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Magnetic Properties of Mixed Uranium and 3d Element Chalcogenides of the MU_8X_{17} Type

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Magnetic susceptibility measurements in the temperature range 4.2–300°K for the MU_8X_{17} type chalcogenides, where M is a 3*d* transition metal or Mg, and X = S or Se, were carried out. For comparison, the magnetic properties of UTe_2 are also given. Almost all the mixed uranium and 3*d*-transition element chalcogenides are induced-antiferromagnets, as indicated from the occurrence of the susceptibility maxima on the χ vs. T curves and large negative values of the paramagnetic Curie temperatures. The influence of the 3*d*-transition metals on setting up the magnetic order in the MU_8X_{17}-type compounds is discussed.

Introduction

The existence of mixed uranium and 3*d*-transition element sulphides and selenides with the general formula of MUX_3, MU_2X_5 and MU_8X_{17}, where M is a 3*d*-transition element, and X = S or Se, were recognized some years ago (*1–3*). Up to now the magnetic properties for only some MUX_3-type compounds have been reported (*4, 5*). All these magnetic studies indicate that such mixed chalcogenides show rather unusual magnetic properties especially in high magnetic fields. In addition, complex magnetic structures for $CrUS_3$ (*4*) and FeU_2S_5 (*6*) have been reported.

In this paper, we present the results obtained from magnetic susceptibility measurements made on a wide class of sulphides and selenides with the chemical formula MU_8X_{17}, where M includes all the 3*d*-transition elements as well as Mg. All of them crystallize in the monoclinic system (space group C2/m), with the lattice parameters being very close to each other (*2, 3*). The crystal structure is of the new type CrU_8S_{17} (*7*).

Experimental

The compounds were synthesized in a similar way to that reported previously (*1–3*), by heating the starting materials UX_2, M and X in appropriate proportions in sealed silica tubes from 800 to 1200°C.

Magnetic susceptibility measurements were performed over the temperature region 4.2–300°K by the Faraday method using an RH Cahn Electrobalance (*8*). An applied continuous recorder output allowed all the details on the susceptibility versus temperature curves to be observed. The measurements at room temperature and liquid helium temperature were made in several

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values of magnetic field strengths, up to 7 koe. A weak field dependence (WFD) of the magnetic susceptibility taken at liquid helium temperature, probably due to some ferromagnetic impurities, particularly for the Fe- and Co-ternaries, was observed. The nature of such impurities is difficult to determine when both the complexity of the binary M-X and U-X systems are taken into account. For the magnetic properties of the latter, see ref. (*9–11*).

Results

Magnetic susceptibility data for the MU_8X_{17} type compounds, in the form of the χ^{-1} vs. T curves are shown in Figs. 1 to 8, and are summarized in Table I. Since two different magnetic atoms are present in the crystal lattice, except for MgU_8Se_{17}, the average effective magnetic moment per uranium atom $\langle\mu\rangle$, obtained fom the slope of a linear part of the χ^{-1} vs. T curves, consists of two contributions which can not be easily separated. Nevertheless, in order to have an idea of the magnitude of the paramagnetic moment of the uranium ion itself in such ternary compounds, we have applied some corrections by subtracting the theoretical "spin only" values for the $3d$-transition ions. As can be deduced from the chemical formula ($MX + 8\ MX_2$), the formal oxidation states of the $3d$-transition (or Mg) and U-ions are 2+ and 4+, respectively. Hence, the effective magnetic moment μ_U per uranium atom can be evaluated from the following expression:

$$\langle\mu\rangle^2 = 8/8\mu_U^2 + 1/8\mu_M^2$$

where 8/8 and 1/8 are the coefficients corresponding to the fraction of the U^{4+} and M^{2+} ions, respectively, in the crystal lattice per uranium atom.

The magnitudes of μ_U estimated this way for all the MU_8X_{17} chalcogenides investigated are listed in Table I in the last column.

Figure 1 displays the magnetic susceptibility data for UTe_2 and only for the selenide MgU_8Se_{17}, as the corresponding magnesium sulphide does not exist (*3*). As seen from the figure, the χ^{-1} vs. T plot for UTe_2, except for the lowest part where a slight positive (convexity) deviation from the straight line is observed, follows the Curie-Weiss law above 60 K, yielding the value μ_{eff} of 3.21 μB. This value is slightly higher than those previously reported (see refs. *10* and *11*). However, in contrast to the earlier data there is the levelling off the χ^{-1} vs. T plot for UTe_2 in the lower temperature region, clearly seen in Fig. 1 associated with a nonmagnetic ground

A strong positive deviation from the Curie–Weiss behaviour below about 60°K is also apparent for MgU_8Se_{17}. As Fig. 1 indicates, the reciprocal susceptibility, χ^{-1}, tends to zero with lowering temperature. No magnetic ordering was observed for this compound down to 4.2°K. Since the Mg^{2+} ions are diamagnetic the determined effective magnetic moment from the straight line part of the χ^{-1} vs. T dependence, being equal to 3.17 μB, is only due to the uranium ions. For both the compounds the paramagnetic Curie temperatures are negative and close to each other (about −65°K).

The deviation from the Curie–Weiss behaviour is also observed from the Ti-U-chalcogenides, as shown in Fig. 2, and occurs almost at the same temperature for the sulphide and selenide, i.e. about 60°K, but in a different way. If for the former the reciprocal magnetic susceptibility below this temperature decreases much slower, showing the tendency for leveling off, then for the latter this decreases much more steeply. As the inset of Fig. 2 illustrates, the magnetic susceptibility for the selenide goes through the maximum at about 5.5°K. This is not observed for the sulphide down to 4.2°K. The occurrence of the maximum in the case of TiU_8Se_{17} can indicate an antiferromagnetic ordering of the magnetic moments in

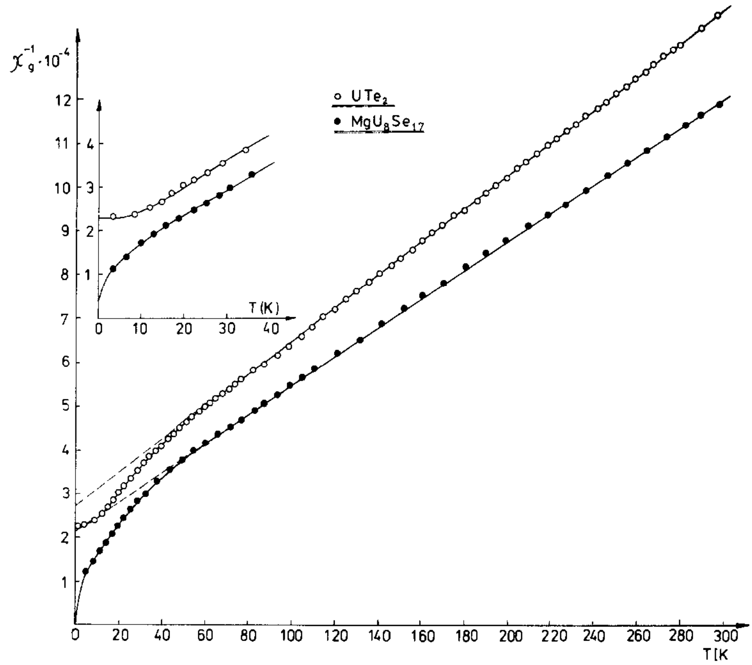

FIG. 1. Temperature dependence of the reciprocal susceptibility for UTe_2 and MgU_8Se_{17}. The inset shows the low temperature behavior of the reciprocal susceptibility for ○ UTe_2 and ● MgU_8Se_{17} on an expanded scale.

TABLE I

MAGNETIC CHARACTERISTICS OF THE MU_8X_{17} TYPE COMPOUNDS

Compounds	$\chi_g^{293} \cdot 10^6$	Field depend. at 4.2°K	θ_p (°K)	temp.* (°K) (above)	T_N (°K)	Effective magnetic moment (μB)		
						⟨μ⟩	μM	μU
UTe_2	7.25	NFD	−67	60	TIP	3.21	—	3.2
MgU_8Se_{17}	8.45	WFD	−65	60		3.17	—	3.2
TiU_8S_{17}	11.5	NFD	−65	60		3.20	2.83	3.0
TiU_8Se_{17}	9.11	NFD	−40	60	5.5	3.16	2.83	3.0
VU_8S_{17}	12.4	NFD	−110	150	19	3.54	3.87	3.2
VU_8Se_{17}	9.16	NFD	−70	160	31	3.31	3.87	3.0
CrU_8S_{17}	14.4	NFD	−30	80	27	3.41	4.90	3.0
CrU_8Se_{17}	11.3	NFD	−60	100	(60)	3.62	4.90	3.2
MnU_8S_{17}	15.1	NFD	−100	160	61	3.86	5.92	3.2
MnU_8Se_{17}	11.6	NFD	−100	110	74	3.88	5.92	3.3
FeU_8S_{17}	14.7	SFD	−80	100	47	3.70	4.90	3.3
FeU_8Se_{17}	11.4	WFD	−60	120	67	3.70	4.90	3.3
CoU_8S_{17}	14.9	WFD	−120	90	41	3.93	4.5	3.6
CoU_8Se_{17}	10.6	SFD	−95	80	30	3.69	4.5	3.3
NiU_8S_{17}	12.7	NFD	−105	130	(40)	3.53	2.83	3.4
NiU_8Se_{17}	9.07	NFD	−125	170	68	3.56	2.83	3.4

NFD, WFD and SFD mean no-, weak and strong field dependence.
* Curie–Weiss law

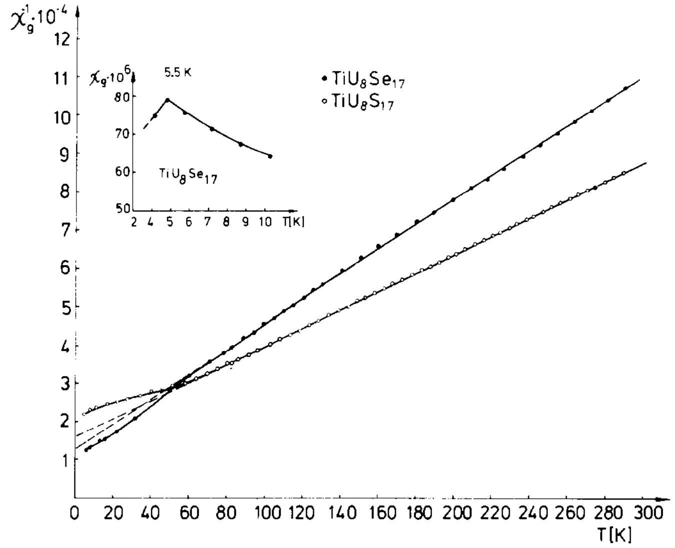

FIG. 2. Temperature dependence of the reciprocal susceptibility for ○ TiU_8S_{17} and ● TiU_8Se_{17}. The inset shows the low temperature behavior of the susceptibility for the selenide.

this compound. It is not excluded that for the sulphide such a maximum is shifted to the lower temperature region. The estimated values of μ_U in both ternaries are close to each other and amount to 3.0 μB.

The results obtained for the V-U-chalcogenides are presented in Fig. 3. As can be seen, the χ^{-1} vs. T curves deviate strongly from a straight line behaviour below about 150–160°K; these curves become very convex for selenide, and less-convex for sulphide against the temperature axis. Both these chalcogenides show probable antiferromagnetic transitions at 19°K for VU_8S_{17} and 31°K for VU_8Se_{17}. Unexpectedly, the values of μ_U for the sulphide is larger than for the selenide (3.2 and 3.0 μB respectively).

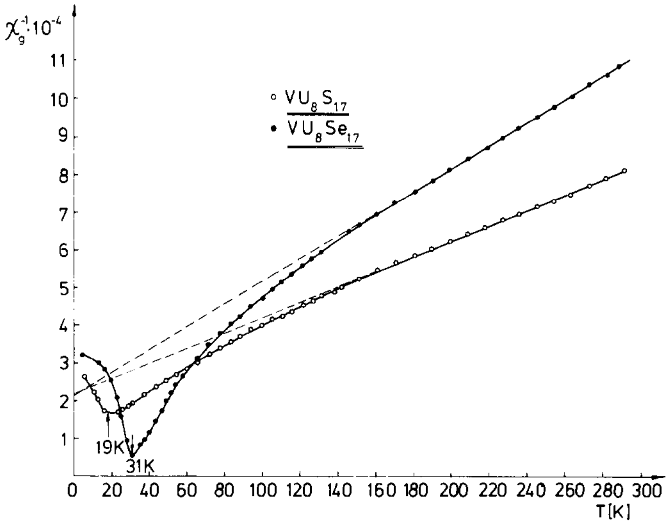

FIG. 3. Temperature dependence of the reciprocal susceptibility for ○ VU_8S_{17} and ● VU_8Se_{17}.

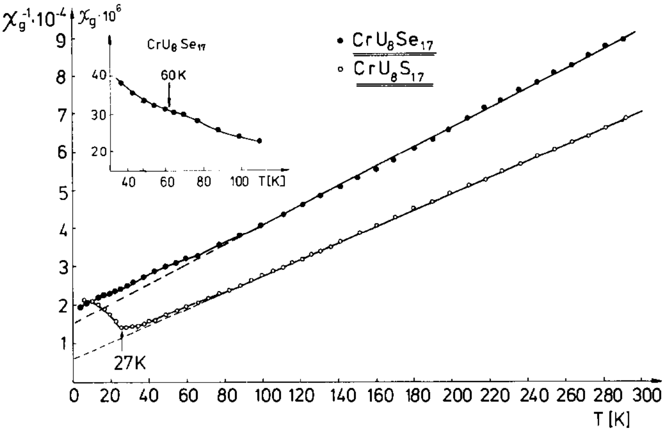

FIG. 4. Temperaure dependence of the reciprocal susceptibility for ○ CrU_8S_{17} and ● CrU_8Se_{17}. The inset shows the low temperature behavior of the susceptibility for the selenide

The thermal variation of the reciprocal susceptibility for the Cr-U-chalcogenides is displayed in Fig. 4. Again, the deviations from the Curie–Weiss behavior are observed below 80 and 190°K for the sulphide and selenide, respectively. However, if for CrU_8S_{17} there is a fairly well pronounced minimum in the χ^{-1} vs. T curve at 27°K, then for CrU_8Se_{17} only an inflection point at about 60°K is observed. This is seen more clearly in the inset of Fig. 4 where the susceptibility as a function of temperature for this selenide is plotted. Nevertheless it seems that both of them are antiferromagnetically ordered, as can be deduced from the fairly large negative values of the paramagnetic temperature θ_p. The low temperature upturn in the susceptibility of CrU_8Se_{17} suggests the existence of unaligned paramagnetic moments, probably of the Cr-ions, down to 4.2°K. The effective moments of uranium calculated for the sulphide and selenide in the temperature range where the Curie–Weiss law is held are 3.0 and 3.2 μB, respectively.

As in the cases described above, the susceptibility of the Mn-U-chalcogenides starts to obey the Curie-Weiss law in the higher temperature region, namely for the sulphide above 160°K, and for the selenide above 110°K. (Fig. 5). Below these temperatures, the χ^{-1} vs. T curves for these two chalcogenides deviate from the straight line behavior: upwards for MnU_8S_{17} and downwards for MnU_8Se_{17}. The observed minima in the temperature variation of χ^{-1} and the large negative values of θ_p (amounting to about −100°K) imply that both of them are antiferromagnetically ordered below 61 and 74°K, respectively.

However, the susceptibility of these two chalcogenides just after it's maximum, increases again with lowering temperature in a complex way. For MnU_8S_{17}, the low temperature upturn is very rapid below 35°K (see the inset of Fig. 5), but for MnU_8Se_{17} the susceptibility goes again through a very broad maximum at about 20°K. Measurements made for the latter compound have shown that the magnitude of the susceptibility maximum changed going from one sample to another and hence influences very strongly the positive deviation from the Curie–Weiss like behaviour below 110°K, probably due to a resultant effect of two contributions. However, no field dependence of χ was found for these two chalcogenides at 4.2°K indicating the lack of any

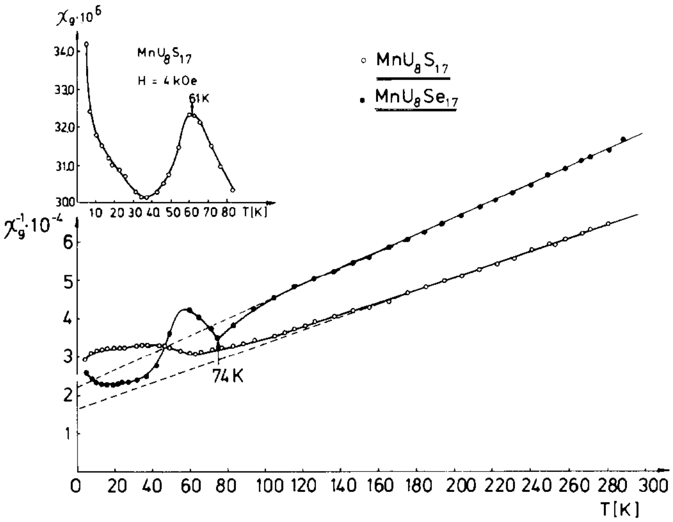

FIG. 5. Temperature dependence of the reciprocal susceptibility for ○ MnU_8S_{17} and ● MnU_8Se_{17}. The insets show the low temperature behavior of the susceptibilities for MnU_8S_{17} and MnU_8Se_{17}.

ferromagnetic impurities in the samples investigated. It seems however that at least for MnU_8S_{17}, the observed low temperature χ upturn suggests that not all the paramagnetic ions participate to the magnetic order.

In the paramagnetic state, the values of μ_{eff} for both these ternaries are almost the same and equal to about 3.3 μB. This value seems to be the best approximation of the paramagnetic moment of the U^{4+} ion because of the $^6S_{5/2}$ configuration of the Mn^{2+} ions ($3d^5$) in these mixed chalcogenides.

A similar magnetic behavior as that described above is exhibited also by the Fe-, Co-, and Ni-U-chalcogenides. Their

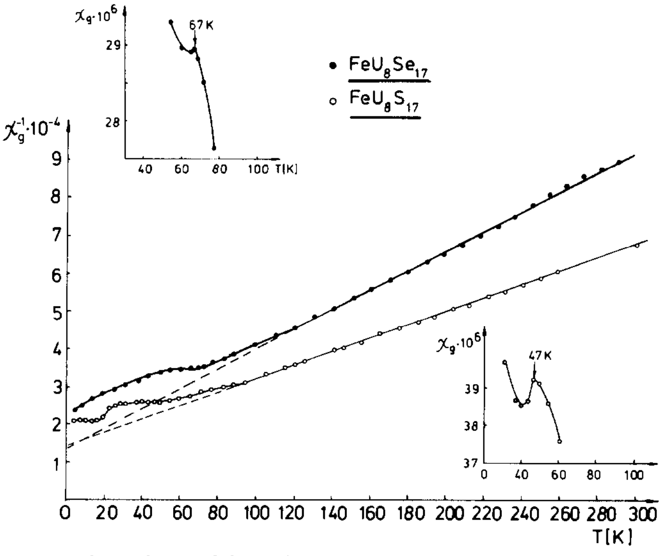

FIG. 6. Temperature dependence of the reciprocal susceptibility for ○ FeU_8S_{17} and ● FeU_8Se_{17}. The insets show the low temperature behavior of the susceptibility for the sulphide and selenide.

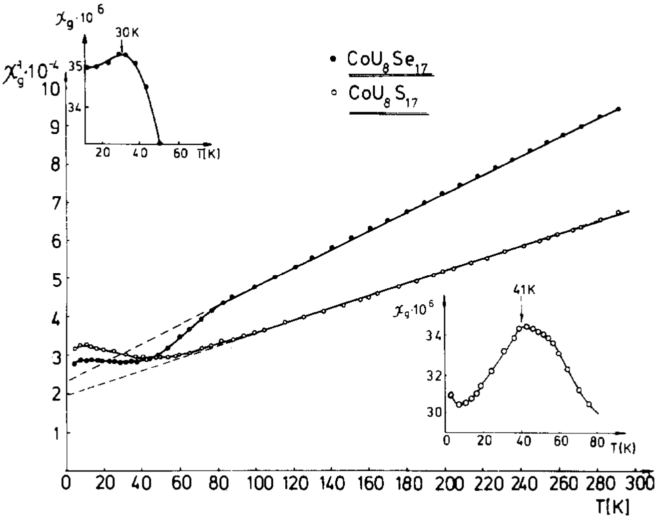

FIG. 7. Temperature dependence of the reciprocal susceptibility for ○ CoU_8S_{17} and ● CoU_8Se_{17}. The insets show the low temperature behavior of the susceptibility for the sulphide and selenide.

susceptibilities follow the Curie–Weiss relation only in the higher temperature region, as illustrated in Figs. 6 to 8. The experimentally obtained values of μ_U in this group of ternary chalcogenides are large and lie between 3.3–3.6 μB. However, the correct values of these moments may be a little different because of the orbital degeneracy of the 3*d*-transition ions which is not completely removed, particularly for the Co-U-chalcogenides. As an example, in Table 1, are shown the results of the U-moments for CoU_8S_{17} and CoU_8Se_{17} which have been calculated by taking into account the experimental value of $\mu_{Co^{2+}}$ being equal to 4.5 μB as cited in the literature.

All these six mixed chalcogenides seem to be magnetically ordered at low

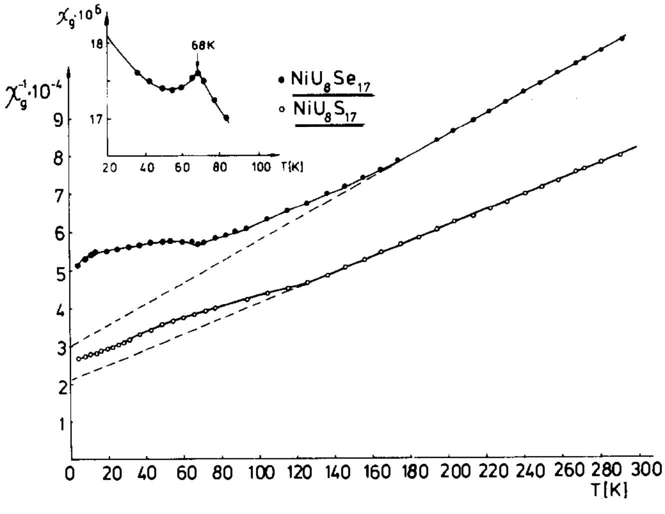

FIG. 8. Temperature dependence of the reciprocal susceptibility for ○ NiU_8S_{17} and ● NiU_8Se_{17}. The inset shows the low temperature behavior of the susceptibility for the selenide.

temperatures. The Néel temperature is difficult to determine due to the fact that the maxima in the susceptibilities are not sufficiently pronounced, and are rather obscured by the complex behavior of the χ^{-1} vs. T plots below T_N, as shown, for example, in the insets of Fig. 6. In addition for the Fe- and Co-U-chalcogenides, the magnetic susceptibilities at liquid helium temperature were field dependent, probably owing to the ferromagnetic impurities of unknown nature. Although this is not the case for the Ni-U chalcogenides; the magnetic susceptibility increases for NiU_8S_{17} below its maximum at 68°K (see the inset of Fig. 8), and for NiU_8Se_{17} below the inflection point at about 40°K. It seems, however, that both these ternary chalcogenides are antiferromagnetically ordered because of their large negative observed values of θ_p. The increase in the susceptibility after attaining a weakly pronounced maximum, found practically for all these six mixed chalcogenides, again supports the idea that not all of the paramagnetic moments are magnetically ordered down to 4.2°K.

Discussion

In view of the magnetic properties, the neighborhood of a magnetic ion play the key role. In the case of these ternary chalcogenides, there are two such ions in the crystal lattice, i.e. the 3*d*-transition and uranium ions.

1 Coordination Polyhedra

Previous accurate crystal structure determination made on a single crystal of CrU_8S_{17} (*7*) has shown that the 3*d*-transition atoms M lie in the *a*-, *b*-planes only. The nearest coordination of these ions was found to form an octahedron for which the two axial M-X distances are a little shorter with respect to the remaining M-X distances. In such a coordination having C_{2h} point symmetry, the M^{2+} ions are expected to exhibit the "spin only" values of the paramagnetic moment (or close to them). The octahedron is analogous to those in the MUX_3 and FeU_2X_5 chalcogenides but in contrast to the latter compounds, the octahedron is well isolated, having no common edge with the others. Hence, the distances M-M are relatively large and are approximately equal to 7.9 Å for sulphides and 8.3 Å for selenides.

The Uranium atoms, in the CrU_8S_{17} type crystal structure occupy three non equivalent positons. All these atoms, labeled U(1), U(2) and U(3), are in the ratio 8 : 4 : 4 in the unit cell respectively and are eight-fold coordinated, as shown in Fig. 9, which represents a part of the CrU_8S_{17} crystal lattice down the *b* axis.

U(1) is located at the center of the bicapped very irregular trigonal prism, as illustrated in an idealized form in Fig. 2 of ref. *7*. Here, for the sake of clarity, the coordination polyhedron around U(1) shown in Fig. 9 is displayed as a octaverticon, which is an intermediate form between a dodecahedron and antiprism having the tetragonal D_{2d} and the axial D_{4d} point symmetries, respectively. According to the Lippard and Russ approach (*12*), this octaverticon is rather closer to a dodecahedron as the calculated dihedral angle between the best least squares planes through the two sets of four atoms, constituting the two trapezoids, is equal to 88.2°.

A similar coordination polyhedron is also characteristic of a number of uranium chalcogenides of which some are given in Table II. For the sake of comparison, in Table II, the structural and magnetic characteristics are given for the listed compounds.

The environment around U(2) and U(3) is very similar to each other and can be related to a dodecahedron, which in an idealized form has the tetragonal D_{2d} symmetry. It is interesting to note that although the two trapezoids constituting the octaverticon (Fig. 9) are perpendicular to each other (dihedral angle $\alpha = 90°$), the central U-atom does not

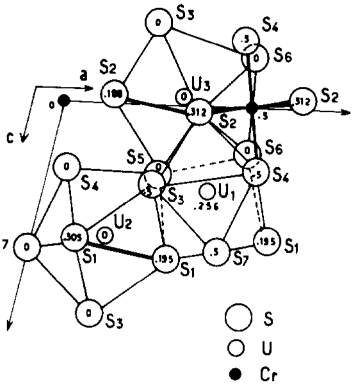

FIG. 9. A part of the view of the CrU_8S_{17} type crystal cell down the *b* axis. The U(1)-, U(2)- and U(3)-octaverticons are presented.

lie on their intersection line (see also Fig. 3 in ref. *7*), as this is required for the idealized form (*12*). The U(2) atom is slightly shifted outside the intersection line but still lying on one of the trapezoids. In consequence, the point symmetry is lower than that for the idealized dodecahedron. Nevertheless, even for the latter dodecahedron, which can be represented, for example, by UCl_4 (*13*) or some U(IV) complexes (*14*), a nonmagnetic crystal field state has been recognized on the basis of the occurrence of the temperature independent paramagnetism (TIP) at low temperatures, and confirmed by the point charge crystal field calculations (*14*, *15*).

2. Paramagnetic State

The very approximate values of the paramagnetic moment of uranium, as deduced from the experimental results, range between 3.0 and 3.6 μB (Table 1). They are close to those reported for several tetravalent uranium compounds (*10*) (*13*), the susceptibilities of which being generally interpreted on the assumption of a localized $5f^2$ electronic structure of U^{4+} ion, and strong crystal field interactions. To a first approximation justified below, similar arguments may be applied in the present study.

The low symmetry of the U(1), U(2) and U(3) coordination polyhedra, being not higher than C_1, removes completely the ninefold degenerated $^3H_4$ ground term of the $5f^2$ electronic configuration and gives rise to a nonmagnetic singlet as a ground crystal field state. Since the excited levels are also singlets, we deal here with the high frequency terms χ_{hf} only in the Van Vleck expression written below:

$$\chi_{hf}(T) = \frac{A + B\exp(-\delta_1/T) + C\exp(-\delta_2/T) + \cdots}{1 + \exp(-\delta_1/T) + \exp(-\delta_2/T) + \cdots}$$

where δ_1 is the energy gaps (in K) between the ground and excited singlets, and A, B, $C, \ldots$ coefficients are the resultant high frequency terms of the paramagnetic susceptibility.

However, it turned out that out of all the compounds investigated in this work, only for UTe_2 the observed TIP at low temperatures supports the conclusion that one of the singlets is a ground state in this uranium di-telluride. At higher temperatures, the Boltzman factors associated with the excited states become appreciable and hence, the temperature dependence of the paramagnetic susceptibility is observed, according to the expression presented above. Since the curvature of the χ^{-1} vs. T dependence is observed for MgU_8Se_{17} down to 4.2°K, it seems that in this case the ground state of uranium is composed of a set of close lying singlets and TIP is expected to appear at still lower temperatures. For the remaining chalcogenides here, the singlet state behavior is obscured by setting up of the magnetic ordering at higher temperatures, as discussed below.

In order to study χ_{hf} as a function of temperature, the composition of the wavefunctions as well as their energies are needed. At present, any estimation of these is completely impossible because as many as 27 crystal field parameters in such a low

TABLE II

STRUCTURAL AND MAGNETIC CHARACTERISTICS OF SOME URANIUM CHALCOGENIDES WITH EIGHTFOLD COORDINATION

Compounds	Symmetry space group	Z	Fraction 8-fold coordination	Separation (Å)									
				M-U*	M-M*	U-U*	U-X	Réf.	θ_p (°K)	$T_{N/C}$ (°K)	μ_{eff}/μ_s (μB)	Volume (Å^3/U-at.)	Réf.
U_3S_5	Orthorhombic Pnam	4	2/3			4.1	2.80	13	−15	12/?	3.1/0.5	59	9
U_3Se_5	Orthorhombic Pnam	4	2/3			4.2	3.05	14	~0	16/?	3.1/0.5	67	9
FeU_2S_5	Monoclinic C2/c	4	1	3.4	4.7	4.1	2.83	15	−190	25/250	3.6/1.0	81	6
$CrUS_3$	Orthorhombic Pnam	4	1	3.5	4.4	4.3	2.85	9	−165	—/110	2.7/0.9	97	4
CrU_8S_{17}	Monoclinic C2/m	2	1	3.9	7.9	4.1	2.83	7	−30	27/—	3.4/—	71	this paper
U_7Te_{12}	Hexagonal $P6_3/m$	1	6/7			3.9	3.22	16	~0	24/110	3.1/1.5	83	11
UTe_2	Orthorhombic	4	1			3.8	3.17	17	−67	TIP	3.2/—	90	this paper, 11

symmetry electrical potential are required to be determined. In general, the curvatures of the temperature dependences of the reciprocal paramagnetic susceptibility, as observed for all the compounds considered here, are due to the thermal population of low lying crystal field states. The convex or concave behavior of the χ^{-1} vs. T plots with respect to the temperature axis, which can be deduced from the χ_{hf} formula given above, arises from the resultant effect of either positive or negative contributions of the B, C, . . . terms. Furthermore, if the excited levels are not too high up in energy, as is probably the case for the compounds considered here, the curvature of the χ^{-1} vs. T graphs becomes successively linearly temperature dependent at higher temperatures, yielding the effective paramagnetic moment of uranium, which is usually close to the free-ion value.

3. Ordered State

The characteristic feature of the MU_8X_{17} chalcogenides as well as the compounds listed in Table II is the onset of the magnetic ordering at low temperatures.

The compounds such as: U_3X_5, FeU_2S_5, U_7Te_{12}, MUX_3 which are crystallographically related to the MU_8X_{17} ternaries as regard the U-U distances and the low point symmetry of the uranium sites, are all characterized by a weak ferromagnetic contribution and a constant high-field susceptibility, the latter reflecting the existence of a strong antiferromagnetic coupling.

It was found from neutron diffraction studies of the ternaries MUX_3 and FeU_2S_5 (*4, 6, 16*) that in both cases the 3*d* transition moments are antiferromagnetically ordered and the U moments form canted structures.

There is a substantial difference in the magnetic behavior of the MU_8X_{17} ternaries as their magnetic susceptibilities at liquid helium temperature are predominantly field independent indicating no ferromagnetic component in their magnetic structure.

At this point a question arises; which of the exchange interactions are the most important in the crystal type MU_8X_{17}, in setting up the antiferromagnetic coupling. It seems that in view of the large distances between M-M atoms, the antiferromagnetic coupling in these ternaries is due to the U moments. This conclusion is supported by the presence of uncoupled paramagnetic ions even at the lowest temperature investigated and by the fact that the U-U distances, e.g. for CrU_8S_{17} (*7*) of about 4.1 Å are comparable with those in the numerous magnetically ordered uranium compounds.

Another important result obtained from accurate neutron diffraction measurements is the evidence of an unusual axial delocalization of the uranium moment in $CrUS_3$ type compounds, besides a diffuse magnetic moment in the thorium vicinity in the isomorphous compound $CrThS_3$ (*16*). Such an unusual behavior has been interpreted as originating from a 6*d* contribution to magnetism, via hydridization with the 3*d* states of the transition metal (*16*). As similar features were not observed in FeU_2S_5 type compounds, the M-U distances (listed in table 1) do not provide a simple criterion on an hypothetical occurrence of moment delocalization; the concentration ratio $n = [M]/[U]$ is more indicative (*16*) and it follows that such a behavior is highly improbable in MU_8X_{17} type compounds, where the 3*d* element is rather "diluted".

Nevertheless it is evident that M-U exchange interactions play a crucial role in the onset of the U moment alignment:
The best illustration for this is a comparison of the magnetic behavior of MgU_8Se_{17} with that of MnU_8Se_{17}. In spite of the fact that the lattice dimensions of both compounds are quite the same, only the latter is magnetically ordered, exhibiting the highest Néel temperature in this 3*d*-transition uranium chalcogenide series. Similarly, taking into account the slight changes in the lattice parameters (*2*), the interatomic spacings and

in a first approximation, the exchange strengths, do not differ significantly within each series. So, the large variety in the magnetic properties observed for the mixed uranium-3*d* transition chalcogenides is mainly due to the influence of 3*d*-transition ion, so that we can not exclude completely the possibility of an antiferromagnetic alignment of 3*d*-transition ions by double superexchange process through the chalcogenide ions (M-X-X-M), the angle M-X-X being equal to 153°.

The influence of 3*d*-transition metal on the ordering temperature can be clearly seen from Fig. 10, where the Néel temperatures of both sulphides and selenides are plotted against a factor defined as the unit cell volume per uranium atom. This factor gives some idea about a magnetic moment dilution in the crystal lattice. As can be seen from this figure, the sulphides or selenides containing the 3*d*-transition metals lying in the perodic table before Mn constitute different T_N-dependences than those containing Mn and the metals beyond. If for the former compounds the T_N falls with increasing magnetic moment dilution according to the expectation, then for the latter compounds it changes in an opposite way; the ordering temperatures increase with increasing volume factor, attaining the highest T_N in the case of the Mn-U-chalcogenides, having simultaneously, in relation to the others, the largest lattice dimensions. Similarly, the selenides with the average volume factor of 82 Å^3/U-atom exhibit higher transition temperatures (except for CoU_8Se_{17}), than the corresponding sulphides for which this factor is equal to about 72 Å^3/U-atom. As for example in Table II, such factors for other uranium chalcogenides are also given. The importance of the U-M exchange interactions in forming the ordered state in the MU_8X_{17} ternaries is also evident by comparison with UTe_2. Although this compound is expected to show much better condition for setting up the magnetic ordering such as: the shorter U-U distances of about 3.8 Å and higher point symmetry of the U nearest surrounding (C_{2v}), it is only a Van Vleck paramagnet at low temperatures.

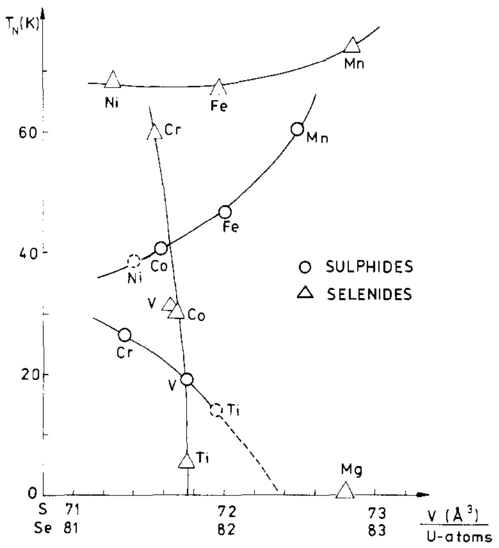

FIG. 10. The ordering temperature of the mixed uranium-3*d* elements chalcogenides as a function of the volume factor: ○ sulphides, ∇ selenides. The dashed points for Ti- and Ni-U-sulphides show the probable Néel temperatures.

Nevertheless, as the M-U(1), M-U(2) and M-U(3) distances differ markedly within each other (they are equal respectively to 3.91 Å, 4.27 Å and 4.97 Å in CrU_8S_{17}), it would be hazardous to present a hypothesis concerning the contribution of each uranium ion to the magnetic order.

Since for all these compounds discussed above the characteristic feature is probably an isolated singlet or a set of closely lying singlets as the ground system of the uranium ions, we deal here with so-called induced moment-ordering which in consequence can lead to complex magnetic structures.

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