Magnetic Properties of Uranium Chalcogenides with Composition Close to UY_2

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The magnetic and some related physical properties of the uranium dichalcogenides are summarized and discussed with regard to their crystal structure. The theoretical magnetic susceptibility calculated on the basis of the usual crystal-field theory is compared with the experimental data. The calculation was carried out under the assumption that the uranium ions have the pure $^3H_4$ term and that there are S^{2-}, Se^{2-} and Te^{2-} ions. Regardless of the crystal environment of the uranium ion in all types of compounds the ground state appears to be a singlet. The results agree with experiment in a considerably broad temperature range. α-Dichalcogenides and U_7Te_{12} exhibit a magnetic transition at low temperatures. Their unusual behavior in this region is discussed in terms of their crystal-field levels, complicated magnetic structure and possible magnetocrystalline anisotropy.

1. Introduction

Because of their refractoriness and satisfactory radiation stability, uranium chalcogenides are the compounds of potential use as both high-temperature nuclear fuel and thermoelectric converter materials. Also, the possibility of using uranium sulfides as catalyst has been reported (*1*). The potential application of the uranium chalcogenides has stimulated the study of their preparation, structures and properties. The magnetic properties of the actinide elements are of undoubted interest due to their electronic structure intermediate between the $3d$ and $4f$ elements. Such an electronic structure of the actinides leads one to expect that their alloys and compounds may realize various types of magnetic order. To date the magnetic properties of uranium chalcogenides have been reviewed in several papers (*2–5*). However, due to limited space the dichalcogenides have received less attention than, for instance the monochalcogenides. Because of their various crystal structures uranium dichalcogenides provide a very convenient material for the examination of the influence of the symmetry of the magnetic atom crystal environment on the magnetic properties of these compounds. In this paper are summarized and reviewed the most up-to-date investigations of the magnetic properties and some related phenomena of the uranium dichalcogenides.

2. Crystal Structure and Preparation of Uranium Dichalcogenides

The existence of some of the uranium dichalcogenides had been known long ago (*6*), the existence of others was reported quite recently [see e.g. (*7, 8*)]. However, there has been much confusion about their crystal structure. Three modifications of disulfides and diselenides had been previously reported: the tetragonal α-modification, the orthorhombic β-modification and, metastable at room temperature, the hexagonal γ-modification (*9–14*). It has been established only recently that, in fact, the tetragonal α-modification contains more uranium than one would expect from stoichiometry, constituting another compound of the composition $UY_{1.9}$ (*15, 16*). Some authors mentioned UTe_2 to be tetragonal (*17, 18*), but even these same authors in other papers (*19, 20*) reported UTe_2 to be orthorhombic. Perhaps the tetragonal compound is tellurium-deficient UTe_{2-x} (*21*). This phase was also obtained in the presence of germanium (*21*) or antimony (*22*). The stoichiometric orthorhombic UTe_2 has been found to have the space group either *Immm* (*23*) or

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TABLE I

A. Crystal Structure of the Uranium Disulfides and Diselenides

Compound	Type of structure or space group	Lattice constants (Å)			Refs.
		a	b	c	
α-US$_2$	$I4/mcm$ (D_{4h}^{18})	10.28		6.31	(9)
(US$_{1.88}$)		10.28		6.327	(12)
		10.278		6.347	(15)
		10.67		6.30	(16)
		10.25		6.30	(24)
		10.312		6.352	(25)
		10.25		6.41	(28)
α-USe$_2$	$I4/mcm$ (D_{4h}^{18})	10.73		6.59	(13, 14, 16)
(USe$_{1.88}$)		10.718		6.605	(15)
		10.731		6.612	(25)
β-US$_2$	$Pmnb$ (D_{2h}^{16})	4.13	7.12	8.47	(9)
		4.22	7.08	8.48	(14)
		4.124	7.117	8.479	(15)
		4.13	7.11	8.44	(16)
		4.1205	7.1139	8.4803	(26)
β-USe$_2$	$Pmnb$ (D_{2h}^{16})	4.26	7.46	8.98	(13, 14)
		4.23	7.46	8.95	(16)
γ-US$_2$	Hexagonal	7.25		4.07	(11)
		7.25		4.06	(16)
γ-USe$_2$	Hexagonal	7.685		4.21	(13, 14)
		7.64		4.24	(16)

TABLE I

B. Crystal Structure of the Uranium Ditellurides

Compound	Type of structure or space group	Lattice constants (Å)			Refs.
		a	b	c	
UTe$_2$	$Immm$ (D_{2h}^{25})	4.162	6.124	13.958	(7)
		4.1617	6.1276	13.965	(23)
		4.180	6.131	13.992	(27)
	$Pnnn$ (D_{2h}^{2})	4.24	6.16	14.52	(19)
		4.17	6.14	13.97	(20)
UTe$_{2-x}$	ZrSiS	4.016		7.49	(18)
		4.243		8.946	(21)
	Tetragonal	4.005		7.469	(22)
U$_7$Te$_{12}$	Th$_7$S$_{12}$	12.309		4.242	(8)
(UTe$_{1.71}$)	Hexagonal	12.320		4.263	(27)

Pnnn (*19*). U_7Te_{12} can also be considered as a substoichiometric ($UTe_{1.71}$) ditelluride. It has not been found while investigating the U–Te phase diagram (*17*). Recently, Breeze et al. reported the existence of this hexagonal compound (*7, 8*). The symmetry type and lattice constants of uranium dichalcogenides are presented in Table I.

The most convenient method for obtaining the uranium dichalcogenides is the direct synthesis from powdered elements taken in the stoichiometric ratio, sealed off in an evacuated quartz capsule, and heated in the temperature range 600–1100°C during a few days (*7, 15, 17, 23, 25, 27, 29–31, 35–38, 42*). The slow increase of the temperature was necessary because of the strong exothermic effect of the reaction. Sometimes additional homogenization was applied (*15, 25, 42*). α-Diselenide was prepared also by thermal decomposition of USe_3 in vacuum at 760°C during 3 hr (*13, 14, 25, 28*). β-Diselenide was obtained by reaction of H_2Se with $UCl_4 \cdot 2NaCl$ at 900°C (*13, 14*). Some disulfides were the products of the reaction of H_2S with U_3O_8 or U (*11, 39, 40*). The synthesis of single crystals was accomplished by the chemical transport method using bromide as transporting agent (*26, 30, 41*). With the exception of the single crystal samples all dichalcogenides are sensitive to air and moisture, and require careful handling in an argon-filled dry-box.

3. Some Physical Properties

Systematic investigations of the electrical properties of uranium selenides and tellurides have been carried through by Matson, Moody, and Himes (*29*). They have found diselenide and ditelluride to be semiconductors, with the electrical resistivity at room temperature being of the order of 10^{-2} Ω cm, and with a high concentration of the charge carriers. The electrical properties of β-US_2 single crystals have been determined in a most detailed way (*26, 30*). This compound appears to be a semiconductor with the room temperature resistivity $\rho \cong 1$ Ω cm. At liquid helium temperature the resistivity amounts to $\rho = 7 \times 10^3$ Ω cm. and decreases as the temperature increases, showing a minimum at about 100 K. Above this temperature the resistivity increases and then, after reaching the intrinsic range (>600 K) again rapidly decreases. The forbidden gap is evaluated as $\Delta E \cong 1.2$ eV. Some thermoelectric data for disulfides are

presented in (*31*), e.g., the electrical resistivity values are equal to 8.3×10^{-3}, 1×10^{-2} and 2.6×10^{-4} Ω cm for α, β and γ disulfides, respectively. The discrepancies between the results given in (*26, 30, 31*) are probably due to the different purity of the samples. Low-temperature heat capacity measurements have been carried out for β-US_2, α-USe_2 and $US_{1.9}$ (α) from 5 to 350 K (*32, 33*). The authors have evaluated the excess heat capacity as being equal to 0.5 cal mole^{-1} K^{-1} around 25 K for β-US_2, and suggested it to be connected with the Schottky transition, with the singlet as ground state. The experimental data have not excluded the same type of transition for $US_{1.9}$ (*33*). In α-USe_2 a λ-type thermal anomaly has been found at 13.1 K.

4. Magnetic Properties

The magnetic properties of the uranium chalcogenides are briefly presented in Table II. We tried to collect only the most up-to-date results. Unfortunately, in the case of β-USe_2 and γ-dichalcogenides the magnetic properties were investigated long ago and only at room temperature. In Table II we omitted the results of these measurements in which the crystal structure was not clearly stated. The most extensive study of the magnetic properties in a wide temperature region and in considerably strong magnetic fields was carried out in our Laboratory (*25–28*, 34, 35), and in this section mainly the results of these studies are discussed. The results of other research groups are compared with ours.

Semimetallic compounds of uranium exhibit a variety of magnetic properties. In analogy with the lanthanide elements it is reasonable to assume that the magnetic properties of these compounds are closely related to the $5f$ electrons of the uranium atom. Whether the f electrons are well localized in the solid state remains a controversial question, since the $5f$ shell of a free actinide atom is spatially more extended than the $4f$ shell of a lanthanide. However, the best evidence is the magnetic form factor determined from thermal neutron scattering experiments, which indicates the spin-density distribution to be quite localized in space and does not support the itinerant electron model. Thus, because of their semiconducting character, in the case of dichalcogenides the application of the point charge model for the description of the

TABLE II

Magnetic Properties of the Uranium Dichalcogenides

Compound	θ (K)	Paramagnetic moment (μ_B)	Ferromagnetic moment (μ_B)	Temp. of magnetic transition (K)	Refs.
α-US$_2$		2.73-2.97[a]			(15)
(US$_{1.88}$)		—[a]		10–35	(25)
α-USe$_2$		2.86–3.07[a]			(15)
				13.1	(33)
(USe$_{1.88}$)		—[a]		8.5–13[b]	(25)
β-US$_2$		2.67–3.08[a]			(15)
		3.08–3.28[a]			(26)
β-USe$_2$	Only room temperature magnetic susceptibility			$\chi_M = 3395 \times 10^{-6}$	(13, 14)
γ-US$_2$	Only room temperature magnetic susceptibility			$\chi_M = 3720 \times 10^{-6}$	(9)
				$\chi_M = 3050 \times 10^{-6}$	(40)
γ-USe$_2$	Only room temperature magnetic susceptibility			$\chi_M = 3550 \times 10^{-6}$	(13, 14)
UTe$_2$	$\theta_{pol.cr.} = -80$	3.12			(38)
	$\theta_\parallel = -100$				
	$\theta_\perp = -70$	—[a]			(27)
UTe$_{2-x}$	-78	3.12			(18)
U$_7$Te$_{12}$		—[a]	0.98	73	(27)
(UTe$_{1.71}$)					

[a] Temperature dependent.   [b] Field dependent.

magnetic properties in the paramagnetic region seems to be justified. We assume that the U^{4+} ion has the pure $^3H_4$ term, and that there are S^{2-}, Se^{2-} and Te^{2-} ions.

4.1. Cation Coordination

a. α-Dichalcogenides. As mentioned above (see Table I) the proposed structure of α-US$_2$ (12) has the symmetry *I4/mcm* or D_{4h}^{18} with the uranium atoms in the two crystallographically different positions. Of the 10 uranium atoms in the unit cell approximately one-fifth is surrounded individually by eight sulfur atoms at the corners of a right antiprism, with the uranium-to-sulfur distance equal to 2.81 Å, and four-fifths are surrounded by 6 sulfur atoms/uranium atom: four of them in the cation plane and two in neighboring planes, all with the uranium-to-sulfur distance equal to 2.77 Å. But it should be noted that the configuration of the sulfur atoms is not octahedral (Fig. 1). According to Khodopdad
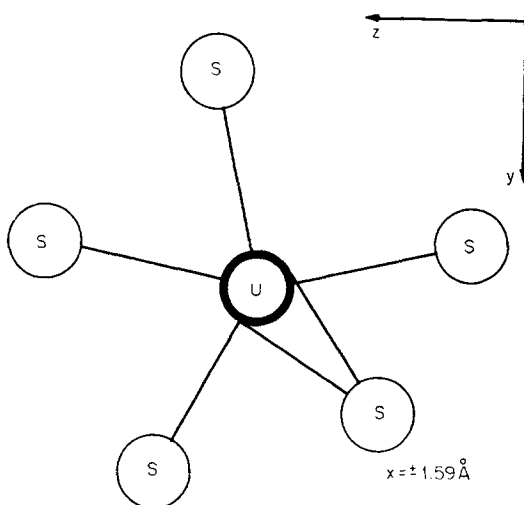

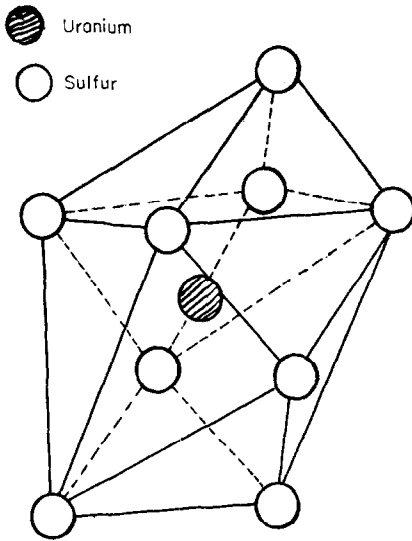Fig. 1. Projection along x axes the coordination polyhedron of the uranium atom with sixfold coordination in α-UY$_2$.

FIG. 2. The coordination polyhedron of the uranium atoms in β-US_2.

FIG. 3. Projection along x axes the coordination polyhedron of the uranium atom in UTe_2.

(13, 14) α-USe_2 has the same structure, but he has not presented the exact atom positions and the interatomic distances. For this reason the crystal-field calculations given below were based on the crystal parameters reported for α-US_2.

b. β-US_2. The reported structure of β-US_2 (9, 15, 16, 24, 26) has the symmetry Pmnb or D_{2h}^{16}. Each uranium atom in the coordination polyhedron is surrounded by nine sulfur atoms (Fig. 2), six of which are placed at the corners of the trigonal prism, while three others occupy the corners of the triangle which is placed in the cation plane and rotated around the threefold axis of the prism by 60°, the uranium-to-sulfur distance varying from 2.713 to 3.141 Å. For calculations the average distance 2.91 Å was assumed.

c. UTe_2. There have been reported two types of symmetry for the orthorhombic UTe_2. This objection was disregarded (27) because in both cases the coordination polyhedron is the same. For the present discussion, however, the atom positions given in (23) were chosen. Uranium is surrounded by eight tellurium atoms which form a trigonal prism with two capped, square faces; the third square face of the prism is topped by another uranium atom (the average U–Te distance is equal to 3.17 Å) (Fig. 3).

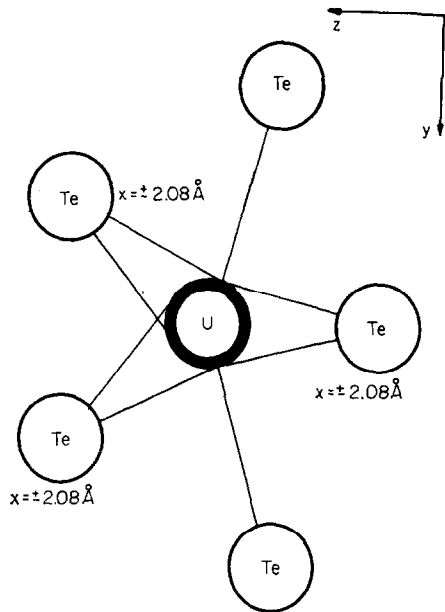d. U_7Te_{12}. The structure of U_7Te_{12} has been reported to be isostructural with Th_7S_{12} and Th_7Se_{12} in which the metal atoms are placed in two geometrically different positions. Of the seven uranium atoms in the unit cell one seventh is surrounded by nine tellurium atoms ordered in the same way as in β-US_2, only the U–Te distances are different. The distance between uranium and the tellurium atoms placed at the corners of the trigonal prism is equal to 3.67 Å, while that between uranium and the tellurium atoms occupying the corners of the triangle is equal to 3.00 Å. Six-sevenths of the uranium atoms are each surrounded by eight tellurium atoms arranged in the same way as in UTe_2; the U–Te distance ranges from 3.10 to 3.26 Å.

4.2. The splitting of the $^3H_4$ term and the magnetic susceptibility of the U^{4+} ion

a. α-Dichalcogenides. As it was said above the structure of α-UY_2 contains uranium atoms in two crystallographically different positions. The energy level diagram for the $^3H_4$ term in a crystal field of D_{4d} symmetry (antiprismatic coordination) and the crystal-field potential were reported by Mulak and Czopnik (43) and are given below:

$$V_{cf} = B_4(O_4^0 + 5 \cdot O_4^4) + B_6(O_6^0 - 21 \cdot O_6^4) \quad (1)$$

where the fourth- and sixth-order crystal-field intensities B_4 and B_6 are defined as:

$$B_4 = -\frac{7}{32}\frac{Ze^2}{R^5}\beta\langle r^4 \rangle, \qquad B_6 = -\frac{39}{256}\frac{Ze^2}{R^7}\gamma\langle r^6 \rangle.$$
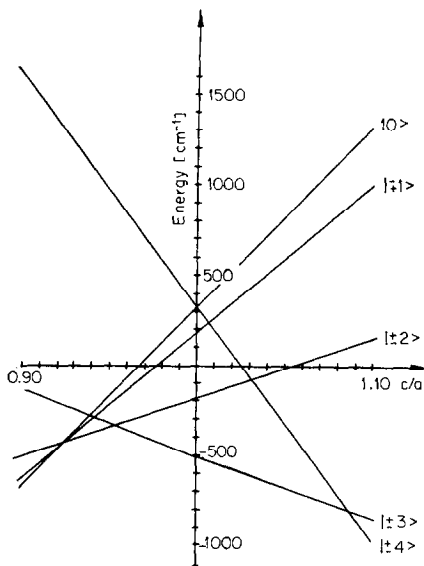
$$(2)$$

FIG. 4. Energy-level diagram for the $^3H_4$ term in a ligand field of D_{4d} symmetry as a function of c/a (43).

In Eqs. (1), (2) and below, $O_2{}^0$, $O_2{}^1$, etc., are specified Stevens operators for a given J (44), Ze is the charge of the ion Y; e, the electron charge; α, β and γ, multiplying factors; $\langle r^n \rangle$
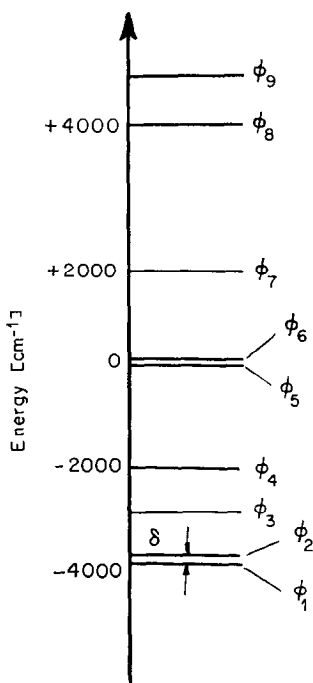

FIG. 5. Diagram of the crystal-field levels for the $^3H_4$ term of the uranium ion with sixfold coordination in α-UY$_2$ (25).

the mean nth power of the radius of the $5f$ electrons; and R, cation–anion distance. According to (45) for U^{4+} we have $\langle r^2 \rangle = 1.68$, $\langle r^4 \rangle = 5.00$ and $\langle r^6 \rangle = 24.4$ atomic units, and for the $^3H_4$ term $\alpha = -2.1 \times 10^{-2}$, $\beta = -7.34 \times 10^{-4}$ and $\gamma = 6.1 \times 10^{-5}$ (46). As it follows from Fig. 4 the doublet $|\pm 3\rangle$ was found to be ground state for c/a close to 1.

The formula for the magnetic susceptibility of the U^{4+} ion in an ideal antiprismatic coordination, within the low-temperature range (0.1 of the total splitting Δ) in which one can assume the population of the lowest doublet only, is given by (43):

$$\chi_{M,8} = \frac{0.72}{T} + \frac{3.89}{\Delta}. \tag{3}$$

The subscript 8 means the eightfold coordination of the uranium ion. In the case of the uranium ion with the sixfold coordination, the crystal-field potential is much more complicated:

$$
\begin{aligned}
V_{cf} = \ & B_2(0.7 \cdot O_2{}^0 - 9.44 \cdot O_2{}^1 + 3.4 \cdot O_2{}^2) \\
& + B_4(0.17 \cdot O_4{}^0 + 0.75 \cdot O_4{}^1 \\
& - 0.16 \cdot O_4{}^2 + 4.6 \cdot O_4{}^3 + 1.4 \cdot O_4{}^4) \\
& + B_6(0.01 \cdot O_6{}^0 + 2 \cdot O_6{}^2 - 1.8 \cdot O_6{}^4 \\
& + 1.7 \cdot O_6{}^6) - 2B_6(O_6{}^1 + O_6{}^3 - 2.0_6{}^5),
\end{aligned}
\tag{4}
$$

where $B_2 = (Ze^2/R^3)\alpha\langle r^2 \rangle$, $B_4 = (Ze^2/R^5)\beta\langle r^4 \rangle$ and $B_6 = (Ze^2/R^7)\gamma\langle r^6 \rangle$.

The other symbols have the same meaning as above. The energy-level splitting scheme of the $^3H_4$ term of the uranium ion surrounded by the six sulfur atoms is presented in Fig. 5. In this case the ninefold degenerated $^3H_4$ term splits into nine singlets with a total splitting about 8000 cm^{-1} (25). For the paramagnetic region at temperatures which do not exceed 300 K, it was assumed that the ground state is composed of two singlets (25):

$$
\begin{aligned}
\phi_1 = \ & -0.072|\pm 4\rangle - 0.335|\pm 3\rangle - 0.471|\pm 2\rangle \\
& + 0.019|\pm 1\rangle + 0.567|0\rangle
\end{aligned}
$$
$$
\begin{aligned}
\text{and } \phi_2 = \ & \pm 0.145|\pm 4\rangle \pm 0.148|\pm 3\rangle \mp 0.268|\pm 2\rangle \\
& \mp 0.621|\pm 1\rangle.
\end{aligned}
$$

Thus, owing to the crystal anisotropy, the average susceptibility can be written in the form (25)

$$\chi_{M,6} = \frac{1}{3}(\chi_M{}^x + \chi_M{}^y + \chi_M{}^z) = \frac{1.0}{T}, \tag{5}$$

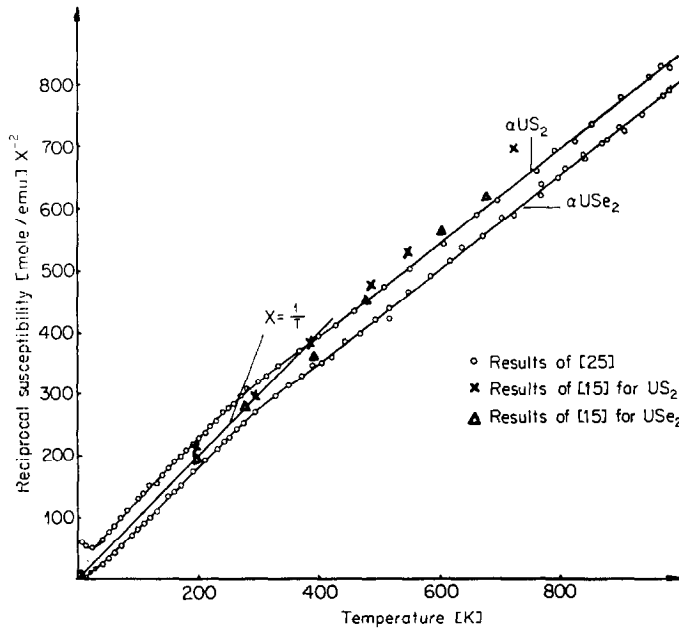if one neglects the high frequency term. The subscript 6 means the sixfold coordination of the

FIG. 6. The reciprocal susceptibility of α-US_2 and α-USe_2 as function of temperature.

uranium ion. Hence, the total susceptibility is equal to (25)

$$\chi_M = \frac{1}{5}\left(\frac{0.72}{T} + \frac{3.89}{\Delta}\right) + \frac{4}{5} \cdot \frac{1.0}{T} = \frac{0.92}{T} + \frac{3.89}{5\Delta}.$$

(6)

The coefficients $1/5$ and $4/5$ correspond to the fractions of the uranium ions in both crystallographic positions. Thus, for relatively low T values Eq. (6) may be approximated by $1/T$, corresponding to a magnetic moment $n_p = 2.83$ μ_B. This value is close enough to that given in (15, 25, 28) obtained in the temperature range up to about 300 K. However, a deviation from the linear χ^{-1} vs T plot (see Fig. 6) above 300 K is observed, which is caused by both the contribution of the temperature-independent term and the population of the higher energy levels.

b. β-US_2. The symmetry of the coordination polyhedron of the uranium atom in β-US_2, assuming all U–S distances equal to 2.91 Å, can be described as C_{3h}. In this case the crystal-field potential is given by

$$V_{cf} = 5B_2O_2{}^0 - 1.5B_4{}^0 + B_6(-0.1 \cdot O_6{}^0$$
$$- 0.5 \cdot O_6{}^6).$$

(7)

The energy-level diagram for the $^3H_4$ term of the uranium ion in β-US_2 is presented in Fig. 7.

According to this scheme the ground level is a doublet. However, the results of magnetic measurements (26) show that the ground state
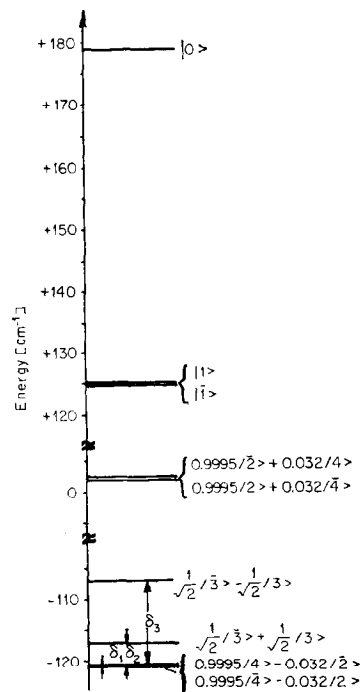

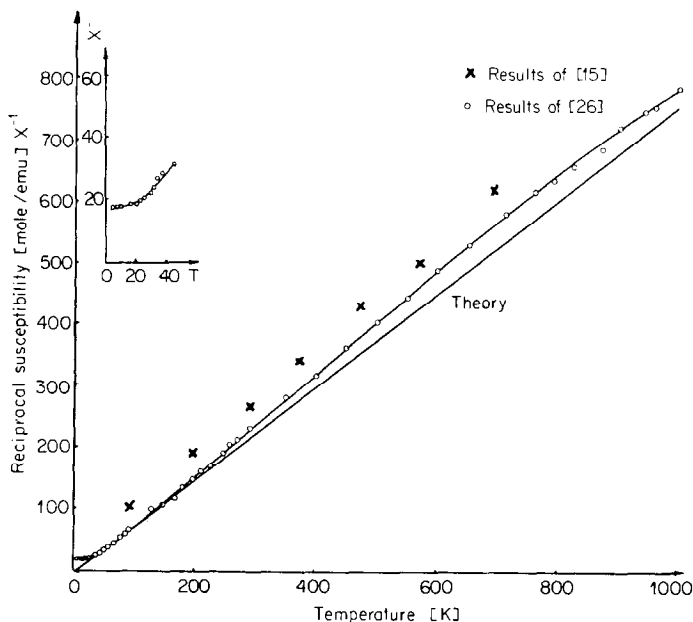FIG. 7. Diagram of the crystal-field levels for the $^3H_4$ term of the uranium ion in β-US_2 (26).

FIG. 8. The reciprocal susceptibility of β-US$_2$ as function of temperature.

has to be a singlet (see Fig. 8). Some evidence for such an assumption is provided also by the measurements of the low-temperature heat capacity (32).

In fact, the real symmetry is lower than C$_{3h}$ and the splitting of the lowest doublet into two singlets is highly probable. From the above considerations it follows that the ground state is composed of four close-spaced singlets which roughly have the form (26)

$$\frac{1}{\sqrt{2}}\Big|4\Big\rangle \pm \frac{1}{\sqrt{2}}\Big|\bar{4}\Big\rangle \quad \text{and} \quad \frac{1}{\sqrt{2}}\Big|3\Big\rangle \pm \frac{1}{\sqrt{2}}\Big|\bar{3}\Big\rangle.$$

Owing to the small value of the coefficient of the $|\pm 2\rangle$ functions in the original doublet, the admixture of this state to the ground state is very small and, for the sake of simplicity, can be neglected. Thus, considering these four singlets the average susceptibility at 0 K can be written in the form (26)

$$\bar{\chi}_0 = \frac{1}{3}\cdot\frac{7.68}{\delta_1} + \frac{2}{3}\cdot\frac{0.96}{\delta_2}. \qquad (8)$$

From preliminary measurements on a single crystal sample it follows that δ_1 is about 30 K. Assuming $\delta_2 \simeq 20$ K we get $\bar{\chi}_0 = 0.050$ while the extrapolation of the experimental curve to 0 K gives 0.054 (26). In the temperature region above 300 K, it seems quite reasonable to use

for the average magnetic susceptibility the simplified expression

$$\bar{\chi} = \frac{1.32}{T}, \qquad (9)$$

which corresponds to the magnetic moment $n_p = 3.25$ μ_B while the experiment gives $n_p = 3.28$ μ_B (26). The theoretical curve calculated from Eq. (9) is presented in Fig. 8. The fit of experimental and theoretical curves is surprisingly good, especially in the temperature range below 300 K. This can be quite incidental, because for exact calculations one needs the values of δ_1, δ_2 and δ_3 (see Fig. 7).

c. UTe$_2$. The crystal-field potential for the uranium ion surrounded by eight tellurium ions, assuming all uranium–tellurium distances to be equal to 3.17 Å (in fact, these distances are ranging from 3.03 up to 3.20 Å—Fig. 3), is given by

$$\begin{aligned}
V_{cf} = {}& B_2(-0.07\cdot O_2^0 + 0.2\cdot O_2^2) \\
& + B_4(-0.22\cdot O_4^0 + 1.48\cdot O_4^2 + 0.13\cdot O_4^4) \\
& - B_6(0.08\cdot O_6^0 + 0.67\cdot O_6^2 + 1.06\cdot O_6^4).
\end{aligned}$$
$$(10)$$

From the energy-level diagram presented in Fig. 9 it follows that also in this case the ninefold degenerated $^3H_4$ term splits into nine singlets. Then, it was assumed (27) that the ground state
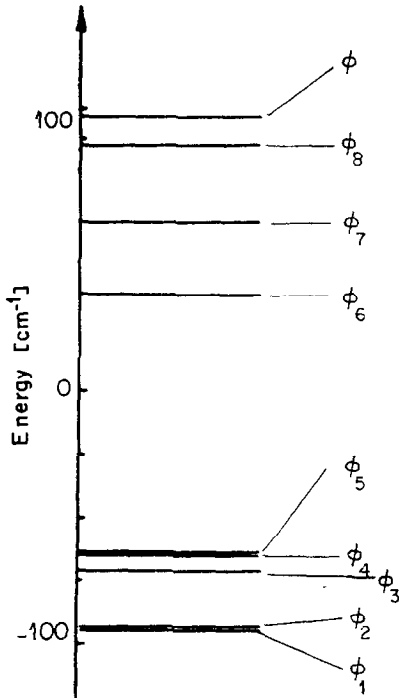
FIG. 9. Diagram of the crystal-field levels for the $^3H_4$ term of the uranium ion in UTe_2 (27).

is composed of three equivalent singlets in the whole investigated region:

$$\phi_1^r = \pm 0.363|\mp 4\rangle \pm 0.607|\mp 2\rangle,$$
$$\phi_2 = 0.355|\pm 4\rangle + 0.607|\pm 2\rangle$$

and $\phi_3 = \pm 0.612|\mp 3\rangle \pm 0.354|\mp 1\rangle$.

Thus, if one neglects the high frequency term, the average magnetic susceptibility can be written in the form (27)

$$\bar{\chi}_M = \frac{1.22}{T}. \qquad (11)$$

The experimental and theoretical curves are presented in Fig. 10. The Eq. (11) corresponds to a magnetic moment $n_p = 3.10$ μ_B, while the experiment gives 3.12 μ_B (38) and 3.06 μ_B at 450 K (27). However, in the low-temperature range the experimental χ^{-1} vs T curve (27) is different from that characteristic for the singlet–ground-state with temperature-independent paramagnetism region. In the author's opinion (27) such a behavior results from the exchange interactions. U_7Te_{12} in which 6/7 of the uranium atoms have very similar crystallographic environments to those in UTe_2, was found to be a ferromagnet below 73 K (27). It may be expected that UTe_2 due to the longer U–U distances 3.77 Å has a lower transition point than U_7Te_{12} with U–U distance equal to 2.12 Å. The assumption of a nonsinglet-ground-state as well as a different valence state from the assumed U^{4+} ion seems to be unreasonable.

d. U_7Te_{12}. The energy-level diagrams for the uranium ions in both crystallographic positions are presented in Figs. 11 and 12. The crystal-
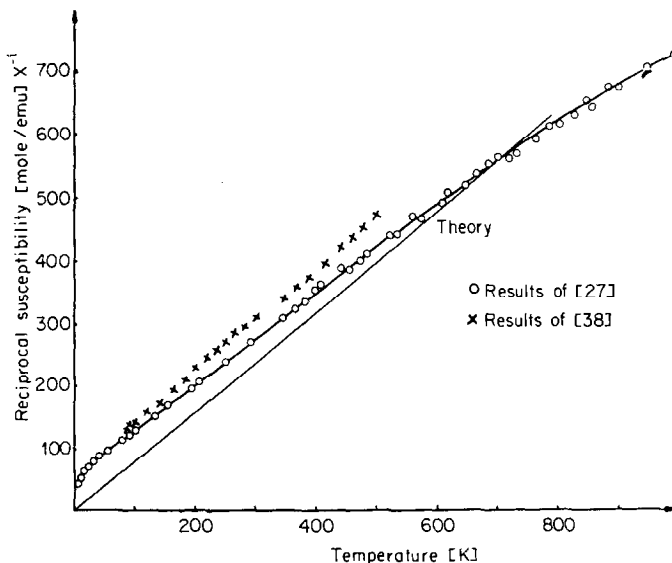

FIG. 10. The reciprocal susceptibility of UTe_2 as function of temperature.
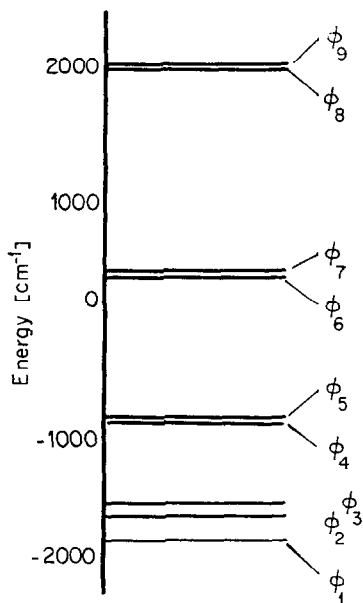
FIG. 11. Diagram of the crystal-field levels for the $^3H_4$ term of the uranium ion with ninefold coordination in U_7Te_{12} (27).
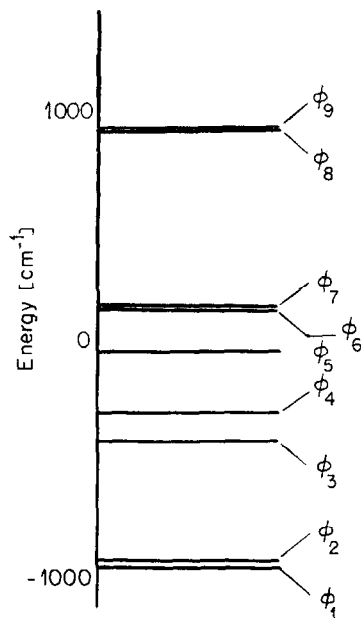

FIG. 12. Diagram of the crystal-field levels for the $^3H_4$ term of the uranium ion with eightfold coordination in U_7Te_{12} (27).

field potential for the ninefold coordinated uranium ion is equal to

$$V_{cf} = B_2(0.7 \cdot O_2{}^0 + 2.1 \cdot O_2{}^2)$$
$$- B_4(0.14 \cdot O_4{}^0 + 2.15 \cdot O_4{}^2 + 1.3 \cdot O_4{}^4)$$
$$+ B_6(0.24 \cdot O_6{}^0 + 0.75 \cdot O_6{}^2 + 0.86 \cdot O_6{}^4$$
$$- 0.6 \cdot O_6{}^6). \tag{12}$$

Thus, assuming the singlets $\phi_1 = 0.532|4\pm\rangle$ $-0.392|\pm2\rangle$ $+0.354|0\rangle$ and $\phi_2 = \pm0.654|\mp4\rangle$ $\mp0.270|\mp2\rangle$ to be the ground state one obtains for the average magnetic susceptibility (27) the formula

$$\bar{\chi}_{M,9} = \frac{0.90}{T}. \tag{13}$$

For the eightfold coordinated uranium ion the crystal-field potential is equal to:

$$V_{cf} = -1.7 \cdot B_2O_2{}^1 - B_4(1.5 \cdot O_4{}^1 + 1.53 \cdot O_4{}^2$$
$$+ 5.5 \cdot O_4{}^3 + 1.17 \cdot O_4{}^4)$$
$$-B_6(1.2 \cdot O_6{}^1 + O_6{}^2 - 1.2 \cdot O_6{}^3$$
$$- 1.1 \cdot O_6{}^4 + 6.7 \cdot O_6{}^5), \tag{14}$$

and the two lowest singlets are as follows (27):

$$\phi_1 = -0.333|-4\rangle +0.476|-3\rangle -0.363|-2\rangle$$
$$+0.170|-1\rangle -0.002|0\rangle - 0.151|1\rangle$$
$$+0.366|2\rangle -0.481|3\rangle +0.336|4\rangle \text{ and}$$
$$\phi_2 = -0.343|-4\rangle +0.484|-3\rangle -0.352|-2\rangle$$
$$+0.144|-1\rangle -0.099|0\rangle +0.160|1\rangle$$
$$-0.348|2\rangle +0.480|3\rangle -0.342|4\rangle.$$

Then the average magnetic susceptibility equals to (27).

$$\chi_{M,8} = \frac{0.65}{T}. \tag{15}$$

It should be pointed out here that, although the polyhedron of the uranium ion with the eightfold coordination in U_7Te_{12} is very similar to that in UTe_2, yet the crystal potentials are different because for UTe_2 the calculations were carried out for average U–Te distances while in the case of U_7Te_{12} for the real ones.

The total magnetic susceptibility is equal to (27)

$$\chi_M = \frac{1}{7} \cdot \frac{0.90}{T} + \frac{6}{7} \cdot \frac{0.65}{T} = \frac{0.70}{T}, \tag{16}$$

when neglecting the high frequency term. The coefficients $1/7$ and $6/7$ correspond to the fraction of the uranium ions in both crystallographic positions. As it follows from Fig. 13 the slopes of the theoretical and experimental curves are close to each other in the temperature region below 200 K only. The occurrence of ferromagnetic order at temperatures below 73 K makes even this agreement disputable. On the other hand, assuming the contribution from the higher singlet ϕ_3 to be the same as that of ϕ_1
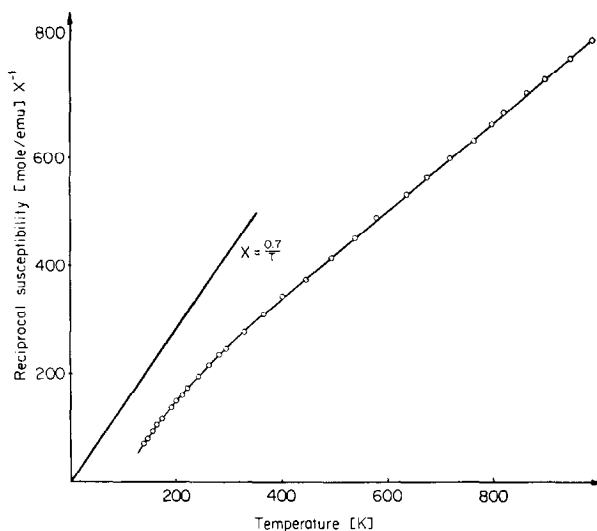
FIG. 13. The reciprocal susceptibility of U$_7$Te$_{12}$ as function of temperature (27).

and ϕ_2 one obtains the following equation for the average magnetic susceptibility (27):

$$\bar{\chi}_M = \frac{1.60}{T}. \qquad (17)$$

The values of the magnetic susceptibility calculated on the basis of Eq. (17) are much higher than the experimental ones. Therefore, one can expect that in fact the two lowest singlets are very close to one another while the third one is markedly higher. Thus, if one does not know the population of the third singlet as a function of temperature, the calculation of the magnetic susceptibility is in vain.

4.3. Region of the magnetic ordering

In the series of compounds described in this paper both α-dichalcogenides and U$_7$Te$_{12}$ appear to be magnetically ordered (25, 27). But their properties are rather complicated, probably due to at least one of the four following causes:

1. As it was shown in the preceding section, all these compounds have most probably the singlet as the crystal-field ground-state. It has been recognized for a number of years (47) that the magnetic properties of such systems, in which the isotropic exchange interactions and the crystal field nearly balance each other, differ in a fundamental way from those of conventional magnetic crystals. In this case the theory predicts a critical value for the ratio of the exchange-to-crystal-field interactions necessary for setting up a magnetic order.

2. Either α-dichalcogenides and U$_7$Te$_{12}$ have a crystal structure with the uranium atoms placed in two geometrically different positions. This type of structure may favor the creation of complicated magnetic orders.

The above points are both in close analogy to the case of the praseodymium metal and its compounds having the same ground term $^3H_4$ and a singlet as the crystal-field ground-state. Moreover, the structure of the elemental Pr contains two groups of crystallographically different ions, namely, in the positions of local cubic and hexagonal symmetry. Cable et al. (48) have shown that in the temperature range below 25 K at least some of the ions carry a moment considerably smaller than the theoretical one. However, recent neutron diffraction on Pr (49, 50) have revealed no magnetic order in zero applied field. A magnetic moment is induced by a considerably strong magnetic field of 46 kOe, which reaches 1.8 μ_B on hexagonal sites and 0.9 μ_B on cubic sites. This discrepancy has as yet no complete explanation.

3. Some magnetically ordered uranium compounds, especially ferromagnets, exhibit strong magnetocrystalline anisotropy. Apart from the distortion of their crystal structure below the point of magnetic transition (51), one observes in these compounds a maximum in the temperature dependence of the magnetization which is sensitive to the strength of the applied magnetic field (37, 52–58). In the case of the here reported compounds we encounter perhaps this anisotropy, too.

4. The presence of a randomly frozen "spin-glass" with magnetic clusters dispersed in it can cause a strange behavior of some alloys and compounds. Such phenomenon is known as micromagnetism (59). Typical micromagnetic materials exhibit a maximum in the temperature dependence of the magnetization which is sensitive to the magnetic field, and a linear dependence of the magnetization on the applied magnetic field in a limited field region.

The dependence of the magnetization on the magnetic field strength for the α-dichalcogenides and U_7Te_{12} is presented in Fig. 14. For diselenide this dependence is linear to about 20 kOe but begins to flatten off above this value. The magnetization of disulfide as a function of the magnetic field is linear up to about 30 kOe, but above this value the curve becomes steeper as the magnetic field is raised. Further, disulfide exhibits also at 4.2 K a small but distinct hysteresis. The behavior of U_7Te_{52} seems to prove it to be a ferromagnet; however, saturation was not observed in magnetic fields up to 80 kOe. The ferromagnetic moment calculated on the basis of the highest measured value of the magnetization is equal to 0.98 BM.

The temperature dependence of the magnetization of α-USe_2 presented in Fig. 15 suggests the possibility of metamagnetism. The value of the critical field between 15 and 18 kOe is sufficient to suppress the antiferromagnetic
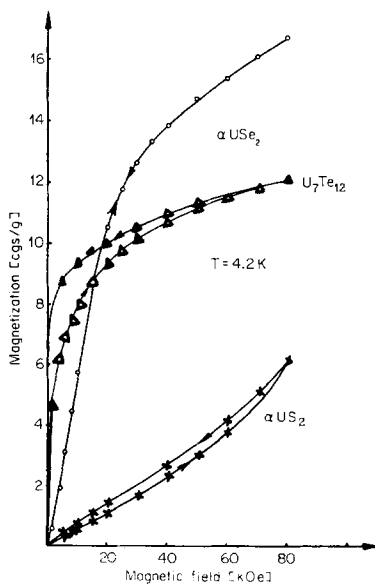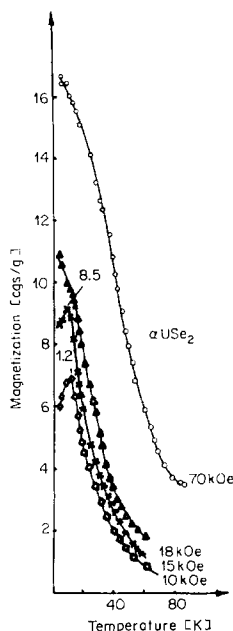

FIG. 15. The magnetization of α-USe_2 as function of temperature (25).

order and create a "ferromagnetic" one. Some evidence for such an interpretation seems to provide the dependence of the magnetization on the magnetic field, which is similar to that reported for rare earth compounds recognized as metamagnets—with the exchange interactions
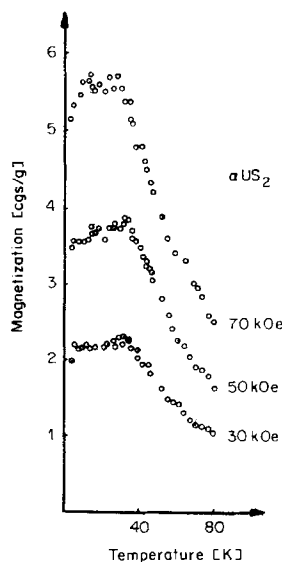

FIG. 14. The magnetization of α-UY_2 and U_7Te_{12} as function of the magnetic field at 4.2 K (25, 27).

FIG. 16. The magnetization of α-US_2 as function of temperature (25).

being weaker than the anisotropy (60). The position of the Néel point of the diselenide appeared (25) to be sensitive to the magnetic field, changing from 12 to 8.5 K as the magnetic field increases from 10 to 15 kOe. In a magnetic field below 10 kOe no change of the Néel point was observed. It is seen from Fig. 16 that the temperature dependence of the magnetization of α-US$_2$ shows a diffuse maximum in the temperature region 10–35 K, which can originate from a magnetic order of antiferromagnetic type. However, no λ-type anomaly was observed in the measurements of the low-temperature specific heat (33).

For U$_7$Te$_{12}$, each magnetization vs temperature curve presented in Fig. 17 showed a maximum below the field intensity of 30 kOe characteristic for the ferromagnetic uranium compounds with high anisotropy. Above 30 kOe the maximum disappears. The Curie point is equal to 73 K. As mentioned above, Westrum and Grønvold (33) have estimated the magnetic entropy of both α-dichalcogenides. For α-USe$_2$ they have obtained 0.19 cal mole^{-1} K^{-1}, while for α-US$_2$ a λ-type anomaly has not been observed. According to their opinion, this small value obtained for α-USe$_2$ indicates that only a fraction of the uranium atoms, i.e., those with antiprismatic coordination are involved in the exchange interactions. However, another ex-

planation is also possible. Recently, Grunzweig-Genossar (61) derived an equation for calculating the magnetic entropy of a singlet-ground-state system, and determined graphically its dependence on the ratio X of the separation δ between the ground and first excited level to the temperature $T_{C, N}$ of the magnetic transition, for the excited level of the 2-, 3- and 4-fold degeneracy. A similar procedure was applied by Suski, Czopnik, and Mydlarz (25) for the singlet as the first excited level. It follows from these works that a magnetic entropy equal to 0.19 cal mole^{-1} K^{-1} can also be obtained for the six coordinated uranium atoms for $T_N = 13$ K, assuming $\delta \sim 56$ K. The latter value is equal to that given in (33) for US$_{1.9}$. Concerning α-US$_2$, the lack of a λ-type anomaly does not exclude in our opinion (25) the possibility of magnetic order, because for $T_{C, N} \approx 20$ K and $\delta \sim 140$ K the magnetic entropy value is as yet well below the experimental finding. A similar behavior was observed for praseodymium metal where a thermal anomaly in the heat capacity occurs (62), but instead of the relatively sharp λ-type excess connected with the breakdown of magnetic order it is very broad, extending over about 190 K.

5. Conclusion

Although the experimental and theoretical results discussed in this paper are significant in revealing the magnetic properties of uranium dichalcogenides, their full explanation requires clearly more sophisticated experiments using, for example, inelastic neutron scattering or heat capacity measurements in a magnetic field.

FIG. 17. The magnetization of U$_7$Te$_{12}$ as function of temperature (27).

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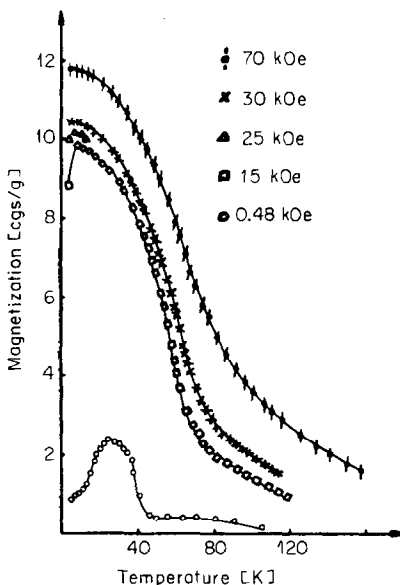
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