Theory of magnetic properties of actinide compounds. II

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The electron-delocalization model of metallic actinide compounds proposed earlier by the present authors is used to interpret additional experimental data concerning the first-order magnetic-phase transitions of these materials. The model is shown to provide a quantitative explanation of the experimental sublattice magnetization, magnetic-phase change, and powder susceptibility of UAs as functions of temperature T. Predictions are made for the low-temperature electronic specific heat and the heats of transition of this compound. The complicated magnetic transitions observed to result from varying x and T in the solid solutions $UAs_{1-x}P_x$, $UP_{1-x}S_x$, and $UAs_{1-x}S_x$ are also theoretically explained. The dependence of the magnetic exchange interactions on the conduction-band occupation is deduced from the experimental data. The agreement between theory and experiment herein reported provides additional confirmation of the present theoretical model.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) we proposed a novel theory of the multiple first-order magnetic-phase transitions observed[2-4] in metallic actinide compounds. The theoretical model takes into account the overlap in energy of the localized $5f$ and the itinerant-electron $6d$-$7s$ band states, the Coulomb interaction between the band and the localized electrons, and the dependence of the magnetic-exchange interaction between ions upon the band occupation. An expression for the free energy or thermodynamic potential of the solid in terms of the occupation numbers of the band and of the magnetic sublevels of the localized states is derived in I. Minimizing this expression yields the temperature dependence of the sublattice magnetization and band occupation, which change discontinuously at certain temperatures. Using the unknown parameters of the band and of the interactions as fitting parameters, the experimental sublattice magnetization,[2] magnetic susceptibility,[5] electronic specific heat,[6] and heats of transition[6] of UP are quantitatively explained in I. The sublattice magnetization,[3] magnetic symmetry change,[3] and electrical resistivity[7] as functions of temperature of NpC are also theoretically explained. In this theory, the "moment-jump" transitions at $T' = 22.5\,^\circ$K in UP[2] and at $220\,^\circ$K in NpC[3] result from a partial delocalization of electrons with decreasing temperature; i.e., the time-averaged configuration of the actinide ion changes from $5f^n(6d\text{-}7s)^\ell$ to $5f^{n-1}(6d\text{-}7s)^{\ell+1}$ as T is lowered below $T = T'$.

In Sec. II of the present paper, the above theory will be applied to the compound UAs, for which the magnetization[4,8] and susceptibility data[9] shown in Fig. 1 are (except for the magnetic symmetry change at $T' \approx 63\,^\circ$K) very similar to what is observed for UP. Predictions are made for the low-temperature electronic specific heat and the heats of transition of UAs, which have not yet to our knowledge been experimentally determined.

The set of parameters obtained for UP in I and for UAs in the present paper permit a calculation in Sec. III of the magnetic-phase diagram (i.e., the most stable magnetic configurations) of $UAs_{1-x}P_x$[8] (see Fig. 2), as a function of temperature and relative composition x, assuming that the parameters of the band and of the interactions vary linearly with x. This provides an important test of the parametrization used in the theory of these two compounds.

The complicated magnetic symmetry changes experimentally induced by varying x and T in the solid solutions $UP_{1-x}S_x$[10-13] (Fig. 3) and $UAs_{1-x}S_x$[4,14] (Fig. 4) are discussed in Sec. IV and yield addi-

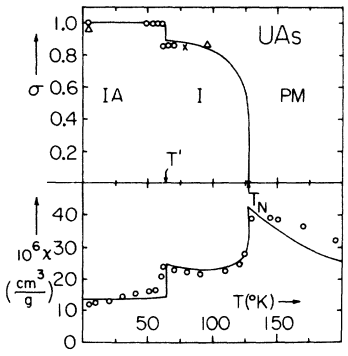

FIG. 1. Relative sublattice magnetization σ and magnetic-powder susceptibility χ of UAs. Top: circles—experiment of Ref. 4; triangles and × —experiments of Ref. 8; solid curve—present theory, $T' = (63 \pm 2)\,^\circ$K and $T_N = 127\,^\circ$K. The symbols IA and I refer to two types of antiferromagnetism (see Ref. 1), and PM is paramagnetism. Bottom: circles—experiment of Ref. 9; solid curve—present theory.

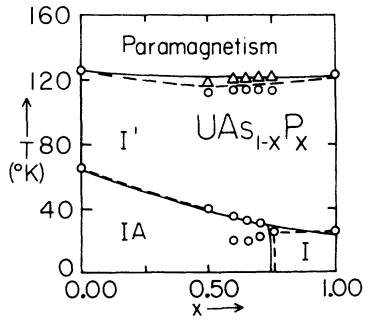

FIG. 2. Magnetic-phase diagram of $UAs_{1-x}P_x$ as a function of temperature T and composition x. Circles and triangles—experiments of Ref. 8, solid curve—present theory; I, IA are types of antiferromagnetic ordering; I' is "low moment" phase of type I.

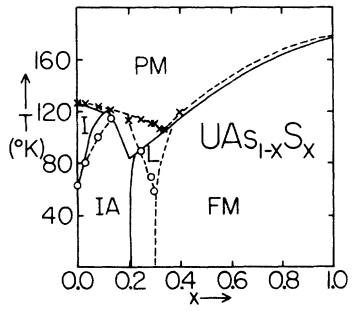

FIG. 4. Magnetic-phase diagram of $UAs_{1-x}S_x$ as a function of temperature T and composition x. Circles and × —experiment of Ref. 8; solid curves—present theory; I, IA, L are types of antiferromagnetic ordering; FM is ferromagnetism; PM is paramagnetism.

tional information concerning the strong dependence of the magnetic-exchange interactions on the conduction-band occupation.

II. THEORY OF URANIUM MONOARSENIDE (UAs)

Uranium monoarsenide has the NaCl-type lattice ($a_0 = 5.779$ Å),[4] is a fairly good conductor with a room-temperature resistivity of $\rho = 238\ \mu\Omega$ cm,[15] and becomes antiferromagnetically ordered below $T_N = 127°$K. Thus, it is a typical member of the class of metallic actinide compounds discussed in I and is especially similar to UP.

The sublattice magnetization from 0–90°K of UAs has been determined from several independent neutron-diffraction experiments,[4,8] and the data are shown in Fig. 1 (top).

At $T = 4.2°$K, the ordered moment per uranium ion is $(2.20 \pm 0.05)\mu_B$[8] or $(2.24 \pm 0.04)\mu_B$[4] and the type of magnetic structure is AFM-IA (antiferromagnetic type IA, i.e., adjacent layers of actinide ions have spin orientation up-up-down-down-···; see Fig. 1 of I). As T is increased, the ordered moment drops suddenly to $(1.92 \pm 0.04)\mu_B$ at $T' = (63 \pm 2)°$K [$T' = (66 \pm 1)°$K was found in Ref. 8] and the magnetic ordering transforms to AFM-I. A transition width of about 7°K was found,[4] which the experimenters were unwilling to ascribe to sample inhomogeneity or temperature differences across the sample. In the case of UP, the first neutron-diffraction results[16] also indicated a width of about 7°K for the "moment-jump" transition, but later the more accurate NMR measurements[2] showed that the transition is really discontinuous and that the high- and low-moment phases coexist over a temperature interval of only ~0.2°K. No NMR results on UAs have yet been reported. The absence of critical scattering[4] at the moment-jump transition of UAs and the steep jump in the magnetic susceptibility[9] (Fig. 1, bottom) also point to a first-order transition.

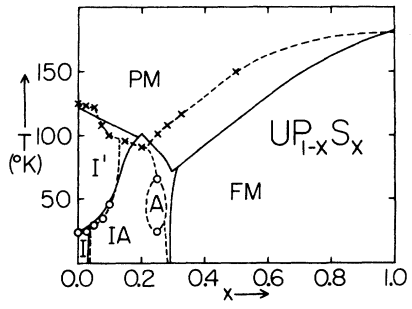

FIG. 3. Magnetic-phase diagram of $UP_{1-x}S_x$ as a function of temperature T and composition x. Circles and × —experiment of Ref. 10; solid curves—present theory; I, IA are types of antiferromagnetic ordering; I' is "low-moment" phase of type I; FM is ferromagnetism; PM is paramagnetism; A is antiphase magnetic structure (see text).

Data concerning the temperature dependence of the sublattice magnetization of UAs near $T_N = 127°$K are also lacking. From the fact that the ordered moment shows no detectable decrease between $T' = 63°$K and $T = 96°$K[4] and from the sudden jump in the susceptibility at $T = T_N$, one expects that for UAs (as for UP) the magnetization falls off quite rapidly as T approaches T_N. This effect has been experimentally observed in the case of $UAs_{0.68}S_{0.32}$.[4] The anomalous "flatness" of the sublattice magnetization vs T above and below $T = T'$, as discussed in I, indicates that elementary magnetic excitations of the effective field or spin wave types are practically absent and that a mechanism other than the entropy of magnetic disorder "drives" the transition at $T = T'$.

The striking similarities in the magnetic susceptibilities and magnetization curves of UP and UAs

indicate that the transitions at T' and T_N result from the same mechanism, even though the moment-jump in UAs occurs at a considerably higher temperature than that of UP and involves a change in the magnetic symmetry. These two differences have been cited[4] as indicating that the source of the transition in UAs is different from that of UP. It will be shown here that despite these differences, our model is capable of explaining the transformations in both compounds.

In estimating the theoretical parameters needed for a quantitative calculation in our model, we can be guided by our previous results for UP. The magnitude ($\approx 2.2\mu_B$) of the ordered moment per U ion in UAs for $T < T'$ and the size ($\approx 10\%$) of the moment jump are sufficiently similar to the corresponding quantities for UP that no changes in the ionic levels or in the parameter $r = \mu_0/\mu_1 = 0.89$ proposed in I are called for. Here μ_0 and μ_1 are the maximum magnetic moments of the crystal-field ground states of the $5f^3$ and $5f^2$ configurations, respectively. The effective mass m^* of the band electrons of UAs is expected to be high; the value $m^*/m \approx 4.0$ (where m is the free electronic mass) was suggested by the observed spin-disorder scattering at T_N.[15] As in the case of UP (see I), this is probably an underestimate. The experimental low-temperature electronic specific heat provides the best value for m^*, but the authors are not aware of such an experiment for UAs.

The number $w_0 = 1 + z$ of electrons per U ion in the band at $T = 0\,^\circ\mathrm{K}$ in the delocalized phase can be estimated from the requirement that the AFM-IA type of ordering be the most stable magnetic phase. In the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory (Fig. 5 of I) the AFM-IA phase never has the lowest magnetic-exchange energy $F_R(w_0)$; although it comes close to having the maximum exchange energy at $w_0 \approx 1.3$, where there is a minimum in $F_R(w_0)$. Kuznietz has shown[12] that when the finite mean free path of the conduction electrons is taken into account the AFM-IA ordering can be the most stable phase in a small interval of w_0 near $w_0 \cong 1.2$ between the regions of stability of the AFM-I and the ferromagnetic (FM) phases. This picture is supported by the experimental results for $UP_{1-x}S_x$ solid solutions (Fig. 3) where the AFM-IA ordering is observed in an interval of x between the AFM-I (near $x = 0$) and FM ($x \gtrsim 0.3$) phases. In our calculations, we use the value $w_0 = 1.2575$ (i.e., $z = 0.2575$), which is slightly larger than the $w_0 = 1.2$ previously derived for UP in I.

As for UP, the steepness of the magnetization curve of UAs near $T = T_N$ shows the need to take into account the dependence of the exchange $J(p)$ on the number $w = z + p$ of band electrons. Here p ($0 \le p \le 1$) denotes the time-averaged probability that an actinide ion has the configuration $5f^2(6d\text{-}7s)^{1+z}$, i.e., that a localized f electron has "jumped" to the itinerant-electron $6d$-$7s$ band. We write as before

$$J(p) = \begin{cases} J(0) + J'(0)p & \text{for } p \approx 0, \\ J(1) = J(0) & \text{for } p \approx 1, \end{cases} \tag{1}$$

taking advantage of the facts that p is small and increasing linearly with T above the localization temperature $T = T'$ and that $p \approx 1$ in the delocalized phase ($T < T'$). The remaining parameters are Δ, the energy required to localize a single electron in the bottom of the band when $p = 1$ and there is no magnetic ordering, and G, the short-range Coulomb repulsion (treated in the approximation of Falicov *et al.*[17,18]) between a localized f electron and a band electron in the same atomic (or Wigner-Seitz) cell. The quantities Δ and G can be estimated from the values used previously for UP and were varied slightly to give the transition at T' in UAs.

For the parameters listed in Table I, the theoretical sublattice magnetization is plotted as a function of temperature in Fig. 1 and compared to experiment. The change from the AFM-IA to the AFM-I type of magnetic ordering as T is raised through T' is consistent with our model, because at $T = T'$, w decreases from $w \approx 1.25$ to $w \approx 0.3$. The latter value lies in the same interval where in the theory of UP in I the exchange is assumed to favor the AFM-I state. In the calculation of the powder magnetic susceptibility χ of UAs there arises, as explained in I, the unknown function $J_{FM}(p)$, describing the p dependence of the ferromagnetic component of the magnetic exchange. This function is written for $T \le T_N$ as follows:

TABLE I. Theoretical parameters for UP, UAS, and US. The energies Δ, G, $J(0)$, and $J'(0)$ are expressed in units of ϵ_0, the Fermi level of the band when occupied by one electron per actinide ion. The corresponding values in eV are given in parentheses.

	UAs	UP	US
r	0.89	0.89	0.89
z	0.2575	0.2	0.7
m^*/m	6.6	8.4	9.7
Δ	1.2176 (0.524 eV)	1.166 (0.421 eV)	1.615 (0.515 eV)
G	0.4051 (0.174 eV)	0.4006 (0.145 eV)	0.44 (0.140 eV)
$J(0)$	0.05275 (0.0227 eV)	0.07 (0.025 eV)	0.075 (0.0239 eV)
$J'(0)$	−0.05125 (−0.0220 eV)	−0.08 (−0.029 eV)	0.17 (0.0542 eV)
	$z_1 = 0.215$	$z_2 = 0.346$	

$$J_{FM}(p)=\begin{cases}J_{FM}(0)+J'_{FM}(0)p+J''_{FM}(0)p^2 & \text{for } p\approx 0,\\ J_{FM}(1) & \text{for } p\approx 1.\end{cases} \quad (2)$$

In order to reduce the number of parameters being freely varied, the quantities $J_{FM}(0)$, $J'_{FM}(0)$, and $J''_{FM}(0)$ were set equal to the corresponding values (0.011, −0.126, and 0.255 eV, respectively) previously found for UP. The fit thereby obtained (Fig. 1, bottom) lends further support to the parametrization introduced in I. The jumps in χ at $T=T'$ and $T=T_N$ and the minimum at $T\approx 100\,^\circ$K are well explained by the theory. Less well explained are the slow linear increase of χ with T for $T<T'$ and the behavior of χ for $T>T_N$. The reason for the former discrepancy is unknown, but the latter can be explained as resulting from the neglect of short-range order and higher-lying crystal-field levels. In the calculation for $T>T_N$, J_{FM} is set equal to the constant value $\theta=32\,^\circ$K determined from an independent experiment.[15]

The predictions of the present model for the heats H_1 and H_2 of the transitions at $T=T'$ and $T=T_N$, respectively, and for the low-temperature band electronic-specific-heat coefficient γ are given in Table II and invite comparison to experiment. The behavior of the free energy, the entropy, and the band occupation as functions of T in the present model of UAs are very similar to the corresponding results for UP described in I. In particular, the entropy of thermally created holes in the localized phase remains the cause of the moment-jump transition at $T=T'_c$ in this theory of UAs.

III. THEORY OF UAs-UP SYSTEM

The compounds UAs and UP form solid solutions with each other.[8] The resulting materials, denoted by the formula $UAs_{1-x}P_x$ ($0\le x\le 1$) retain the NaCl lattice structure, the As and P ions being randomly distributed over the anion sublattice. The magnetic-phase diagram of $UAs_{1-x}P_x$ has been investigated by neutron diffraction and magnetic susceptibility experiments,[8] and the results are shown in Fig. 2. In the region from $x\approx 0.6$ to $x\approx 0.75$ the samples appear to have been inhomogeneous, as reflections characteristic of both the types AFM-I and AFM-I*A* magnetic phases are found below $T\approx 30\,^\circ$K. This effect, together with the small number of experimental points, leads to ambiguity in assigning the phase boundaries in some regions. The dashed lines in Fig. 2 are the authors' extrapolation of the data.

Inasmuch as the theoretical parameters for UP and UAs have been derived (see Table I), predictions can be made for the system $UAs_{1-x}P_x$ by assuming that the parameters to be used for each fixed x are given by interpolating between their values at $x=0$ (UAs) and $x=1$ (UP). In this way, our model of these two compounds can be put to an additional test.

Furthermore, information about the magnetic exchange can be deduced as follows. As x varies from $x=0$ to $x=1$ at $T=0\,^\circ$K (lower boundary of phase diagram), the number of conduction electrons $w_0(x)$ is given by $w_0(x)=1+z(x)$, assuming that the ground state remains the delocalized phase ($p=1$). We saw in I that the type of magnetic ordering of lowest exchange energy varies with w. If $z(x)$ is given by

$$z(x)=z(0)(1-x)+z(1)x, \quad (3)$$

the critical value z_1 of z (or of w_0) separating the AFM-I and AFM-I*A* phases can be found by substituting into Eq. (3) the experimental result for x_1, where one phase transforms to the other at $T=0\,^\circ$K. The sample inhomogeneity around $x=0.7$ obscures x_1 somewhat; the choice $x_1=0.74$ yields the result $z_1=0.215$ (see Fig. 5).

The lattice constant a and the effective mass m^* are also assumed to vary linearly with x:

$$a(x)=a(0)(1-x)+a(1)x, \quad (4)$$

$$m^*(x)=m^*(0)(1-x)+m^*(1)x. \quad (5)$$

Equation (4) is reasonably well verified experimentally.[8] However, energies which occur in the theo-

TABLE II. Low-temperature electronic specific-heat coefficient λ and heats H_1 and H_2 of the transitions at $T'=65\,^\circ$K and $T_N=127\,^\circ$K of UAs, as predicted by the theory of Table IA, column 1.

γ (cal/mole °K^2)	H_1 (cal/mole)	H_2 (cal/mole)
2.12×10^{-3}	20.2	71.0

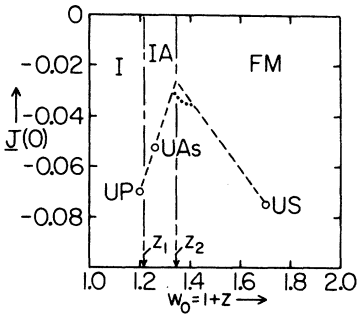

FIG. 5. Variation of the exchange interaction J(0) (dashed lines) with the number w_0 ($=1+z$) of band electrons per U ion at $T=0\,^\circ$K. The circles mark the w_0 and J(0) values deduced from the theory of UP, UAs, and US proposed here and in Ref. 1. The quantities z_1 and z_2 define the intervals of stability of the I and I*A* antiferromagnetic orderings and of the FM ferromagnetic ordering as shown. The dotted line suggests how J(0) is modified by the *L* phase occurring in the $UAs_{1-x}S_x$ phase diagram.

ry change in a more complicated way because of Eq. (4). For example, the Fermi energy ζ_0 of the band at $T = 0\,^\circ\mathrm{K}$ is given by

$$\zeta_0(x) = \epsilon_0(x)[z(x)+p]^{2/3}, \tag{6}$$

defining a characteristic band energy $\epsilon_0(x)$ (a constant for fixed x) as follows:

$$\epsilon_0(x) = \hbar^2[3\pi^2(N/V)^{2/3}[2m^*(x)]^{-1}$$
$$= \hbar^2(12\pi^2)^{2/3}[2m^*(x)a^2(x)]^{-1}. \tag{7}$$

The quantity $\epsilon_0(x)$ is the Fermi level of the band when occupied by N electrons. In the numerical program, which calculates the thermal behavior of the system for fixed x, all energies are measured with respect to $\epsilon_0(x)$; i.e., $\underline{\epsilon}_0(x) = 1$ in these units, where the underlining denotes an energy expressed in these units. In the calculations of the phase diagram of $UAs_{1-x}P_x$, the parameters $\underline{\Delta}$, $\underline{G}$, $\underline{J}$, $\underline{J}'$ are assumed to depend linearly on x; i.e.,

$$\underline{\Delta}(x) = \underline{\Delta}(0)(1-x) + \underline{\Delta}(1)x, \tag{8}$$

and analogous equations hold for $\underline{G}$, $\underline{J}$, and $\underline{J}'$. Other ways of specifying the x dependence of the parameters without introducing any new ones are possible, but only the above method produced reasonable results.

The results of the calculation (solid curves of Fig. 2) show that the theoretical models of UP and UAs can also be used to explain the variations of the transition temperatures and magnetic ordering as UAs is changed continuously into UP. Thus, important additional support for our model of actinide compounds has been found.

IV. THEORY OF UP-US AND UAs-US SYSTEMS

A. Uranium monosulfide (US)

The metallic actinide compound US forms solid solutions with UP and UAs [4,10–14] and Figs. 3 and 4 show that the corresponding magnetic-phase diagrams $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ are even more complicated than that of the $UAs_{1-x}P_x$ system treated in Sec. III. It is, therefore, highly desirable to apply the present model to US so that a calculation can be made for the UP-US and UAs-US systems.

Uranium monosulfide has the NaCl lattice ($a = 5.489$ Å) and is ferromagnetic (FM) with a Curie temperature of $T_C = 178\,^\circ\mathrm{K}$. [4] The magnetization curve as a function of temperature is reported to be a "normal" Brillouin-type curve, [10] but the corresponding data have not to our knowledge appeared in print. The magnetic moment at $T = 0\,^\circ\mathrm{K}$ is reported as $1.7\mu_B$. [19] This value is rather smaller than the $2.0\mu_B$ predicted for the triplet ground state of the $5f^2$ configuration assumed here (see I) and indicates either the influence of higher crystal-field levels or a moment reduction caused by hybridization. There is also a rhombohedral distortion in US of about 0.5% setting in below T_C and a strong anisotropy ($\approx 10^6$ G) with easy [111] axes. [19] The distortion is neglected in the present model. Note that since no first order moment-jump or localization transitions are observed in UAs, the parameter Δ must be chosen large enough that the model does not yield such a transition.

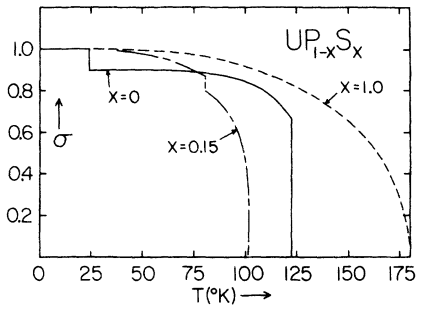

FIG. 6. Theoretical curves of reduced magnetic moment σ per U ion as a function of temperature T for three values of x corresponding to the calculation of the $UP_{1-x}S_x$ phase diagram shown in Fig. 3.

The effective mass has been estimated [15] from the spin-disorder resistivity to be $m^*/m \approx 10$, and galvanomagnetic measurements [20] indicate that conduction at $T = 0\,^\circ\mathrm{K}$ is by 0.45 holes per U ion. If the conduction band is s-like, one can interpret this result as implying $w_0 = 1.55$ (i.e., $z = 0.55$) electrons per U ion. The value $w_0 \approx 2.0$ (i.e., $z = 1.0$) has been proposed by Kuznietz and Grunzweig-Genossar. [15] Because there are very few data concerning US to be explained, the theoretical parameters are far from uniquely determined. Several sets of parameters consistent with the known properties of US were considered, and those listed in Table I (col. 3) provide the best fit to the UP-US and UAs-US systems discussed below. The theoretical magnetization curve for US is shown in Fig. 6. The ferromagnetic ordering of US is predicted by the RKKY model (see Fig. 5 of I) for the value of w_0 ($w_0 = 1.7$) listed in Table I. This is also consistent with the previous results for ferromagnetic NpC, for which in I we proposed $w_0 = 1.5 - 1.7$.

B. Magnetic interactions in the UP-US and UAs-US systems

Having now obtained a model for UP, UAs, and US, we can calculate the phase diagrams of the UP-US and UAs-US systems as was done in Sec. III for $UAs_{1-x}P_x$. Due to the greater complexity of the former materials, however, several difficulties arise. First, spin structures of small periodicity (i.e., long "repeat distance" in the lattice) are observed [4,10] in narrow intervals of x separating the AFM-IA and AFM-I phases in $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ (see Figs. 3 and 4). In Fig. 3, the region marked

A is an antiphase structure[21] consisting of ferromagnetic layers stacked in the sequence $5+$, $4-$, $5+$, $4-, \ldots$, where the symbols $+(-)$ denote that the moments of the associated layers point up (down) with respect to a given crystal axis. In Fig. 4, the region marked L represents a longitudinal-wave arrangement[4] which is not commensurate with the lattice, i.e., the magnitude of the moments varies from layer to layer in a sinusoidal form. The A and L phases are not taken into account in the RKKY calculations presented in I and indicate the complexity of the long-range magnetic exchange interactions in these materials.

A second problem arises from the variation of the magnetic exchange with w_0. In the case of $UAs_{1-x}P_x$ (Sec. III) a linear dependence of $\underline{J}$ on x was adequate, because UAs and UP are very similar and their theoretical parameters are not much different. However, as x is varied between $x=0$ and $x=1$ in $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ the parameters traverse a much larger range of values inasmuch as US is physically quite different from UP or UAs. In particular, $w_0(x)$ varies from $w_0(0)=1.2$ to $w_0(1)=1.7$ in $UP_{1-x}S_x$, in which region the absolute magnitude of the exchange interaction in the RKKY theory (Fig. 5 of I) first decreases in the AFM-I regime and then increases in the FM phase. This correlates well with the initial sharp decrease of the Néel temperature T_N (i.e., the AFM-I $\rightarrow$ FM transition temperature) as x is varied from $x=0$ in $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ and with the subsequent increase of T_C with x in the FM phase.

In order to take this into account, the exchange $\underline{J}$ is assumed to depend on x (or on z which depends linearly on x) like two linear segments intersecting at z_2, a critical value of z separating the regions of stability of the AFM-IA and FM phases. Note that the intervening L and A structures are neglected here. The equations for $\underline{J}$ are

$$\underline{J}(z)=\begin{cases}0.07-0.3(z-0.2) & \text{for } z\le z_2\\ \underline{J}(z_2)+[0.075-\underline{J}(z_2)/(0.7-z_2)] & \\ \quad\times(z-z_2) & \text{for } z\ge z_2.\end{cases} \tag{9}$$

The upper part of Eq. (9) is uniquely specified by the condition that $\underline{J}(z)$ pass through the points ($z=0.2$, $\underline{J}=0.07$) and ($z=0.2575$, $\underline{J}=0.05275$) previously derived for UP and UAs, respectively. The lower part of Eq. (9) is determined by requiring that $\underline{J}(z=0.7)=0.075$, the value derived for US, and that $\underline{J}(z)$ be continuous at $z=z_2$. Thus, the parametrization of Eq. (9) introduces only the one new unknown z_2. Figure 5 shows the relationship between z_1, z_2, and $\underline{J}(z)$.

In $UAs_{1-x}S_x$, the AFM-IA phase transforms to the FM phase at $x\approx 0.3$ at $T=0\,^\circ$K (Fig. 4). Using Eq. (3) with $z(0)=0.2575$ and $z(1)=0.7$, one finds $z_2=0.39$. In $UP_{1-x}S_x$ the critical value of x is hard to estimate because of the intervening A structure and because of the scarcity of data in this region, but it must lie in the interval $x=0.2$ to $x=0.3$. The corresponding interval for z_2, taking $z(0)=0.2$ and $z(1)=0.7$, is $z_2=0.3$ to $z_2=0.35$. Inasmuch as the value $z_2=0.39$ deduced for $UAs_{1-x}S_x$ lies outside this interval, one sees that the magnetic exchange in the UP-US and UAs-US systems is not a function of w_0 (or z) only but depends also on the particular anions involved. This may be due to short-range cation-anion-cation superexchange interactions competing with the long-range RKKY-type exchange.

Not desiring to introduce any more parameters into our model, we use the compromise value $z_2=0.346$ in the calculation of both phase diagrams shown in Figs. 3 and 4. The parameter z_1 separating the AFM-I and AFM-IA phases at $T=0\,^\circ$K is also needed for the calculation of $UP_{1-x}S_x$. Substituting the corresponding value of $x\approx 0.03$ determined from the data of Fig. 3 into Eq. (3) with $z(0)=0.2$ and $z(1)=0.7$, one finds $z_1=0.215$. This is the same result found in Sec. III from the analysis of $UAs_{1-x}P_x$ and thus supports the parametrization used there.

C. Calculation of magnetic-phase diagrams

The variation of the exchange $\underline{J}$ with z is given in Eq. (9) and the remaining parameters of $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ are assumed to depend on x according to the same interpolation introduced in Sec. III [see Eqs. (3)–(5) and (8)]. Considering first the $UP_{1-x}S_x$ phase diagram (Fig. 3), we see that the theory reproduces well the data for small x. The transitions AFM-I $\rightarrow$ AFM-I$'$ and AFM-IA $\rightarrow$ AFM-I with increasing temperature involve a sharp drop of about 10% in the ordered moment and a partial localization of electrons as in UP and UAs. The transition to paramagnetism (PM) is of the second order for larger x. Magnetization-vs-temperature curves for several values of x are shown in Fig. 6. The theory does not agree so well with experiment for intermediate values of x because of the ambiguity noted above in connection with the parameter z_2.

A new kind of transition is represented by the boundary between the AFM-IA and FM phases near $x\approx 0.3$. If x lies only slightly to the right of this boundary at $T=0\,^\circ$K, $z>z_2$, and the ground state is FM. As T increases, however, the occupation of the band $w=z+p$ slowly decreases from its maximum value $w_0=z+1$ at $T=0\,^\circ$K due to the continuous thermal decrease of p. Thus, w may cross over the critical value $w_2=1+z_2$ at which temperature there will be a transition to the AFM-IA phase. Since there is no discontinuity in p at this transition, no discontinuity in the ordered moment is predicted. A similar type of transition is found experimentally in $UP_{0.75}S_{0.25}$,[21] where there is observed a change from the A (antiphase) to the FM

structure with increasing temperature at $T \approx 70\,^{\circ}\mathrm{K}$ without any discernible discontinuity in the ordered magnetic moment.

The calculation of the $UAs_{1-x}S_x$ phase diagram (Fig. 4) results in good agreement with experiment for $x \lesssim 0.05$ and for $x \gtrsim 0.4$. Otherwise the quantitative agreement is not so good, principally because of the occurrence of the L phase, which results in T_N being larger than the calculated values in the interval $0.2 \leq x \leq 0.3$. The estimated exchange interaction in the L phase is sketched in Fig. 5, but no calculation involving this phase was attempted. The transitions at $T = T_N$ and on the AFM-IA – AFM-I phase boundary are of the first order in the theory for $x \lesssim 0.1$. For $x \gtrsim 0.1$, the transition to paramagnetism (PM) is of the second order.

V. DISCUSSION

The theory of UAs and the UP-UAs, UP-US, and UAs-US systems herein described lends additional support to the theoretical model of metallic actinide compounds proposed in Ref. 1 (I) by the present authors. In particular, the sublattice magnetization and susceptibility of UAs are explained using the same or similar theoretical parameters as were introduced in I to explain UP. The theoretical predictions made in Sec. II for the conduction electronic specific heat and heats of transition of UAs make possible an experimental test of the model. The analysis of the magnetic-phase diagrams in connection with the previous applications shows that the present theory is capable, in principle, of explaining the wide variety of observed phase transitions within the context of a single unified model. For example, the moment jump transitions, either with an associated change in magnetic symmetry (as in UAs and NpC) or without such a change (e.g., UP), steep or first-order transitions at T_N (e.g., UP, UAs), and changes in magnetic symmetry not involving a moment jump (e.g., $UP_{0.25}S_{0.75}$) are all accounted for in this model.

The qualitative agreement between theory and experiment of $UP_{1-x}S_x$ and $UAs_{1-x}S_x$ is imperfect for some intervals of x due to the great complexity of these materials but allows some important deductions about the magnetic-exchange interactions to be made. First, the variations of the magnitude of the exchange and of the most stable magnetic configuration with the number of conduction electrons w_0 at $T = 0\,^{\circ}\mathrm{K}$ are in approximate agreement with the RKKY theory except near $w_0 = 1.3$, where the AFM-IA and more complicated structures are observed. The critical values of w_0 separating the most stable magnetic phases have been estimated from the data. Also, short-range superexchange interactions appear to be present in these materials.

The theory could be improved by taking into account the mean free path of the band electrons, as suggested by Kuznietz.[12] Furthermore, the effects of the substitutional disorder of the anion sublattice of the solid solutions might be considered. Finally, recent experiments[22] show an additional phase boundary in the $UP_{1-x}S_x$ phase diagram separating the cubic FM from the rhombohedrally distorted FM phases near $x = 0.75$. Taking account of this distortion might improve the results shown in Fig. 3.

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