

## New Ternary Molybdenum Chalcogenides $M_{1+x}Mo_6Se_8$ , with $M =$ Np, Pu, Am

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The ternary molybdenum selenides  $An_{1.0}Mo_6Se_8$  and  $An_{1.2}Mo_6Se_8$  ( $An =$  Np, Pu, Am) have been synthesized, and characterized by X-ray powder diffraction. They crystallize in the rhombohedral system and are isomorphous to the corresponding rare-earth compounds. The magnetic susceptibilities and electrical resistivities of the Pu- and Am-based compounds have been measured; the actinide ions are found to be trivalent in both compounds. No superconducting transition was found for  $Pu_{1+x}Mo_6Se_8$  and  $Am_{1+x}Mo_6Se_8$  down to 2.5 and 3.5 K respectively, contrary to the case of  $Np_{1+x}Mo_6Se_8$  for which  $T_c = 5.6$  K. The reasons of this different behavior are discussed.

### Introduction

Chevrel phases are ternary molybdenum chalcogenides of general formula  $M_{1+x}Mo_6X_8$ , where  $X$  stands for S or Se, while  $M$  stands for a metal which can be monovalent ( $Li^+$ ,  $Na^+$ ), divalent ( $Mg^{2+}$ ,  $Pb^{2+}$ ), trivalent (rare earth $^{3+}$ ), or tetravalent ( $Th^{4+}$ ,  $Sn^{4+}$ ) (1). All the rare-earth (RE) molybdenum sulfides and selenides are superconductors, except Ce and  $Eu_{1+x}Mo_6X_8$ , with, in most cases, critical temperatures higher in the selenides than in the sulfides (2). The reasons why the cerium compounds are not superconductors are not clear, but it is believed that the interactions between the  $4f$  electrons and conduction electrons are strong enough to destroy superconductivity (2); these interactions are thought to be much weaker in the other trivalent RE

compounds. In this context, it was interesting to study the behavior of the transuranium elements in ternary molybdenum selenides.

We report here the preparation and X-ray characterization of the three following ternary molybdenum selenides:  $Np_{1+x}Mo_6Se_8$ ,  $Pu_{1+x}Mo_6Se_8$ , and  $Am_{1+x}Mo_6Se_8$ , with  $x = 0.0$  and  $0.2$ , and the magnetic and electrical properties of the Pu- and Am-based compounds. The occurrence of superconductivity in the neptunium compound  $Np_{1+x}Mo_6Se_8$  has been recently reported in another paper (3).

### I. Experimental

The experimental techniques have been described in detail in Ref. (3), and will be recalled here only briefly.

(1) The samples were prepared by reacting the corresponding actinide diselenide (Am, Pu) or triselenide (Np) (4) with the appropriate amount of molybdenum and selenium powders. After a first heating step at 850°C, the so-formed products were pelletized and heated again in evacuated quartz tubes up to 1140°C, and held at this temperature for 24 hr. Two different compositions were achieved for each element:  $M_{1.0}\text{Mo}_6\text{Se}_8$  and  $M_{1.2}\text{Mo}_6\text{Se}_8$ , respectively ( $M = \text{Np, Pu, Am}$ ). The samples were synthesized starting with about 1 g of neptunium or plutonium and ~100 mg of americium. As indicated by spark mass analysis, the purities of the starting actinide metals were 99.8% for Np, 99.97% for Pu, and 99.5% for Am. The obtained products were analyzed by powder X-ray diffraction techniques using a 114.6-mm-diameter Norelco camera and  $\text{CuK}\alpha$  radiation.

(2) The magnetic susceptibility was measured by the Faraday method under low helium pressure. Temperature was measured with an iron-gold/chromel thermocouple, which had been calibrated with a certified carbon resistance. The distance between the sample and the thermocouple was about 2 mm.

(3) The electrical resistivity measurements were performed using the four-points method on 3-mm-diameter cold-pressed pellets which were stuck in sealed copper containers with a glue of high thermal conductivity. This technique has been developed by A. Blaise (5). Temperature was measured with a certified carbon sensor attached to the sample holder; this allowed us to take into account as completely as possible the self-heating effects due to the radioactive nature of the  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  isotopes used in this study (see discussion of these effects in Ref. (6)).

(4) Pumping over the helium bath allowed to obtain nominally (on the temperature sensors): 2.5 K in the magnetic susceptibility apparatus and 3 K in the electrical resistivity apparatus.

## II. X-Ray Results

The X-ray powder patterns of all the obtained samples are quite similar, in line positions as well as in their intensities. With the exception of a few weak lines, all the diffraction lines could be indexed in the rhombohedral-hexagonal system. For example, we show in Table I the rhombohedral indexation of the  $\text{Np}_{1.2}\text{Mo}_6\text{Se}_8$  spectrum. Only two very weak nonindexed lines are found at  $2\theta = 24.80$  and  $48.46^\circ$ . The comparison of observed intensities with those calculated using the  $\text{PbMo}_6\text{S}_8$  atom coordinates (7) gives qualitative agreement.

The lattice parameters ( $a_R - \alpha_R$  in the rhombohedral system, and  $a_H - c_H$  in the equivalent hexagonal system) were refined with a computer program (8) in which the Nelson-Riley extrapolation function was included. They are presented in Table II.

In the Chevrel phases  $M\text{Mo}_6\text{Se}_8$ , the structure consists ideally of  $\text{Mo}_6\text{Se}_8$  clusters surrounding the metal  $M$  sites. The cations  $M$  themselves are considered to be surrounded by eight selenium ions in a quasi-cubic symmetry. In such a structure, the lattice parameters are not very sensitive to the size of the metal  $M$ . In the case of the actinides  $An$ , neptunium, plutonium and americium have so close ionic radii (9) that, within the experimental errors, no systematic trend can be deduced from the lattice parameters of their compounds  $An_{1+x}\text{Mo}_6\text{Se}_8$ .

## III. Magnetic Susceptibility Results

### 1. $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$

As mentioned in the Introduction, the magnetic susceptibility measurements on  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$ , which show a diamagnetic transition around 6 K, have been presented in another paper (3).

### 2. $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$

The inverse molar susceptibilities of  $\text{Pu}_{1.0}\text{Mo}_6\text{Se}_8$  and  $\text{Pu}_{1.2}\text{Mo}_6\text{Se}_8$  are shown on

Fig. 1. The samples were found to be paramagnetic in all the studied temperature range (2.5–300 K) with no field dependence of the susceptibility. Superconductivity and/or long-range magnetic order were not detected down to 2.5 K by this experiment. The  $1/\chi$  curves show both a strong negative curvature. In the low-temperature range from 2.5 to 30 K, a Curie-Weiss law  $\chi =$

$C/(T - \Theta_p)$  is followed with  $\Theta_p = 0 (\pm 1 \text{ K})$ ,  $C = 0.091$  and  $0.111 \text{ emu cgs/mole}$  for  $\text{Pu}_{1.0}\text{Mo}_6\text{Se}_8$  and  $\text{Pu}_{1.2}\text{Mo}_6\text{Se}_8$ , respectively. This corresponds to the same plutonium effective moment in the two compounds:  $p = 0.85 \pm 0.05 \mu_B/\text{Pu atom}$ . Such a low moment suggests a +3 oxidation state of the Pu ion. The fact that the susceptibility followed a Curie law when pumping  $\chi$  over

TABLE I  
OBSERVED X-RAY ( $\text{CuK}\alpha$ ) DIFFRACTION ANGLES AND INTENSITIES FOR  $\text{Np}_{1.2}\text{Mo}_6\text{Se}_8$ . COMPARISON WITH CALCULATED DIFFRACTED ANGLES WITH  $a_R = 6.754 (3) \text{ \AA}$  AND  $\alpha_R = 88.93 (4)^\circ$

<i>hkl</i>	$2\theta$ ( $^\circ$ )		Observed intensity	<i>hkl</i>	$2\theta$ ( $^\circ$ )		Observed intensity
	Observed	Calculated			Observed	Calculated	
100	13.31	13.36	MS	410			
110	18.58	18.66	M	014	56.07	56.12	VW
$\bar{1}10$	18.97	19.00	M	$41\bar{1}$			
111				$\bar{1}14$	58.30	58.22	M
$\bar{1}\bar{1}1$	23.09	23.20	VW	330	58.91	58.74	VW
?	24.80	—	VW	024			
200	26.86	26.64	VW	420	61.16	61.12	W
210				$42\bar{1}$			
012	29.52	29.60	M	$\bar{1}24$	63.40	63.18	VW
$\bar{2}10$				$\bar{3}32$			
012	30.02	30.04	M	233	65.25	65.51	W
211	32.17	32.21	W	430			
$\bar{2}11$	32.93	33.02	S	034	69.23	69.12	MS
220	37.47	37.55	W	134			
$\bar{2}20$	38.20	38.27	W	431	70.23	70.30	W
221	39.48	39.61	M	511	72.38	72.34	W
$22\bar{1}$				$\bar{3}33$			
300	40.14	40.29	W	$\bar{5}11$	73.84	73.49	W
$\bar{2}21$				520	76.42	76.64	W
122	40.73	40.63	S	440	79.84	79.75	VW
310				522			
013	42.28	42.32	M	441	80.85	80.82	VW
$\bar{3}10$				$44\bar{1}$	81.77	81.71	VW
013	42.81	42.80	VW	522			
$\bar{1}13$				441	82.93	83.04	VW
$31\bar{1}$	44.96	44.81	} S	$14\bar{4}$			
$\bar{3}11$	44.96	45.12		433			
222	45.82	45.91	VW	334	83.90	84.15	W
320				442	84.98	84.89	W
023	48.46	48.18	VW	532			
$\bar{3}20$				235	87.94	87.94	VW
023	49.43	49.28	VW	611	89.02	88.92	MW
$32\bar{1}$				$\bar{5}32$			
$\bar{1}23$	50.81	50.73	MW	235	90.68	90.68	W
$\bar{3}21$				444	101.66	102.01	MW
123	51.38	51.30	W	741			
?	52.96	—	VW	147	133.13	133.20	M

TABLE II

RHOMBOHEDRAL ( $a_R$  AND  $\alpha_R$ ) AND EQUIVALENT HEXAGONAL ( $a_H$  AND  $c_H$ ) LATTICE PARAMETERS OF THE TERNARY MOLYBDENUM CHALCOGENIDES  $Am_{1+x}Mo_6Se_8$ , AS DEDUCED FROM X-RAY POWDER DIFFRACTION SPECTRA (CuK $\alpha$  RADIATION)

Sample	$a_R$ (Å)	$\alpha_R$ (°)	$a_H$ (Å)	$c_H$ (Å)
Np <sub>1.0</sub> Mo <sub>6</sub> Se <sub>8</sub>	6.747(8)	88.90(8)	9.449(11)	11.907(14)
Np <sub>1.2</sub> Mo <sub>6</sub> Se <sub>8</sub>	6.754(3)	88.93(4)	9.462(5)	11.915(6)
Pu <sub>1.0</sub> Mo <sub>6</sub> Se <sub>8</sub>	6.759(5)	89.01(5)	9.476(10)	11.908(13)
Pu <sub>1.2</sub> Mo <sub>6</sub> Se <sub>8</sub>				
Sample 1	6.757(3)	89.02(3)	9.474(5)	11.902(6)
Sample 2	6.753(4)	89.04(4)	9.469(8)	11.891(10)
Am <sub>1.0</sub> Mo <sub>6</sub> Se <sub>8</sub>	6.747(4)	88.89(5)	9.449(8)	11.906(10)
Am <sub>1.2</sub> Mo <sub>6</sub> Se <sub>8</sub>				
Sample 1	6.749(4)	88.99(2)	9.460(8)	11.894(10)
Sample 2	6.747(4)	88.96(4)	9.455(8)	11.897(10)

the He bath, showed that the temperature of the sample was not significantly different of that given by the thermocouple.

Two main contributions may account for the curvature of  $1/\chi$  above 30 K:

—The diamagnetic susceptibilities of the ions Pu<sup>3+</sup>, 6Mo<sup>2+</sup> and 8Se<sup>2-</sup>, superposed to the Pauli susceptibility of conduction electrons. For LaMo<sub>6</sub>Se<sub>8</sub>, the susceptibility has

been measured to be  $\chi = (345 - 0.363 T) 10^{-6}$  emu cgs/mole (10) (the room temperature susceptibility of PuMo<sub>6</sub>Se<sub>8</sub> is 798  $10^{-6}$  emu cgs/mole).

—*Eventual crystal field effects.* We have first tried to fit  $\chi$  by the law  $\chi = \chi_0 + C/T$  using the low temperature Curie constants. The best fits are given in Fig. 1. They correspond to the formulae  $\chi = 504 10^{-6} + 0.091/T$  for Pu<sub>1.0</sub>Mo<sub>6</sub>Se<sub>8</sub> and  $\chi = 538 10^{-6} + 0.111/T$  for Pu<sub>1.2</sub>Mo<sub>6</sub>Se<sub>8</sub>. The fits are good up to 100 K and less above. The  $\chi_0$  terms are much larger than the LaMo<sub>6</sub>Se<sub>8</sub>  $\chi$  value. As La and Pu are both trivalent in these compounds with close lattice constants, the Pauli susceptibilities should be about the same (the difference between the La<sup>3+</sup> and Pu<sup>3+</sup> diamagnetic susceptibilities,  $10 \times 10^{-6}$  emu cgs/mole, can be neglected). Therefore, the  $\chi_0$  term in Pu<sub>1+x</sub>Mo<sub>6</sub>Se<sub>8</sub> contains also a Van Vleck contribution due to the low-lying excited states of the Pu ions. If this is the case, it is due to crystal field effects and the Pu effective moment  $p$  should increase with temperature. We have then calculated:

$$p(\mu_B/\text{Pu atom}) = \left[ \frac{3k_B T (\chi_{\text{PuMo}_6\text{Se}_8} - \chi_{\text{LaMo}_6\text{Se}_8})}{N} \right]^{1/2} \quad (1)$$

( $k_B$ , Boltzmann constant;  $N$ , Avogadro's number).

The thermal dependence of  $p(T)$  is shown on Fig. 2: it increases from 0.85  $\mu_B$  (in the low-temperature limit) to 1.12  $\mu_B$  at room temperature, approaching the free Pu<sup>3+</sup> effective moment (1.23  $\mu_B$ ).

### 3. Am<sub>1+x</sub>Mo<sub>6</sub>Se<sub>8</sub>

The molar magnetic susceptibility of Am<sub>1.0</sub>Mo<sub>6</sub>Se<sub>8</sub> measured at the maximum field (approximately 5 kOe), is shown on Fig. 3. The sample was found paramagnetic in all the studied temperature range: no magnetic ordering and/or superconductive transition were observed, even at low field.

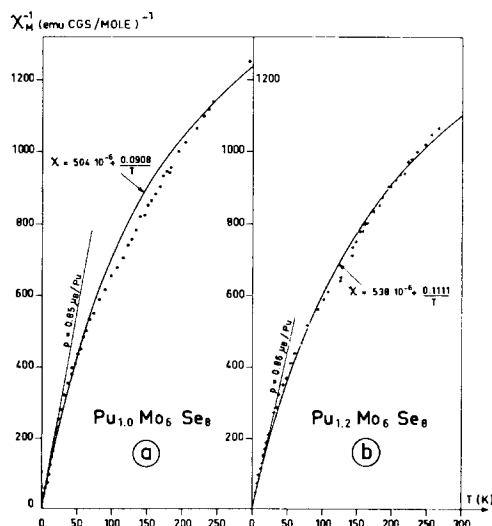


FIG. 1. Temperature dependence of the reciprocal molar susceptibility of Pu<sub>1.0</sub>Mo<sub>6</sub>Se<sub>8</sub> and Pu<sub>1.2</sub>Mo<sub>6</sub>Se<sub>8</sub>. Comparison with a fit in  $\chi = \chi_0 + C/T$ .

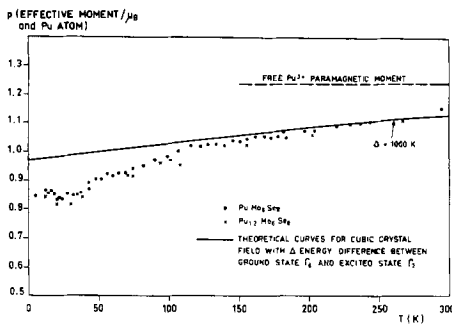


FIG. 2. Temperature dependence of the plutonium effective moment (in Bohr magnetons units) in  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$ . Comparison with a theoretical curve for  $\text{Pu}^{3+}$  with a cubic crystal field splitting of  $\Delta = 1000$  K between ground state  $\Gamma_8$  and excited state  $\Gamma_7$ .

The numerical value of  $\chi$  is rather low and weakly dependent of temperature between 150 and 300 K, but it shows a Curie-type contribution  $\chi_i$  below 150 K. This low-temperature term is approximately equal to  $10/T$  emu cgs/mole; it has probably to be attributed to strongly paramagnetic impurities, either  $\text{Cm}^{3+}$  or  $\text{Am}^{2+}$  (divalent americium in precipitates or in the neighborhood of impurities). An atomic concentration of  $2 \times 10^{-3}$   $\text{Cm}^{3+}$  or  $\text{Am}^{2+}$  ions (with a paramagnetic moment of  $7.9 \mu_B$ ) is consistent with

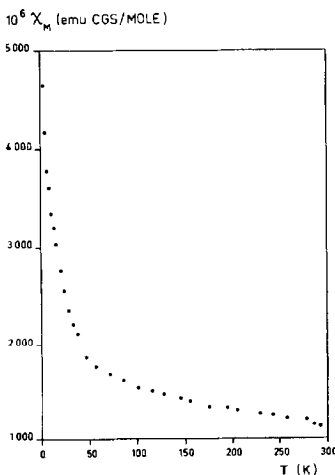


FIG. 3. Temperature dependence of the molar susceptibility of  $\text{Am}_{1.0}\text{Mo}_6\text{Se}_8$ , measured with an applied field of approximately 5 kOe.

the observed  $\chi_i$  values. By assuming that this low-temperature contribution follows a Curie law, the lowest temperature obtained is estimated to be 3.5 K (instead of 2.5 K given by the thermocouple).

The magnetic susceptibility of the sample showed a slight field dependence at all temperatures. This was corrected by the classical Honda-Owen extrapolation at infinite field  $H$  of  $\chi_{\text{apparent}} = \chi_{\text{corrected}} + B/H$  (11). Between 150 and 300 K, where the impurity Curie-type contribution  $\chi_i$  is negligible, the corrected molar magnetic susceptibility may be written:

$$\chi_{\text{AmMo}_6\text{Se}_8} = (1287 - 1.206 T) \times 10^{-6} \text{ emu cgs/mole.}$$

After subtracting the  $\chi_{\text{LaMo}_6\text{Se}_8}$  value (10) which is thought to correct for the diamagnetic and Pauli paramagnetic contributions as in  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$  (see above), one obtains the remaining contribution of the Am ions:  $(942 - 0.843 T) \times 10^{-6}$  emu cgs/mole, which suggests a trivalent state for Am, as will be discussed in Section V.1.

#### IV. Electrical Resistivity Results

To confirm the absence of superconductive transition inferred from the magnetic susceptibility results, the electrical resistances of the compounds  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$  and  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$  were measured from 3 to 300 K, as described in Section I.3. For both types of samples, the electrical resistances lie in the ohm range and are practically temperature independent. No transition was detected down to 3 K, confirming the magnetic susceptibility results.

#### V. Discussion

##### 1. The Trivalent State of Pu and Am in $(\text{Pu}, \text{Am})_{1+x}\text{Mo}_6\text{Se}_8$

(a)  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$ . If one takes into account the departure from Russel-Saunders cou-

pling due to the large spin-orbit interaction, the free  $\text{Pu}^{3+}$  ion effective moment is  $1.23 \mu_B$  in the ground state  $J = \frac{5}{2}$  (Landé factor  $g_J = 0.416$  (12) instead of 0.285 for R.S. coupling). Such a value is found in the plutonium halogenides  $\text{PuCl}_3$  and  $\text{PuF}_3$  (13). One sees in Fig. 2 that the effective moment  $p(T)$  approaches the free  $\text{Pu}^{3+}$  moment at room temperature. If we consider in first approximation that each  $\text{Pu}^{3+}$  ion is at the center of a cube of negative charges, the ground state of  $\text{Pu}^{3+}$  is a  $\Gamma_8$  quadruplet and the first excited state at an energy  $\Delta$  is a  $\Gamma_7$  doublet (14). If one treats the cubic crystal field as a perturbation on the free ion ground state  $J = \frac{5}{2}$ , the effective moment in Bohr magnetons per Pu atom is given by:

$$p^* = 0.269 \left[ \frac{32x(1 - e^{-1/x}) + 5e^{-1/x} + 26}{2 + e^{-1/x}} \right]^{1/2},$$

with  $x = \frac{k_B T}{\Delta}$ .

The calculated curve  $p^* = f(T)$  with  $\Delta = 1000$  K is shown on Fig. 2. The agreement with the effective moment  $p(T)$  deduced from experimental data by Eq. (1) of Section III.2 is rather good between 150 and 300 K. Below 150 K,  $p^*(T)$  is larger than  $p(T)$  and at 0 K,  $p^*(T) = 0.97 \mu_B$  (effective moment of  $\Gamma_8$ ) while the measured value is  $0.85 \mu_B$ .

The discrepancy may be due to:

—The small crystal field approximation which is known to be insufficient in the actinides (15). Here  $\Delta \approx 1000$  K which is not very small compared to the  $J = \frac{7}{2} - J = \frac{5}{2}$  difference of 4700 K ( $3268 \text{ cm}^{-1}$ ) (12).

—The splitting of  $\Gamma_8$  by the noncubic crystal field component due to a distortion of the selenium cube.

The latter effect has been observed in  $\text{CeMo}_6\text{Se}_8$  for which the magnetic susceptibility was also analyzed in terms of crystal field (10). It is reasonable to find in

$\text{PuMo}_6\text{Se}_8$  a  $\Gamma_8 - \Gamma_7$  crystal field splitting three times larger than in  $\text{CeMo}_6\text{Se}_8$ . The noncubic crystal field is of the order of 150 K in  $\text{PuMo}_6\text{Se}_8$  compared to 30 K in  $\text{CeMo}_6\text{Se}_8$ .

(b)  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$ . The americium ion contribution to the magnetic susceptibility of  $\text{AmMo}_6\text{Se}_8$ , determined in Section III.3, was  $(942 - 0.843 T) \times 10^{-6} \text{ emu cgs/mole}$ . This is in the range of the molar susceptibilities of trivalent americium compounds: Am metal ( $780 \times 10^{-6}$ ) (6), AmN ( $777 \times 10^{-6}$ ) (14),  $\text{AmRh}_2$  and  $\text{AmAl}_2$  ( $(1000 - 0.60 T) \times 10^{-6}$ ) (15),  $\text{AmRu}_2$  ( $(720 - 0.30 T) \times 10^{-6}$ ) (15) AmSb ( $1250 \times 10^{-6}$ ) (16), and is much weaker than the susceptibilities of  $\text{Am}^{4+}$  and  $\text{Am}^{2+}$  compounds.

$\text{Am}^{3+}$  is known to have a singlet ground state ( $J = 0$ ), whatever the local symmetry. For the free ion, the first excited state ( ${}^7F_1$ ) is a triplet at an energy  $2720 \text{ cm}^{-1}$  (17), and the calculated Van Vleck susceptibility at 0 K is  $764 \times 10^{-6} \text{ emu cgs/mole}$ , quite near the AmN and Am metal values. The Am contribution to the susceptibility of  $\text{AmMo}_6\text{Se}_8$  is somewhat larger. However, Dunlap *et al.* (16) showed that crystal field effects, when treated in the  $J$ -mixing formalism with the order of magnitude that one expects in actinide compounds, can explain the higher value of the susceptibility found in some trivalent Am compounds such as AmSb (for this compound their fit corresponds to crystal field parameters  $A_4 \langle r^4 \rangle = 2315 \text{ cm}^{-1}$ ,  $A_6 \langle r^6 \rangle = 500 \text{ cm}^{-1}$ ). With the  $A_4 \langle r^4 \rangle$  value ( $772 \text{ cm}^{-1}$ ) deduced for  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$  (see above), one may infer a 0 K value of the  $\text{Am}^{3+}$  susceptibility of  $\approx 900 \times 10^{-6} \text{ emu cgs/mole}$ , in reasonable agreement with the value of  $942 \times 10^{-6} \text{ emu cgs/mole}$  estimated for  $\text{AmMo}_6\text{Se}_8$ .

(c) *Conclusion.* The analysis of the magnetic susceptibility of  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$  (3), supported by recent  $^{237}\text{Np}$  Mössbauer isomer shift measurements in this compound (18), had led to similar conclusions: the assignment of a 3+ oxidation state for

neptunium, with an important noncubic component to the crystal field.

In conclusion, the actinide ions are found primarily trivalent in the three Chevrel phases  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$ ,  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$ , and  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$ , whatever the composition ( $x = 0.0$  or  $0.2$ ); the crystal field splitting ( $\sim 0.1$  eV) is one order of magnitude larger than in isomorphous rare-earth compounds  $\text{REMo}_6\text{Se}_8$ , and presents a noncubic component.

## 2. The Occurrence of Superconductivity in the Actinide-Based Chevrel Phases

Taking into account the trivalent state of Np, Pu, and Am in their corresponding Chevrel phases  $\text{An}_{1+x}\text{Mo}_6\text{Se}_8$ , it is surprising to find  $T_c = 5.6$  K for  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$  (3), while the hypothetical  $T_c$  is  $< 2.5$  and  $3.5$  K for  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$  and  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$ , respectively. Indeed, in the corresponding trivalent rare-earth compounds  $\text{RE}_{1+x}\text{Mo}_6\text{Se}_8$ ,  $T_c$  decreases slowly from  $11.2$  K for La to  $8$  K for Nd,  $6.5$  K for Sm and  $5.4$  K for Gd (19). The fact that  $T_c$  is smaller than  $0.05$  K in  $\text{EuMo}_6\text{Se}_8$  is not understood, but it is likely connected to the primarily divalent state of Eu in this compound. Some part of the depression of  $T_c$  in the RE series can be explained by pair-breaking effects due to the exchange interaction between the conduction electrons and RE spins; for example, in  $\text{GdMo}_6\text{Se}_8$ , this effect is thought to have decreased  $T_c$ , from  $8.5$  K (value interpolated between those of  $\text{LaMo}_6\text{Se}_8$  and  $\text{LuMo}_6\text{Se}_8$ ) to the experimental value of  $5.4$  K (10).

As the lattice parameters are practically the same in RE and actinide Chevrel phases, two causes for lowering of  $T_c$  in  $\text{An}_{1+x}\text{Mo}_6\text{Se}_8$  compared to the corresponding trivalent RE values, may be involved:

—One is the larger mass of the actinide ion, which decreases many lattice vibration frequencies and the Debye temperature  $\Theta_D$ .

—The other is the larger exchange parameter between localized An electrons and

conduction electron spins, because of the spatial extent of the  $5f$  wavefunctions. (The same argument is generally used to discuss the absence of superconductivity in  $\text{CeMo}_6\text{X}_8$  (2, 10)).

It is clear that these two arguments cannot explain the dramatic decrease of  $T_c$  in the Pu and Am Chevrel phases compared to  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$ .

In our present state of knowledge, two explanations may be cited for this difference:

—Because of the large crystal field effects, the low-temperature actinide localized moments are generally smaller than in the corresponding RE, especially for  $5f$  shells with even occupation numbers; for example, in  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$  ( $5f^4$ ), the low-temperature behavior of the magnetic susceptibility suggests a singlet ground state (3); this might have favored the occurrence of superconductivity in this compound compared to  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$  in which the fundamental level is a Kramer's doublet; but it does not explain the case of  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$ .

—Another explanation is in terms of self-radiation damage effects, due to the strong  $\alpha$ -radioactivity of the  $^{239}\text{Pu}$  and (moreover) the  $^{241}\text{Am}$  isotopes. Indeed, fast-neutron radiation damage is known to decrease dramatically the critical temperature of Chevrel phase superconductors such as  $\text{PbMo}_6\text{S}_8$  and  $\text{SnMo}_6\text{S}_8$  (20). In our opinion, this is the main explanation for the disappearance of superconductivity in  $\text{Am}_{1+x}\text{Mo}_6\text{Se}_8$  ( $T_c < 3.5$  K) and it has to be checked by similar work using the  $^{243}\text{Am}$  isotope. In the case of  $\text{Pu}_{1+x}\text{Mo}_6\text{Se}_8$ , measurements on samples prepared with the less radioactive  $^{242}\text{Pu}$  isotope, would also allow to solve this problem.

A more complete understanding of the occurrence of superconductivity in actinide molybdenum ternary chalcogenides needs the study of uranium-, protactinium-, and thorium-based compounds. Preliminary studies on the ternary sulfides  $\text{ThMo}_6\text{S}_8$  and

UMo<sub>6</sub>S<sub>8</sub> have shown that they are not superconductors down to 1.5 K (21). But complications arise from the fact that certainly Th and perhaps U are tetravalent in these compounds.

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