pi^2\nu^2\omega Z_{9/2}\theta^{7/2}+\cdots], \quad \text{(A10)}$$

$$I_4=N^{-2}\Sigma_{\mathrm{kk'}}(J_{\mathrm{k}}+J_{\mathrm{k'}}-J_{\mathrm{k'-k}}-J_0)\phi_{\mathrm{k}}\phi_{\mathrm{k'}}=-\pi^2\nu^2\mathfrak{z}J(Z_{5/2})^2\theta^5-\cdots. \quad \text{(A11)}$$

In evaluating I_3, a partial integration transforms the original form to a form linear in ϕ_{k}.

In the statistical perturbation treatment of Sec. 7, we required integrals quadratic in ϕ_{k}. These are carried out in the same manner as the above integrals. The expansion of ϕ_{k}^2 according to (A3) leads to a double sum; the integrals are then evaluated, and the double sum is transformed to Z_q functions with the aid of the following relation:

$$\sum_{m=1}^{\infty}\sum_{m'=1}^{\infty}\frac{e^{-(m+m')\beta g\mu H}}{(m+m')^{q+\frac{1}{2}}}=Z_{q-\frac{1}{2}}-Z_{q+\frac{1}{2}}. \quad \text{(A12)}$$

Illustrative integrals are evaluated as follows:

$$I_5=N^{-1}\Sigma_{\mathrm{k}}(J_0-J_{\mathrm{k}})\phi_{\mathrm{k}}^2=(\pi\nu\mathfrak{z}J)[(Z_{3/2}-Z_{5/2})\theta^{5/2}+(5/4)\pi\nu(Z_{5/2}-Z_{7/2})\theta^{7/2}+\cdots], \quad \text{(A13)}$$

$$I_6=N^{-2}\Sigma_{\mathrm{kk'}}(J_{\mathrm{k}}+J_{\mathrm{k'}}-J_{\mathrm{k'-k}}-J_0)\phi_{\mathrm{k}}^2\phi_{\mathrm{k'}}=-\pi^2\nu^2\mathfrak{z}JZ_{5/2}(Z_{3/2}-Z_{5/2})\theta^5-\cdots. \quad \text{(A14)}$$

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Neutron-Diffraction Investigation of $CuCr_2Se_4$ and $CuCr_2Te_4$†

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Neutron-diffraction measurements at 508°K as well as x-ray–diffraction measurements at room temperature show the compounds $CuCr_2Te_4$ and $CuCr_2Se_4$ to have a normal spinel structure. The coherent scattering length of Se was found to be 0.779×10^{-12} cm. The neutron-diffraction diagrams below the transition temperature confirm the ferromagnetic behavior proposed by Lotgering. The magnetic moment of the Cu ion in the tetrahedral site is zero, whereas the magnetic moments of the Cr ions in the octahedral site are approximately three Bohr magnetons, corresponding with Cr^{3+}.

INTRODUCTION

THE compounds $CuCr_2Se_4$ and $CuCr_2Te_4$ have been synthesized for the first time by Hahn *et al.*[1] Their magnetic properties have been investigated by Lotgering.[2] Magnetization and susceptibility curves as a function of temperature, the transition temperature, and the positive paramagnetic Curie temperature showed a ferromagnetic behavior which is anomalous for magnetic spinels. From the saturation magnetization, a moment of 4.9 Bohr magnetons per molecular unit was derived. To explain this, Lotgering[2] assumed that the Cu atoms are diamagnetic and that the Cr^{3+} and Cr^{4+} atoms are distributed at random over the B sites. However, no indication of ordering of the electron is found down to 1°K. It therefore seemed worthwhile to undertake a neutron-diffraction study of these compounds.

EXPERIMENTAL

The samples were prepared by heating stoichiometric quantities of the elements in evacuated silica tubes to 550°C for the $CuCr_2Se_4$ and 600°C for the $CuCr_2Te_4$. After the first heating, the samples were quenched, powdered, and reheated to ensure homogeneity.

A chemical analysis showed that the samples were practically pure, except for the presence of traces of binary compounds such as CuSe and CuTe, whose diffraction peaks could easily be separated.

The neutron wavelength was 2.57 Å, using the (111) reflection of a copper monochromating crystal.[3] Slits of 30′ angular divergence were placed between the reactor and the monochromator and in front of BF_3 detector. As a second-order filter, a block of pyrolytic graphite with a thickness of 7.5 cm was employed.

X-ray–diffraction diagrams were obtained at room temperature with a Philips diffractometer, scanning in steps of 0.02′ and counting at each position during 4 min. Copper radiation was used to obtain the diagram of $CuCr_2Se_4$ and Mo radiation for $CuCr_2Te_4$.

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TABLE I. Final parameters (with standard deviations) in the paramagnetic state for $CuCr_2Se_4$ and $CuCr_2Te_4$.

	$CuCr_2Se_4$			$CuCr_2Te_4$	
	X ray	Neutrons		X ray	Neutrons
x	0.065 (0.078)	0.023 (0.019)	x	−0.163 (0.256)	0.012 (0.018)
u	0.25756 (0.00034)	0.25738 (0.00021)	u	0.25595 (0.00099)	0.25628 (0.00038)

TABLE II. Final parameters (with standard deviations) in $CuCr_2Se_4$ and $CuCr_2Te_4$.

	$CuCr_2Se_4$		$CuCr_2Te_4$	
	$T=298°K$	$T=4.2°K$	$T=298°K$	$T=4.2°K$
μ_1	2.31787 (0.14420)μ_B	2.80788 (0.11231)μ_B	1.98204 (0.10940)μ_B	3.11183 (0.16388)μ_B
μ_2	−0.05454 (0.16281)μ_B	0.01421 (0.12817)μ_B	0.02611 (0.11773)μ_B	0.05322 (0.14094)μ_B
u	0.25761 (0.00034)	0.25907 (0.00024)	0.25606 (0.00027)	0.25610 (0.00049)
B	0.4332 (0.1913) Å^2	−0.0755 (0.1259) Å^2	0.7881 (0.2207) Å^2	0.0775 (0.4103) Å^2
R	1.266%	1.106%	1.092%	1.485%

RESULTS AND DISCUSSION

The atomic positions will be described in the centrosymmetric space group $Fd3m(O_h^7)$ with the anions (Se, Te) in $32(e)$, the Cr atoms in $16(d)$, and the Cu atom in $8(a)$.

For the determination of the crystallographic structure, an x-ray–diffraction diagram at room temperature and a neutron-diffraction diagram taken at 508°K were available. A full-matrix least-squares refinement program was used which minimizes the quantity $\sum_i w(\sum_r I_{\text{obs}}-\sum_r I_{\text{calc}})^2$, where w is the weight of the observation, $\sum_i$ is the summation over the composite peaks in the diagram, $\sum_r$ is the summation over the constituent peaks, and I_{obs} and I_{calc} are the observed and calculated intensities.[4]

In principle there are only two parameters which have to be determined, i.e., the position of the anion u and the degree of inversion x. As the neutron-scattering lengths of copper and chromium are 0.79×10^{-12} and 0.352×10^{-12} cm, respectively, the neutron diagram should be much more sensitive to the degree of inversion than the x-ray diagram. However, from the refinement of the neutron data of $CuCr_2Se_4$, the standard deviations came out very large, although the values of the parameters were the same as those that were obtained from the refinement of the x-ray data. In particular, in both cases the degree of inversion was zero within the limits of error. A refinement of the scattering length of selenium with fixed values of u and x using the neutron data resulted in $b=(0.779\pm0.014)\times10^{-12}$ cm, as compared with the value 0.89×10^{-12} cm given in the literature.[5] Using this value, the refinement of the u and x parameters gave the results listed in Table I. In this refinement, the value of 0.59×10^{-12} cm was used for the scattering length of tellurium.

As the diffraction diagrams obtained at room temperature and at liquid-helium temperature had the same over-all appearance, it was concluded that the magnetic structure remains essentially unchanged.

TABLE III. Comparison of the calculated and observed intensities of the x-ray diagram and of the neutron-diffraction diagram at 508°C for $CuCr_2Se_4$. In the column (e.s.d.), the estimated standard deviations of the observed intensities are listed.

X ray ($\lambda=1.5418$ Å)			Neutrons ($\lambda=2.5689$ Å)		
$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)	$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)
1 1 1	871	887 (46)	1 1 1	429	467 (102)
2 2 0	1548	1668 (55)	2 2 0	6011	6485 (118)
3 1 1	3861	4196 (78)	3 1 1	9664	9988 (140)
2 2 2	6496	6091 (89)	2 2 2	24860	24651 (183)
4 0 0	9177	9174 (109)	4 0 0	23248	24180 (178)
3 3 1	181	176 (33)	3 3 1	2451	2559 (89)
4 2 2	531	522 (40)	4 2 2	3737	3749 (100)
5 1 1 3 3 3	2783	2783 (65)	5 1 1 3 3 3	12493	12751 (146)
4 4 0	10308	10490 (114)	4 4 0	56574	56774 (260)
5 3 1	156	126 (30)	5 3 1	13	1 (20)
6 2 0	169	159 (30)	6 2 0	2249	2545 (113)
5 3 3	422	381 (37)	5 3 3 6 2 2	27822	28852 (230)
6 2 2	2008	2002 (60)			
4 4 4	1696	1618 (55)	4 4 4	13596	13813 (172)

TABLE IV. Comparison of the calculated and observed intensities of the x-ray diagram and of the neutron-diffraction diagram at 508°C for $CuCr_2Te_4$.

X ray ($\lambda=0.7109$ Å)			Neutrons ($\lambda=2.5689$ Å)		
$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)	$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)
1 1 1	303	500 (34)	1 1 1	85	0 (90)
2 2 0	889	758 (37)	2 2 0	7167	7129 (133)
3 1 1 2 2 2	11142	12110 (121)	3 1 1	12279	12604 (152)
			2 2 2	12100	12610 (149)
4 0 0	8394	7700 (98)	4 0 0	13582	12953 (147)
3 3 1	190	170 (33)	3 3 1	1750	1532 (96)
4 2 2	328	313 (29)	4 2 2	4694	4307 (113)
5 1 1 3 3 3	1532	1399 (49)	5 1 1 3 3 3	11253	11434 (141)
4 4 0	8600	8289 (104)	4 4 0	42780	42972 (230)
6 2 0	110	106 (27)	6 2 0	2905	2603 (102)
5 3 3 6 2 2	3172	3241 (70)	5 3 3 6 2 2	14938	14715 (185)
4 4 4	1514	2004 (61)	4 4 4	7180	7720 (148)
5 5 1 7 1 1	186	242 (33)			

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TABLE V. Comparison of the calculated and observed intensities of the neutron diagrams at 4.2 and 298°K for $CuCr_2Se_4$. The intensities are calculated for the collinear model, the parameters are given in Table I.

	$T=4.2°K$			$T=298°K$	
$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)	$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)
1 1 1	5838	5964(132)	1 1 1	1887	1929(86)
2 2 0	6507	7339(128)	2 2 0	2944	3084(85)
3 1 1	14005	14099(155)	3 1 1	5624	5782(101)
2 2 2	31286	31220(219)	2 2 2	13350	13020(135)
4 0 0	27529	27604(194)	4 0 0	11886	12097(128)
3 3 1	4446	4292(104)	3 3 1	1792	1762(69)
4 2 2	4476	4652(109)	4 2 2	1935	1878(74)
3 3 3 5 1 1	16144	16312(160)	3 3 3 5 1 1	6867	6922(108)
4 4 0	70837	70920(296)	4 4 0	29872	29869(192)
5 3 1	1044	843(86)			
6 2 0	2983	3135(111)			
5 3 3 6 2 2	38934	38866(252)			
4 4 4	18699	19209(193)			

The calculations were performed with a full-matrix least-squares refinement program which minimizes the same function as for the crystallographic structure, but which could refine simultaneously the position parameter of the anion and the direction and magnitude of the magnetic moments.

To check the hypothesis of Lotgering, the 16-fold *B*-site was split into two 8-fold (face-centered-cubic) magnetic subsites in the same way as is the case of Fe_3O_4. Different noncollinear models were tried, but the best agreement was obtained for a parallel arrangement of the spin vectors. The moments of the two sublattices were then refined starting from various orientations of the common spin axis. The refinement gave equal values for the two chromium moments and zero for the copper moment. For the models with the spin in the {110} planes, the agreement was slightly better than for the others. According to Lyons, Kaplan, Dwight, and Menyuk,[6] the energy has a minimum for a magnetic spinel structure with spins in these planes and it has therefore been assumed that this arrangement represents the true one.

TABLE VI. Comparison of the observed and calculated intensities of the neutron diagrams at 4.2 and 298°K for $CuCr_2Te_4$. The intensities are calculated for the collinear model, the parameters are given in Table I.

	$T=4.2°K$			$T=298°K$	
$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)	$h\ k\ l$	I_{calc}	I_{obs}(e.s.d.)
1 1 1	8324	8427(154)	1 1 1	1841	1765(103)
2 2 0	7678	7734(135)	2 2 0	3998	3965(101)
3 1 1	12640	18220(173)	3 1 1	7986	7872(119)
2 2 2	19356	20212(177)	2 2 2	8087	8307(119)
4 0 0	17840	17460(168)	4 0 0	8186	8136(115)
3 3 1	4232	4060(114)	3 3 1	1449	1483(78)
4 2 2	5459	5597(120)	4 2 2	2718	2607(88)
3 3 3 5 1 1	14729	14800(154)	3 3 3 5 1 1	6725	6693(111)
4 4 0	52986	52962(262)	4 4 0	25212	25265(177)

Finally, a refinement was carried out in which the following parameters were used: μ_1, the magnetic moment of *B* site (in Bohr magnetons); μ_2, the moment magnetic of *A* site (in Bohr magnetons); *u*, the position of the anion; *B*, the over-all isotropic temperature factor in Å^2.

This gave a satisfactory agreement, as is shown by the values of

$$R=\frac{\sum_i(\sum_r I_{obs}-\sum_r I_{calc})^2}{\sum_i \sum_r I_{obs}}.$$

The form factors for Cu and Cr were taken from the data given by Watson and Freeman.[7]

From the low values of the *R* factors given in Table II, it is concluded that it is very improbable that the two chromium atoms have different moments. This is in agreement with the result of the conductivity measurements which show no indication of electronic ordering down to 1°K, in contrast with analogous magnetic compounds, such as $LaSrMnO_4$ [2] or Fe_3O_4.[8] The magnitude of the moments is compatible only with the assumption that all chromium atoms are present in the Cr^{3+} state, while copper occurs as Cu^+. From this, a magnetic moment of about 6 Bohr magnetons per molecule is calculated, as compared with a measured value of 4.9 Bohr magnetons.[1]

It must be concluded that there is a nonlocalized moment of 1 Bohr magneton which is opposite to the chromium moments.

From conduction measurements, it has been found that these substances have a *p*-type conduction. This seems in agreement with the present result that an electron is transferred from the conduction band to the copper sites.

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