

New Ternary Uranium Copper Chalcogenides $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$: Crystal Structure and Magnetic Properties

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The new compounds $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$ have been synthesized by direct reaction between UX_2 ($X = \text{S, Se}$), Cu, and chalcogens at 600°C. Single crystals were obtained using the chemical vapor transport method. The compounds crystallize in the hexagonal system with $a = 9.7308(8)$, $c = 5.7045(6)$ Å for $\text{Cu}_2\text{U}_3\text{S}_7$ and $a = 10.138(1)$, $c = 5.9525(7)$ Å for $\text{Cu}_2\text{U}_3\text{Se}_7$. The crystal structures of the two compounds were solved in the space group $P6_3$ and refined to the final values of the reliability factors $R = 0.031$, $R_w = 0.038$ for $\text{Cu}_2\text{U}_3\text{S}_7$ and $R = 0.036$, $R_w = 0.044$ for $\text{Cu}_2\text{U}_3\text{Se}_7$. They are isotypic with $\text{La}_3\text{CuSiS}_7$. Magnetic measurements showed that $\text{Cu}_2\text{U}_3\text{S}_7$ presents a paramagnetic behaviour down to 5 K while $\text{Cu}_2\text{U}_3\text{Se}_7$ exhibits an antiferromagnetic transition at $T_N = 13$ K. © 1996

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SYNTHESIS

The systematic search for new ternary compounds in the Cu–U–X (S, Se) systems was carried out by heating calculated mixtures of UX_2 , Cu powder, and chalcogen, with variable composition ratios $\text{Cu}_2\text{X}/\text{UX}_2$, in evacuated and sealed silica tubes. All materials were handled in a dry argon filled glove box in order to avoid any contamination by oxygen and moisture. The reaction products were analyzed by X-ray powder diffraction using an INEL CPS 120 diffractometer and $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54059$ Å).

Heating the stoichiometric mixtures $\text{Cu}_2\text{S} + 3\text{US}_2$ and $\text{Cu}_2\text{Se} + 3\text{USe}_2$ at $T = 600^\circ\text{C}$ for 3 days led to diffraction patterns characteristic of isotypic single phase materials having thus the formulas $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$. Above this temperature, the compounds were found to decompose to a mixture of the binaries Cu_2X and the ternaries $\text{Cu}_2\text{U}_6\text{X}_{13}$. Single crystals were obtained by the chemical vapor transport method using UBr_4 as transporting agent for $\text{Cu}_2\text{U}_3\text{S}_7$ and iodine for $\text{Cu}_2\text{U}_3\text{Se}_7$ in a two-zone furnace with the temperature gradient 600–540°C for two weeks.

CRYSTALLOGRAPHIC STUDY

Single crystal X-ray diffraction intensities were measured on a Nonius-CAD-4 four-circle diffractometer. The lattice parameters were determined from a least-squares analysis of the setting angles of 25 reflections, revealing $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$ to crystallize in the hexagonal system. The indexed X-ray powder diffraction patterns are given in Tables 1 and 2; the lattice parameters and the experimental conditions for data collection are given in Table 3.

The single crystal X-ray diffraction data processing was carried out on a VAX 3100 computer using the MOLEN package (6). At the final stages of the refinements, an absorption correction was performed using the program DIFABS (7).

The systematic absences $00l:l \neq 2n$ indicated $P6_3$, $P6_3/m$, and $P6_3/22$ as possible space groups, but after aver-

INTRODUCTION

The search for new uranium chalcogenides has led to the synthesis and characterization of a great number of new ternary compounds, especially with 3d and 4d transition metals and lanthanides (1–3). These compounds display a wide variety of structural features and unusual magnetic behaviors, the latter resulting from strong magnetic interactions between two different (d and f) magnetic sublattices.

This work is a continuation of our study of the uranium–copper–chalcogen system, where the influence of copper on the magnetic properties of the ternary compounds is considered to be negligible. The uranium-rich compounds $\text{Cu}_2\text{U}_6\text{S}_{13}$ and $\text{Cu}_2\text{U}_6\text{Se}_{13}$ have been previously isolated and characterized (4, 5). These compounds are situated on the $\text{Cu}_2\text{X}-\text{UX}_2$ line in the ternary Cu–U–X ($X = \text{S, Se}$) system. We report here on the synthesis, crystal structure, and magnetic properties of two other compounds, $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$, which form in the same pseudo-binary system.

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TABLE 1
X-Ray Powder Diffraction Pattern
of $\text{Cu}_2\text{U}_3\text{S}_7$

<i>h k l</i>	d_{obs} (Å)	d_{cal} (Å)	<i>I/I</i> ₀
1 1 0	4.8632	4.8647	4
1 0 1	4.4270	4.4277	38
2 0 0	4.2093	4.2130	18
1 1 1	3.7017	3.7034	18
2 0 1	3.3894	3.3904	100
2 1 0	3.1857	3.1847	45
0 0 2	2.8572	2.8557	26
2 1 1	2.7831	2.7815	4
1 0 2	2.7061	2.7061	9
3 0 1	2.5222	2.5204	39
1 1 2	2.4639	2.4627	9
2 2 0	2.4337	2.4324	44
2 0 2	2.3642	2.3638	22
3 1 0	2.3376	2.3369	15
3 1 1	2.1627	2.1629	30
2 1 2	2.1259	2.1261	60
4 0 0	2.1073	2.1065	17
3 0 2	2.0025	2.0025	3
4 0 1	1.9769	1.9764	9
3 2 0	1.9293	1.9330	13
2 2 2	1.8539	1.8517	20
3 2 1	1.8319	1.8310	28
3 1 2	1.8091	1.8086	8
1 1 3	1.7738	1.7729	<3
4 1 1	1.7509	1.7502	35
2 0 3	1.7354	1.7349	19
4 0 2	1.6960	1.6952	<3
5 0 0	1.6856	1.6852	<3
5 0 1	1.6166	1.6163	<3
3 2 2	1.6016	1.6008	<3
3 0 3	1.5752	1.5759	12
3 3 1	1.5596	1.5599	5
4 1 2	1.5456	1.5460	6
4 2 1	1.5327	1.5339	<5

aging, an internal residual of 50% excluded $P6_322$. The crystal structure was solved in the noncentrosymmetric space group $P6_3$, the model obtained being inconsistent with centrosymmetry.

The positional parameters for the uranium atoms in the sulfide $\text{Cu}_2\text{U}_3\text{S}_7$ were obtained by the direct method (program MULTAN (8)) and those of the other atoms were derived from a Fourier difference synthesis. Uranium was found to occupy the 6c crystallographic site, copper to be in 2a and 2b sites, and sulfur to be in 6c, 6c, and 2b sites.

Refinements of the positional and isotropic thermal parameters for all the atoms led to $R = 0.033$ and $R_w = 0.041$. Subsequent refinement cycles with anisotropic thermal factors for all atoms yielded the final values $R = 0.031$ and $R_w = 0.038$. The highest residual electron density peak corresponded to 0.5% of that of an uranium atom.

The positional parameters found for the sulfide $\text{Cu}_2\text{U}_3\text{S}_7$

were used as initial values for the refinement of the crystal structure of the selenide $\text{Cu}_2\text{U}_3\text{Se}_7$. Refinements with the isotropic thermal parameters gave the the reliability factors values $R = 0.038$ and $R_w = 0.046$, and the final refinements with anisotropic thermal parameters resulted in the values $R = 0.036$ and $R_w = 0.044$, with a highest residual electron density peak corresponding to 0.7% of that of an uranium atom.

The positional parameters were standardized using the program STRUCTURE TIDY included in the TYPIX database (9), and the search for parent structure-types revealed $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$ to be isotypic with the sulfosilicide $\text{La}_3\text{CuSiS}_7$ (10). The U, Cu(1), and X atoms in $\text{Cu}_2\text{U}_3\text{X}_7$ occupy the same positions as La, Cu, and S atoms, respectively, in $\text{La}_3\text{CuSiS}_7$, while Cu(2) occupy the same position as that of Si.

The final values of the positional parameters and of the isotropic thermal factors for both compounds are given in Table 4. Anisotropic displacement parameters and the main interatomic distances are given in Tables 5 and 6

TABLE 2
X-Ray Powder Diffraction Pattern
of $\text{Cu}_2\text{U}_3\text{Se}_7$

<i>h k l</i>	d_{obs} (Å)	d_{cal} (Å)	<i>I/I</i> ₀
1 1 0	5.0678	5.0687	<3
1 0 1	4.9295	4.9327	37
2 0 0	4.3848	4.3896	15
1 1 1	3.8617	3.8620	20
2 0 1	3.5338	3.5350	85
2 1 0	3.3166	3.3183	30
0 0 2	2.9825	2.9816	32
2 1 1	2.9004	2.8995	28
1 0 2	2.8250	2.8231	32
3 0 1	2.6287	2.6271	87
1 1 2	2.5714	2.5698	16
2 2 0	2.5357	2.5344	85
2 0 2	2.4679	2.4663	58
3 1 0	2.4358	2.4349	25
3 1 1	2.2539	2.2542	54
2 1 2	2.2173	2.2177	100
3 0 2	2.0872	2.0885	20
4 0 1	2.0582	2.0597	9
3 2 0	2.0143	2.0141	7
3 2 1	1.9084	1.9082	50
3 1 2	1.8867	1.8859	15
1 1 3	1.8517	1.8504	7
4 1 1	1.8245	1.8240	54
2 0 3	1.8109	1.8106	18
4 0 2	1.7681	1.7675	5
2 1 3	1.7054	1.7051	10
5 0 1	1.6849	1.6843	25
3 2 2	1.6689	1.6690	3
3 0 3	1.6435	1.6442	28
4 1 2	1.6119	1.6117	<3
4 2 1	1.5985	1.5984	6

TABLE 3
Intensity Collection Parameters

	Cu ₂ U ₃ S ₇	Cu ₂ U ₃ Se ₇
Cell parameters (Å)		
<i>a</i>	9.7308(8)	10.138(1)
<i>b</i>	5.7045(6)	5.9525(7)
Unit cell volume (Å ³)	467.8	529.9
Crystal dimensions (mm ³)	0.16 × 0.12 × 0.08	0.06 × 0.08 × 0.01
Linear absorption coefficient (cm ⁻¹)	550.1	710.45
<i>Z</i>	2	2
<i>d</i> _{cal} (g/cm ³)	7.565	8.735
Radiation	λ Mo(Kα ₁)	λ Mo(Kα ₁)
Scan mode	ω - 2θ	ω - 2θ
Scan range	θ < 40°	θ < 40°
Measurement limits	-17 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 10	0 ≤ <i>h</i> ≤ 18 0 ≤ <i>k</i> ≤ 18 0 ≤ <i>l</i> ≤ 10
Number of observed reflections	2215	1311
Number of independent reflections <i>I</i> > 3σ(<i>I</i>)	863	777
Reliability factors:		
$R = \Sigma [F_o - F_c] / \Sigma F_o $	0.031	0.036
$R_w = [\Sigma_w (F_o - F_c)^2 / \Sigma_w F_o ^2]^{1/2}$	0.038	0.044
Goodness of fit	1.033	1.061

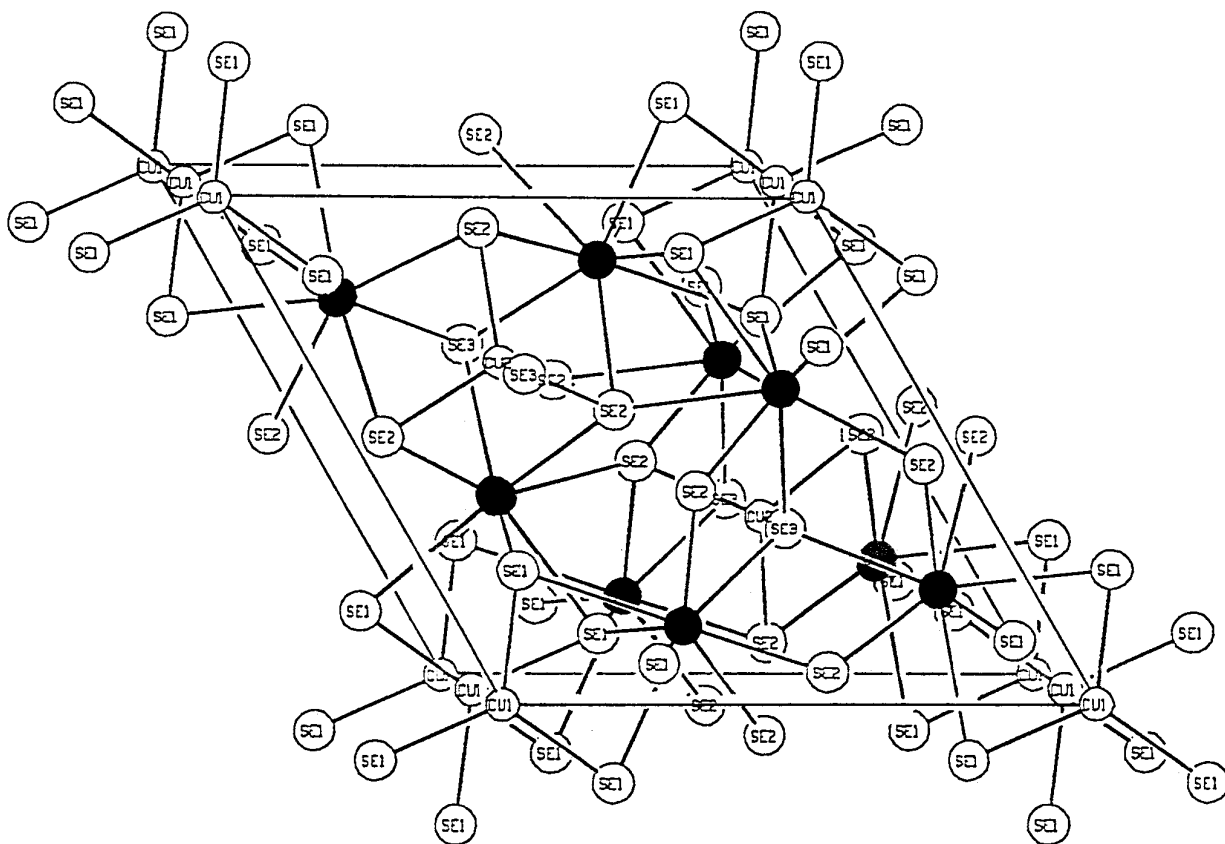


FIG. 1. ORTEP view of the crystal structure of Cu₂U₃Se₇ (filled circles are uranium atoms).

TABLE 4
Positional and Thermal Parameters of $\text{Cu}_2\text{U}_3\text{X}_7$ ($X = \text{S}, \text{Se}$)

Atom	Site	x	y	z	B_{eq} (\AA^2)
$\text{Cu}_2\text{U}_3\text{S}_7$					
U	6c	0.15146(3)	0.38079(3)	0.0290(2)	0.264(3)
Cu(1)	2a	0	0	0	0.74(3)
Cu(2)	2b	1/3	2/3	0.6479(4)	0.53(2)
S(1)	6c	0.2616(2)	0.1545(2)	0.0156(6)	0.40(3)
S(2)	6c	0.5129(2)	0.0802(2)	0.2832(5)	0.32(3)
S(3)	2b	1/3	2/3	0.2519(7)	0.38(4)
$\text{Cu}_2\text{U}_3\text{Se}_7$					
U	6c	0.15327(5)	0.37965(5)	0.0243(3)	0.588(6)
Cu(1)	2a	0	0	0	1.20(5)
Cu(2)	2b	1/3	2/3	0.6579(7)	0.91(4)
Se(1)	6c	0.2642(1)	0.1542(1)	0.0129(4)	0.66(2)
Se(1)	6c	0.5122(2)	0.0770(2)	0.2821(3)	0.65(2)
Se(3)	2b	1/3	2/3	0.2553(5)	0.65(2)

respectively. Structure factor tables are available upon request to the authors.

CRYSTAL STRUCTURE DESCRIPTION

An ORTEP view of the $\text{Cu}_2\text{U}_3\text{Se}_7$ structure is illustrated in Fig. 1. In this structure, uranium atoms have an eightfold coordination of chalcogen atoms (Fig. 2) with uranium to chalcogen distances ranging from 2.645 to 3.099 \AA in the sulfide and from 2.767 to 3.212 \AA in the selenide. The mean U–S distance of 2.86 \AA and U–Se distance of 2.98 \AA are slightly larger than those which were derived for uranium in the tetravalent state in such a chalcogen coordination (11). A larger crystal radius, particularly in the sulfide, may suggest uranium to be in some intermediate valence state (between U^{4+} and U^{3+}).

TABLE 5
Anisotropic Thermal Parameters of $\text{Cu}_2\text{U}_3\text{X}_7$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$\text{Cu}_2\text{U}_3\text{S}_7$						
U	0.208(5)	0.285(5)	0.274(6)	0.108(3)	-0.07(1)	-0.06(2)
Cu(1)	0.66(3)	β_{11}	0.94(9)	β_{11}	0	0
Cu(2)	0.58(3)	β_{11}	0.43(6)	β_{11}	0	0
S(1)	0.34(4)	0.43(4)	0.43(5)	0.18(2)	-0.12(8)	0.14(9)
S(2)	0.19(4)	0.43(4)	0.42(6)	0.20(3)	0.10(5)	0.03(5)
S(3)	0.53(6)	β_{11}	0.1(1)	β_{11}	0	0
$\text{Cu}_2\text{U}_3\text{Se}_7$						
U	0.545(8)	0.608(8)	0.61(1)	0.274(6)	-0.05(2)	-0.09(2)
Cu(1)	0.98(6)	β_{11}	2.0(2)	β_{11}	0	0
Cu(2)	1.05(7)	β_{11}	0.7(1)	β_{11}	0	0
Se(1)	0.56(3)	0.77(3)	0.63(4)	0.34(2)	-0.13(4)	-0.04(5)
Se(2)	0.56(3)	0.78(3)	0.64(4)	0.34(2)	0.15(4)	0.02(4)
Se(3)	0.77(5)	0.77(5)	0.46(7)	β_{11}	0	0

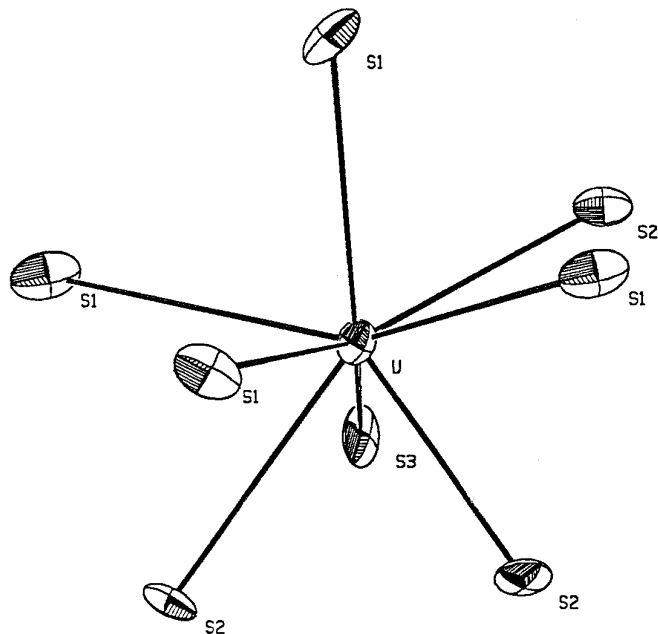


FIG. 2. Environment of uranium.

The copper atoms Cu(1) and Cu(2) have different chalcogen coordination polyhedra. Cu(1) has a trigonal environment (Fig. 3) with normal $X\text{--Cu(1)--}X$ angles of 119.84° for $X = \text{S}$ and 119.90° for $X = \text{Se}$. The Cu(1)–3S distance of 2.219 \AA in $\text{Cu}_2\text{U}_3\text{S}_7$ is shorter than those usually found for such a coordination: 2.33 \AA in TiCu_3S_2 (12), 2.32 \AA in Cu_4SnS_4 (13), where copper is expected to be monovalent.

Each Cu(1) atom has two other Cu(1) neighbors, forming a chain running along the c axis, with interatomic distances equal to half of the c axis value, i.e., 2.852 \AA in the sulfide and 2.976 \AA in the selenide.

The Cu(2) atoms are surrounded by four chalcogens forming a flattened tetrahedron (Fig. 4), with copper

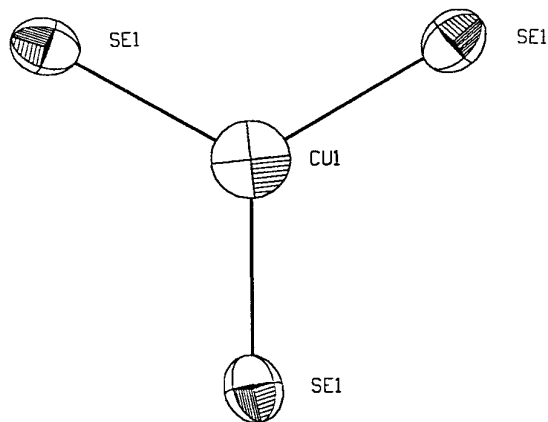


FIG. 3. Environment of Cu(1).

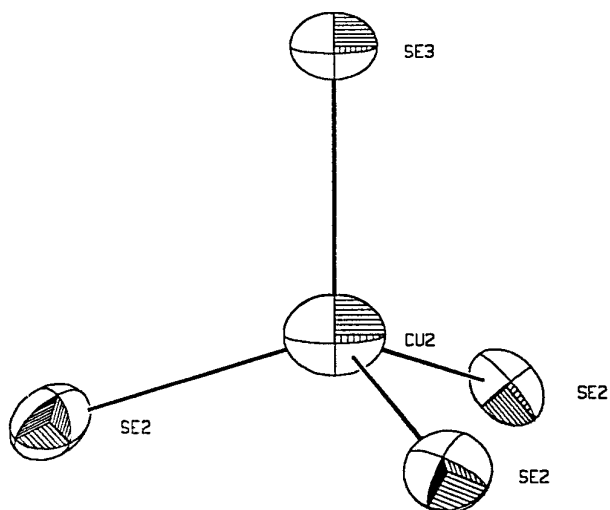


FIG. 4. Environment of Cu(2).

slightly closer to one corner within the CuX_4 tetrahedron. The mean $\text{Cu}(2)\text{-X}$ distances of 2.278 Å and 2.387 Å for $X = \text{S}$ and Se, respectively, are also slightly shorter than those generally found in ternary or quaternary copper chalcogenides with similar coordination around Cu: 2.348 Å in $\text{K}_3\text{Cu}_3\text{Nb}_2\text{S}_8$ (14), 2.307 Å in KCuZrS_3 (15), 2.422 Å in KCuZrSe_3 (15), and 2.433 Å in $\text{KCu}_2\text{NbSe}_4$ (16).

Such a shortening of copper to chalcogen distances, and

especially for $\text{Cu}(1)\text{-X}$, suggests also that copper should not be purely monovalent. This assumption agrees well, in terms of charge compensation, with the expected valence state of uranium.

MAGNETIC PROPERTIES

Magnetic measurements on polycrystalline samples were performed in the temperature range 5–300 K using a S.H.E SQUID magnetometer. The thermal variation of the reverse susceptibility for the two compounds is shown in Fig. 5. $\text{Cu}_2\text{U}_3\text{S}_7$ exhibits paramagnetic behavior down to 5 K. A curve fitting using the modified Curie–Weiss law $\chi = \chi_0 + C/T - \theta$ in the temperature range 50–300 K led to the value $\theta_p = -33$ K for the paramagnetic Curie temperature and to an effective paramagnetic moment of $2.50 \mu_B/\text{U}$.

The magnetic susceptibility of $\text{Cu}_2\text{U}_3\text{Se}_7$ shows a maximum at $T_N = 13$ K (see inset in Fig. 5) indicating an antiferromagnetic transition. Analysis using the modified Curie–Weiss law in the temperature range 80–300 K leads to the values $\theta_p = -28$ K for the paramagnetic Curie temperature and $2.64 \mu_B/\text{U}$ for the effective paramagnetic moment.

These values for the effective paramagnetic moments of uranium are significantly lower than the theoretical U^{4+} free ion value of $3.58 \mu_B$ ($^3\text{H}_4$ ground term) and are also

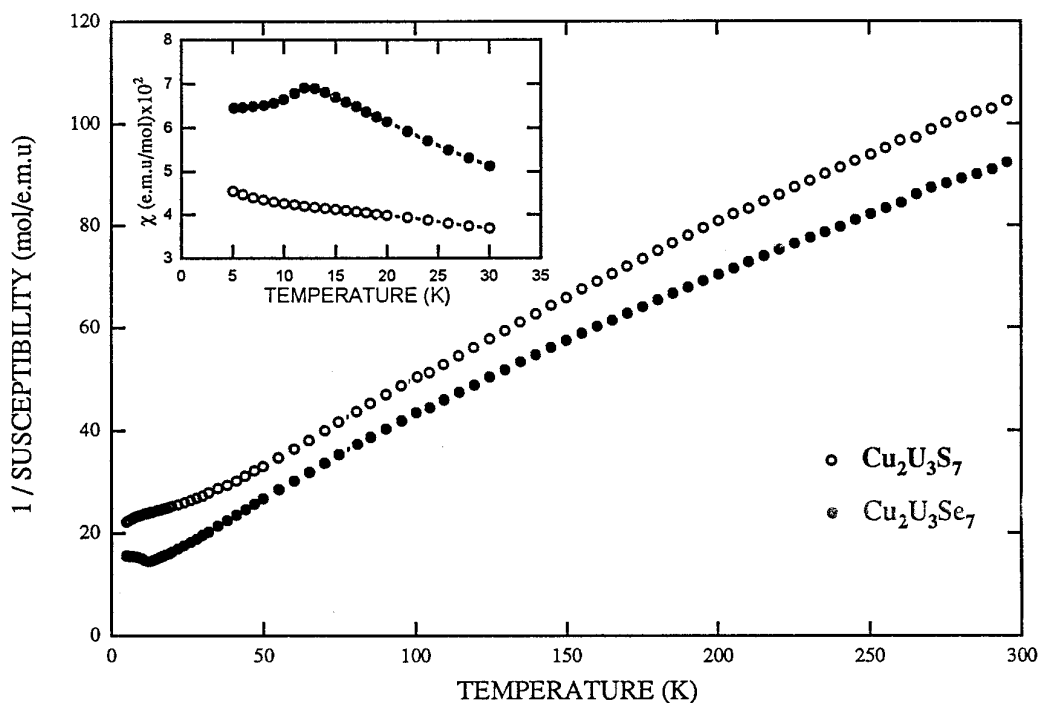
FIG. 5. Thermal variation of the reverse susceptibility of $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$. Inset: Susceptibility as a function of temperature.

TABLE 6
Principal Interatomic Distances (Å)

		X = S	X = Se	
U-	X(2)	2.645(2)	2.767(2)	
	X(3)	2.750(2)	2.866(1)	
	X(2)	2.755(2)	2.894(2)	
	X(1)	2.835(2)	2.945(2)	
	X(1)	2.892(2)	3.011(2)	
	X(2)	2.929(2)	3.072(2)	
	X(1)	2.956(3)	3.084(2)	
	X(1)	3.099(3)	3.212(2)	
	Cu(1)	3.235(3)	3.357(1)	
	Cu(2)	3.267(2)	3.353(3)	
Cu(1)-	2 U	4.224(2)	4.411(2)	
	3 X(1)	2.219(2)	2.332(1)	
	2 Cu(1)	2.852(4)	2.976(8)	
Cu(2)-	3 U	3.235(3)	3.357(1)	
	X(3)	2.259(5)	2.384(5)	
	3 X(2)	2.284(3)	2.397(2)	
X(1)-	3 U	3.267(2)	3.353(3)	
	Cu(1)	2.219(2)	2.332(1)	
	U	2.835(2)	2.945(2)	
	U	2.892(2)	3.011(2)	
	U	2.956(3)	3.084(2)	
	U	3.099(3)	3.212(2)	
	X(2)	3.256(3)	3.387(2)	
	X(2)	3.299(3)	3.431(2)	
	X(2)	3.467(3)	3.604(2)	
	Cu(2)	3.503(2)	3.645(2)	
	Cu(1)	3.542(3)	3.720(5)	
	X(2)-	Cu(2)	2.284(3)	2.384(2)
		U	2.645(2)	2.767(2)
U		2.755(2)	2.866(2)	
U		2.929(2)	3.072(2)	
2 X(2)		3.200(4)	3.312(3)	
X(1)		3.256(3)	3.387(2)	
X(3)-	X(1)	3.299(3)	3.431(2)	
	3 X(3)	3.431(4)	3.615(3)	
	Cu(2)	2.259(5)	2.397(5)	
	3 U	2.750(2)	2.894(1)	
	3 X(2)	3.431(4)	3.615(3)	
	Cu(2)	3.445(5)	3.556(5)	

lower than that for a totally quenched orbital moment ($2.83 \mu_B$). The large reduction of the effective moment probably results from the crystal field interactions. This is supported also by high values of the temperature-independent part of the susceptibility χ_0 (large curvature of the χ^{-1} curve) inferred from the modified Curie-Weiss law, i.e., 2.38×10^{-3} and 2.76×10^{-3} e.m.u./mol for $\text{Cu}_2\text{U}_3\text{S}_7$ and $\text{Cu}_2\text{U}_3\text{Se}_7$ respectively.

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