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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE HEXAGONAL URANIUM DICHALCOGENIDES γUS_2 AND γUSe_2

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ABSTRACT

The crystal structure of the hexagonal uranium disulfide γUS_2 (hexagonal $P\bar{6}2m$, a = 7.236(2) Å, c = 4.062(1) Å, γ = 120°) has been determined from single crystal X-ray diffraction data and confirmed by Rietveld refinements from X-ray powder diffraction intensities of the isostructural selenide γUSe_2 (a = 7.6328(3) Å, c = 4.1897(2) Å, γ = 120°). They crystallize with the anti-Fe_2P-type structure. The sulfide γUS_2 exhibits weak ferromagnetism below ≈10 K, and the selenide is a ferromagnet with a Curie temperature of ≈20 K and an ordered moment of 0.72 μB/U under 20 kGauss.

KEYWORDS: A. chalcogenides, D. crystal structure, D. magnetic properties

INTRODUCTION

The uranium binary chalcogenides form a large family of compounds with compositions ranging from UX to UX_3 (for X = S and Se) and up to UX_5 (for X = Te). They exhibit a wide variety of magnetic properties, with the uranium ion generally being tetravalent, and in intermediate (in UX) and ordered mixed valent (in U_3X_5) states in those compounds with low chalcogen content. The crystal structure types are known for all these binaries except the hexagonal form of the dichalcogenides γUX_2 (X = S, Se). As part of our program on crystallochemical characterization of these binary systems [1–6], we have determined the

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structure and magnetic properties of these compounds. Some preliminary results were previously reported [7,8].

EXPERIMENTAL

The binary uranium chalcogenides γUX_2 are thermally unstable (above ≈450 °C for X = S and above ≈700 °C for X = Se), and it was not possible to grow single crystals using the classical gas phase transport method. The selenide γUSe_2 can be prepared by thermal decomposition of a higher selenide (USe_3) at 650–670 °C under vacuum [9]. The sulfide γUS_2 was prepared with the binary U_3S_5 as a starting material, by a gas–solid reaction under a stream of H_2S at 410 °C [10] or by adding the complementary stoichiometric amount of sulfur and heating in a sealed silica tube at the same temperature [11]. After two weeks of heat treatment, the latter method yielded single crystals of γUX_2 suitable for X-ray diffraction, which formed directly in the sample.

The X-ray diffraction intensities were collected on a Nonius CAD4 four circle diffractometer, with the experimental conditions shown in Table 1.

STRUCTURE DETERMINATION

All calculations and structure refinements were performed with the Molen program package [12]. The lattice parameters, calculated from a least-squares refinement of a collection of 25

TABLE 1
Intensity Collection Parameters of γUS_2

Symmetry	Hexagonal
Space group	$P\bar{6}2m$ (no. 189)
Lattice parameters (Å)	$a = 7.236$ (2) $c = 4.026$ (1)
Unit cell volume (Å^3)	184.2
Formula units per cell	Z = 3
Formula weight	302.16
Calculated density	8.17
Crystal dimensions (mm^3)	0.18 × 0.06 × 0.04
Linear absorption coefficient	639.2
Radiation	λ (Mo Kα)
Scan mode	$\omega - 2\theta$
Measurement conditions	$\theta \leq 30°$ $-10 \leq h \leq 10$ $0 \leq k \leq 10$ $0 \leq l \leq 5$
Number of data collected	652
Number of unique data	138
Number of unique data with $I > 3\,\sigma\,(I)$	116
Ponderation factor p	0.02
Reliability factors:	
$R = \Sigma\,[\lvert F_o\rvert - \lvert F_c\rvert] / \Sigma\,\lvert F_o\rvert$	0.035
$R_\omega = [\Sigma_\omega\,(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma_\omega\,\lvert F_o\rvert^2]^{1/2}$	0.036
Goodness of fit (GOF)	0.99

TABLE 2
Positional Parameters, Anisotropic $\beta(i,j)$ and Equivalent Isotropic B (Å^2) Thermal Parameters* for γUS_2

Atom	Site	x	y	z	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	B(Å^2)
U(1)	1a	0	0	0	3.7(4)	$\beta_{1,1}$	4(1)	$\beta_{1,1}$	0.48(3)
U(2)	2d	1/3	2/3	1/2	2.8(2)	$\beta_{1,1}$	8.9(8)	$\beta_{1,1}$	0.49(2)
S (1)	3g	0.256(2)	0	1/2	3(2)	3(3)	10(6)	$\beta_{2,2}$	0.6(2)
S (2)	3f	0.600(2)	0	0	6(3)	5(3)	15(6)	$\beta_{2,2}$	0.9(2)

* The form of the anisotropic thermal parameters is

$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$.

The values of $\beta_{i,j}$ are multiplied by 10^3, and $\beta_{1,3} = \beta_{2,3} = 0$.

reflections, are a = 7.236(2) Å, c = 4.062(1) Å, γ = 120°. No systematic extinctions were observed, and the structure was solved in the $P\bar{6}2m$ space group (no. 189). The uranium atoms were found by the Patterson method to occupy the special positions 1a and 2d, and a difference Fourier map revealed the sulfur atoms to be on 3g and 3f Wyckoff sites. However, two electron density peaks with similar intensities were present for the latter site (x,0,0) and the refinement of their variable positional parameter x gave very close and equally reliable values for the final residual factors: R = 0.035 for x(S(2)) = 0.60, and R = 0.031 for x(S(2)) = 0.40. These positions are not symmetrically equivalent in the noncentrosymmetric space group $P\bar{6}2m$ and lead to two different structural models. The first one refers typically to the anti-Fe_2P-type of structure (Table 2), giving uranium-to-sulfur distances ranging from 2.73 to 3.00 Å, and a shortest S1–S2 distance of 3.21 Å. (Table 3, Fig. 1). The second model, with a slightly lower final residual factor, leads to a different bonding scheme, with the formation of S(1)–S(2) bonds (d = 2.283 Å) similar to those usually encountered in polysulfides, which could explain the weak thermal stability of these chalcogenides. In the sulfide γUS_2, the uncertainty between the two models arises from the fact that the diffusion factor of sulfur is much lower than that of uranium, which occupies two pseudo centrosymmetric positions (1a and 2d) in the noncentrosymmetric $P\bar{6}2m$ space group. So far it has not been possible to grow single crystals of the isotypic selenide γUSe_2, where the higher scattering power of selenium compared to that of sulfur would more clearly indicate the correct structural solution.

X-ray powder diffraction intensities were then collected for γUSe_2 on an Inel CPS 120 curved counter and the refinements of the two models were carried out by the Reitveld method, with the program Fullprof [12]. The unit cell parameters calculated from least-

TABLE 3
Interatomic Distances (Å) for γUS_2

U(1)	–6S(1)	2.75(1)	U(2)	–3S(1)	2.74(1)
	–3S(2)	2.89(1)		–6S(2)	3.003(4)
	–2U(1)	4.062(1)		–2U(2)	4.062(1)
S(1)	–6U(2)	2.74(1)	S(2)	–1U(1)	2.90(1)
	–2U(1)	2.75(1)		–8U(2)	3.003(4)
	–2S(1)	3.21(2)		–4S(2)	3.83(1)
	–2S(2)	3.21(2)		–2S(1)	3.21(2)

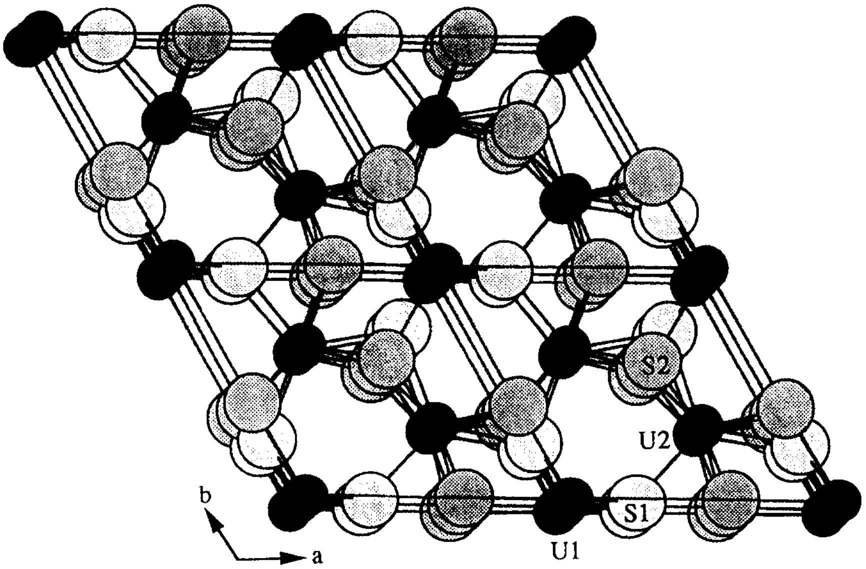

FIG. 1
View of the structure along the *c* axis.

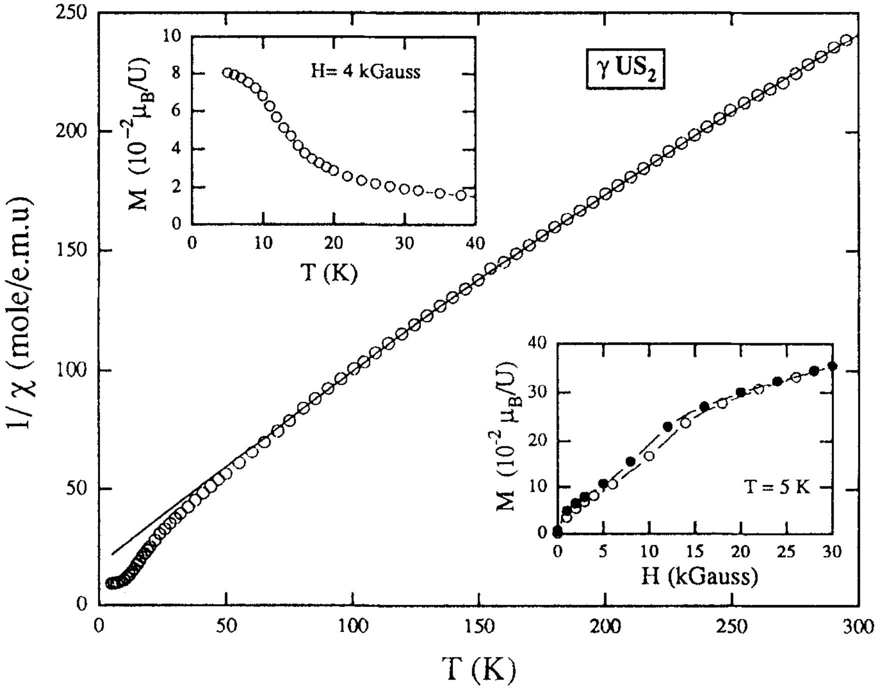

FIG. 2
Reverse susceptibility versus temperature, magnetization versus temperature (upper inset), and magnetization versus magnetic field (lower inset) for γUX_2.

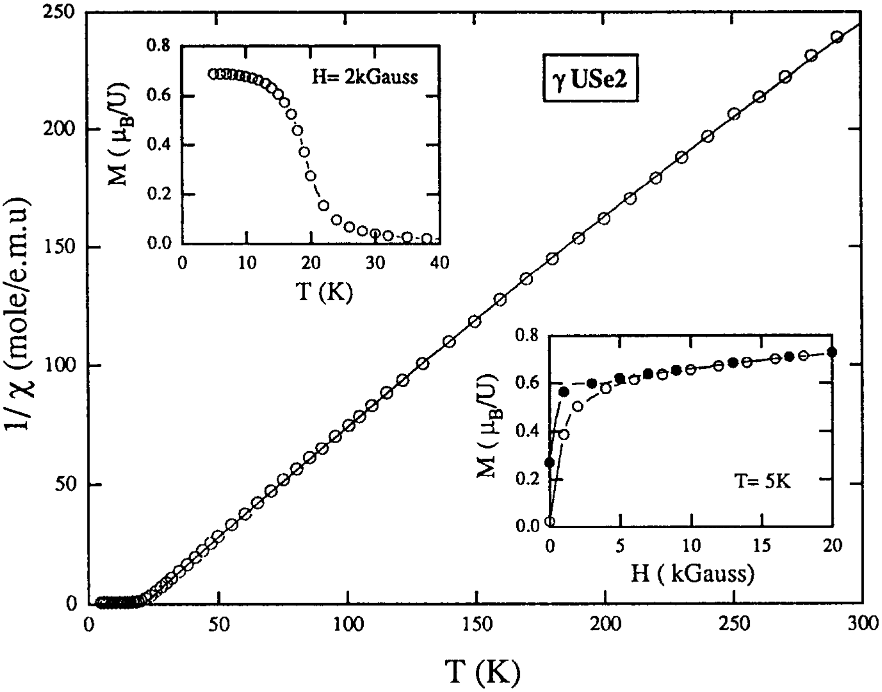

FIG. 3

Reverse susceptibility versus temperature, magnetization versus temperature (upper inset), and magnetization versus magnetic field (lower inset) for γUXe_2.

squares refinements of the powder pattern are a = 7.6328(3) Å, c = 4.1897(2) Å, and γ = 120°. The structure refinements proved unambiguously that the anti-Fe_2P-type structure was the correct structural model, with a conventional R factor of 0.06, compared to R = 0.10 for the other structural model.

MAGNETIC PROPERTIES

Magnetic measurements were performed on compacted powders, with a SQUID magnetometer in the temperature range of 5–300 K and in the field range of 0–20 kGauss.

Figures 2 and 3 display the temperature dependence of the reciprocal susceptibility and the thermal and field dependence of the magnetization of γUS_2 and of γUSe_2, respectively. The γUS_2 exhibits weak ferromagnetism below ≈10 K, with a remanent magnetization of 2.6 × 10^{-2} μB/U. The susceptibility was fitted between 100 and 300 K according to the modified Curie-Weiss law $\chi = \chi_0 + c/T - \theta p$, giving an averaged paramagnetic effective moment of 2.99 μB/U atom, a temperature independent term $\chi_0 = 648 \times 10^{-6}$ emu/mole. The negative paramagnetic Curie temperature $\theta p = -20$ K indicates that the weak ferromagnetism probably originates from a noncolinear antiferromagnetic lattice. The selenide γUSe_2 is a ferromagnet with a Curie temperature Tc ≈ 20 K, an ordered uranium magnetic moment (as measured on powder) of 0.72 μB under 20 kGauss, and a remanent value of 0.27 μB/U. In the paramagnetic region, the effective magnetic moment calculated using the modified Curie-Weiss law in the temperature range of 40–300 K is 2.89 μB/U with $\chi_0 = 377 \times 10^{-6}$ emu/mole and $\theta p = 21$ K. This value of the effective paramagnetic moment is close to that of the sulfide and to those usually found in uranium chalcogenides. Due to large crystal field interactions, the valence state of uranium cannot be unambiguously derived from these values; but on account of the stoichiometry, uranium should be in the tetravalent state in these compounds.

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