CALORIMETRIC STUDY ON THE ELECTRONIC STRUCTURE IN UP-US SYSTEM

HARUMI YOKOKAWA

National Chemical Laboratory for Industry, 2-19-19, Mita, Meguro, Tokyo, Japan

and

YOICHI TAKAHASHI

Department of Nuclear Engineering, University of Tokyo, 7-3-1, Hongo, Tokyo, Japan

(Received 7 September 1978; accepted in revised form 27 December 1978)

Abstract—The heat capacity of $UP_{1-x}S_x$ (x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) has been measured from 80 to 670 K by laser-flash calorimetry. All samples exhibit an anomaly corresponding to the magnetic transition. The magnetic transition temperatures determined are in good agreement with literature values. $UP_{0,x}S_{0.6}$ shows an additional small peak at 86 K below T_c . It has been derived that the US-rich ferromagnetically ordered state should be divided into two phases in terms of the direction of the moments. Above 250 K, the heat capacities of all samples increase monotonically with temperature and are well represented in the form of $C_p = 6R + AT - BT^{-2}$. The conduction band structure has been derived from the high-temperature linear term and has been compared with that in literature. It has been suggested that the magnetically ordering behavior such as the direction of the moments would be closely correlated with the band structure.

1. INTRODUCTION

The NaCl-type uranium semi-metallic compounds with Group Vb and VIb elements have been widely investigated in recent years, because the compounds exhibit strong similarities, and in some cases diversities, in their physical properties [1, 2]. Attempts to account for the magnetic and other properties have given rise to great controversy concerning the nature of the 5f electrons; that is, itinerant vs localized [2-4].

The thermal properties have provided important information on the electronic structure of these compounds. Firstly, the entropy changes associated with the magnetic transition have been found to be small, suggesting the probable effects of the crystal field on the localized 5f states [5, 6]. Correspondingly, the existence of the Schottky heat capacity[7] is suggested in the paramagnetic region. However, this type of anomaly has not been hitherto detected in an apparent manner despite several analyses on UP[8], US[5], UN[9] and $U_{1-x}Th_xS[6]$. Secondly, the large values of the electronic heat capacity coefficients [6, 10-12] lead to the suggestion that the narrow 5f bands[13] or the virtual bound 5f states [14] would contribute to the Fermi level, although no experimental evidence is shown to confirm the origin of the large γ being of 5f character.

In order further to clarify the electronic structure, it becomes of considerable interest to investigate the heat capacity over a wide temperature range, especially at high temperatures. Detailed analysis of the high-temperature heat capacity will make it possible to detect the Schottky heat capacity or to derive the electronic heat capacity coefficients in the paramagnetic state.

We reported previously on the heat capacity measurements of UP and the analysis on the basis of the localized model [8]. In the present study, measurements are extended over the series of the pseudobinary $UP_{1-x}S_x$ samples. The results are discussed with emphasis on the correlation between the thermal properties and the magnetically ordering behavior.

2. EXPERIMENTAL

(a) Materials

The samples used were sintered pellets of uranium monophosphide, monosulfide and their solid solutions. These were prepared by following methods: (1) UP: Uranium metal of 99.9% purity was hydrided at 550 K for 3 hr and subsequently dehydrided into metal powder. This was allowed to react with phosphorus at 570 K for 7 days in argon atmosphere and annealed at 900 K for 12 hr in vacuum. After being pressed, the pellets of UP were heated at 2200 K for 3 hr in vacuum. (2) US: The uranium hydride powder was allowed to react with H₂S at 900 K for 5 hr. Mixtures in proper amounts of the resulting US₂ and the uranium metal powders were pressed and heated at 1700 K for 2 hr in vacuum. The US pellets obtained were ground into powder. After being pressed, the pellets of US were again sintered in order to be homogenized at 2300 K for 3 hr in vacuum. (3) Solid solution samples were prepared by mixing UP and US powders in proper amounts in argon atmosphere, and the mixed powders were pressed into pellets and were heated in vacuum at 2100 K for 1 hr and then at 1920 K for 16 hr.

Seven samples of different compositions in the $UP_{1-x}S_x$ system were taken for heat-capacity measurements, that is, x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0. The size of samples was about 10 mm in diameter and 5 mm thick except 10 mm⁴ × 2.5 mm for UP_{0.4}S_{0.6} and 7 mm⁴ × 3 mm for US. These samples were supplied by the Central Research Laboratory, Mitsubishi Metal Co., Ltd. Chemical and spectroscopic analyses for the samples of UP and US were done by the Laboratory; the

(a)	Results o	f che	mical	analys	is	(in we	eight	per ce	ent)			
			U	Р		S		о	N	P/U	:	s/u
	UP	8	8.10	11.7	9			0.05	_	1.027		
	US	8	8.09			11.8	17	0.04	0.01		1	.002
(b)	Results o	f spe	ctros	copic a	nal	ysis (in p	pm)				
		Ca	Si	Al,Fe	Cu	v	в	Cr,Mo	Mq,Mn,Ni	Bi,Pb,Sn	Cd	Ag
	UP	25	16	14	11	11	4	3	2	1	0.3	0.2
	US	25	34	14	2	11	10	3	2	1	0.3	0.2

Table 1. Results of chemical and spectroscopic analyses for uranium monophosphide and monosulfide. (a) Results of chemical analysis (in weight per cent). (b) Results of spectroscopic analysis (in ppm)

results listed in Table 1 proved clearly that the both samples are satisfactorily freed from oxygen contaminations (about 0.04 wt%). Although nonmetal elements of sulfur and phosphorus might be expected to evaporate from the pellets during the sintering process in high vacuum and at high temperatures, the results also proved that essentially no significant change of chemical composition occurs during the heat treatment. The ratio of P/U obtained for UP, which is slightly deviated from the unity, might not mean that the present sample is hyperstoichiometric, but probably might be resulted from the insufficient precision in the chemical analysis. The results on UP and US lead to the expectation that also in the solid-solution samples for which no chemical analysis was done, changes of chemical compositions from the initial values for mixtures would be virtually small. X-Ray diffractometric analyses of the UP, US, and solid-solution samples confirmed the materials to be a single phase.

In order to obtain the consistent set of data throughout the series, the molecular weights adopted for the present samples were evaluated from the initial compositions for mixtures of UP and US, both of which were assumed to be stoichiometric.

(b) Procedure

Heat-capacity measurements were made with a laser flash calorimeter described elsewhere [15]. The inaccuracy in the measurements on α -alumina [15] and platinum [16] was confirmed to be within $\pm 0.8\%$ below 670 K.

The evaluated inaccuracy for the present samples by using available data of thermal diffusivity on $UP_{1-x}S_x[27]$ ranges from $\pm 0.8\%$ at 300 K to $\pm 1.2\%$ at 670 K. Above 300 K, measurements were made on the samples coated with a thin layer of graphite film, while below 300 K where the samples undergo the magnetic transition, an absorbing disk made of glassy carbon was used. Apiezon-N or silicone grease was used for thermal contact between the absorbing disk and the samples. Corrections for the glassy carbon [17] and the grease [18] were made using available data.

3. RESULTS

Smoothed heat-capacity values, listed in Table 2 at selected temperatures, were obtained by least-square

method from experimental values [19], except for the transition region where the values were obtained graphically.

(a) Uranium monosulfide

The present results on US from 80 to 670 K are shown as a function of temperature in Fig. 1. A λ -type anomaly associated with the ferromagnetic ordering was observed at 180 ± 0.5 K. The present results agree within ± 1% with those of Westrum *et al.*[11] by adiabatic calorimetry (1.5-350 K) throughout the overlapping temperature region. Both results for the maximum heat capacity value at T_c agree excellently with each other as well as for the values of T_c .

(b) Uranium monophosphide

The present results on UP from 80 to 670 K are also plotted against temperature in Fig. 1. These results agree well with those reported previously by the present authors; it is expected that the present results are more reliable than the previous ones, because the calibration of thermocouples was found to be partly insufficient at low temperatures in the previous measurements. A very sharp peak associated with the antiferromagnetic transition was observed at 120.8 ± 0.2 K, which agrees well with that of Counsell *et al.* [10], while the present maximum value of the heat capacity is quite higher than theirs. Above the Néel temperature, the heat capacity shows a usual monotonic increase with temperature.

(c) Solid solutions

The present results are shown in Figs. 2 and 3, together with those of UP and US for comparison. UP_{0.9}S_{0.1} and UP_{0.9}S_{0.2} exhibit a sharp peak at 95.5 and 84.5 K, respectively, and both samples shown an additional small anomaly near 121 K. The agreement of this temperature with the Néel temperature of UP suggests the existence of a small amount of non-homogenized UP. From the excess enthalpy around 121 K, the quantities of the contaminated UP are estimated to be about 0.21 and 0.23% for UP_{0.9}S_{0.1} and UP_{0.9}S_{0.2}, respectively. In the US-rich region, no such sign of the existence of non-homogenized US was observed. For UP_{0.4}S_{0.6}, an extra, small and broadened anomaly around 86 K was found in addition to that associated with the magnetic ordering.

Calorimetric stud	y on	the electronic	structure	ìn	UP-US system
-------------------	------	----------------	-----------	----	---------------------

x	0.0	0.1	0.2	0.4	0.6	0.8	1.0
T/K			c _p / .	JK ⁻¹ mo	1-1		
80	26.6	29.8	34.7	28.8	27.0	26.2	26.3
90	30.8	36.2	35.4	32.6	30.6	29.3	29.0
100	35 2	38 1	34 8	36.0	32 6	32.2	31.9
100	JJ.L	50.1	54.0	50.0	52.0	52.2	5117
110	41.3	37.9	36.2	39.6	35.6	35.2	34.9
120	130	39.1	37.2	43.0	38.8	38.5	37.9
130	41 34	38.96	38.43	45.9	41.8	41.7	41.2
140	41 66	40 10	39 65	41 38	45 7	45 1	44.8
150	42 30	41 11	40.82	41 63	49.7	49 1	49 0
150	42.50	41.11	40.02	41.03	47.0	42.1	45.0
160	43.05	42.16	41.91	42.23	45.7	54.3	53.8
170	43.83	43.14	42.92	42.97	43.2	62.5	61.1
180	44 58	44.03	43.84	43.75	43.34	46.9	87.0
100	45 28	44.05	44 68	44 52	44 11	45 82	47.8
200	45.20	14.04	44.00	46.36	44.90	45.02	46 80
200	43.74	47.70	43.44	43.20	44.00	43.74	40.00
210	46 54	46 24	46 15	45 94	45 43	46 24	47 00
220	47 09	46 84	46 79	46 57	45 99	46 63	47 29
220	47.00	40.04	40.75	47 15	45.50	40.05	47 63
230	47.30	47.30	47.37	47.13	40.50	47.00	49 00
240	40.04	4/.0/	47.91	40.00	40.90	47.51	40.00
230	40.40	40.33	40.41	40.1/	47.33	47.90	40.57
260	48 85	48 74	48 87	48.61	47.78	48.40	48.74
270	40.03	40 13	40.07	49 02	48 14	48 81	49 09
270	49.21	49.15	49.50	49.02	19 17	40.01	49.03
200	49.34	49.49	50 00	49.40	40.47	49.20	49.45
290	49.00	49.02	50.00	49.70	40.70	49.00	50.06
300	50.14	50.13	50.41	50.08	49.07	49.92	50.08
250	51 36	51 45	51 85	51 44	50 26	51 39	51 38
400	52 34	52 51	57 94	52 49	51 17	52.49	52.42
450	57 10	52.01	52.20	52 70	51 07	53 40	53 20
430	22.12	53.42	54 64	54 17	53.52	54 10	54 06
500	53.90	54.24	54.04	54.1/	52.33	24.13	54.00
550	54.68	55.06	55.31	54.90	55.10	54.91	34./8
600	55.36	55.73	55.93	55.60	53.61	55.60	55.4/
650	56.03	56.42	56.49	56.27	54.07	56.26	56.14
298.15	50.09	50.08	50.35	50.02	49.01	49.86	50.01
m							
	269.00	269.11	269.22	269.44	269.66	269.87	270.09
g mol ⁻¹							

Table 2. Smoothed heat capacity values of $UP_{1-x}S_x$ and molecular weights adopted



Fig. 1. Molar heat capacity of US and UP; open and closed circles represent the present results on US and UP, respectively. Literature values for US: ----, □, Westrum et al.[11]; ◆, Nakai et al.[20]; ---, Murabayashi et al.[21]; ----, MacLeod [23]; -----, Moser and Kruger [22]. For UP, comparison with literature values is given in Ref.[8]. The lattice contribution is also presented by the broken curve.



Fig. 2. Low temperature heat capacities of $UP_{1-x}S_{x}$ (a) Antiferromagnetic region. (b) Ferromagnetic region.



Fig. 3. High temperature heat capacities of $UP_{1-x}S_x$.

4. ANALYSIS OF THE HEAT CAPACITY

The heat capacity of $UP_{1-x}S_x$ can be separated into the following contributions: $C_p = C_1 + C_{el} + C_{mag}$, where C_1 is the lattice contribution at constant pressure, C_{el} is the heat capacity due to the conduction electrons, and C_{mag} is the magnetic heat capacity.

(a) Lattice contribution

Information on the lattice contribution in the NaCltype actinide compounds has been accumulated from neutron inelastic scattering experiment [24] and from heat-capacity analysis of the corresponding thorium compounds [5, 6, 11]. The general features of the lattice term can be summerized in terms of the characteristic temperature as follows: (1) The characteristic temperatures of the uranium compounds are about 10% higher than those of the corresponding thorium compounds and (2) the sulfides and phosphides of an actinide element have the values essentially of the same magnitude.

In this study, therefore, the lattice heat capacity for the UP-US system was estimated from the heat capacity of ThS in a manner similar to that used by Flotow *et* al.[5], by assuming the composition independence of the lattice term throughout the series. The estimated lattice term is presented in Fig. 1.

(b) Heat capacity anomaly and its relation with magnetic phase diagram

The magnetic heat capacity has been examined in the vicinity of the magnetic transition with emphasis on its correlation with the magnetically ordering properties. The transition temperatures were determined from the maximum point of the heat capacity anomaly. These are

in good agreement with those determined from the magnetic [25, 26] and electric [27] properties, as shown in Fig. 4. The excess heat capacity of $UP_{1-x}S_x$ in the region of heat capacity anomaly, obtained by subtracting the lattice contribution, is presented in Fig. 5.

The magnetic phase diagram in the UP-US system, which is shown in Fig. 4, has been extensively studied by neutron diffractometry [25] and by measurements of the magnetic susceptibility [26] and of other properties [27]. UP orders antiferromagnetically at about 121 K [28, 29] with the type I magnetic structure. Below the Néel temperature the magnetic moments are probably aligned along the [001] direction [30] and they change in magnitude abruptly at 23 K without change of the magnetic structure [31]. The stepwise replacement of phosphorus in UP with sulfur produces a rapid lowering of the Néel



Fig. 4. Magnetic phase diagram in the UP-US system. Open circles are the transition temperatures determined in the present study; △, Counsell et al. [10, 12]; +, Kuznietz et al. [25]. I and IA represent the antiferromagnetic structures of type I and IA, respectively. The ferromagnetic region is divided into two phases, Fa and Fb, in terms of the direction of the magnetic moments; in Fa, the moments are along the [111] direction, and along the [001] direction in Fb.

temperature and a gentle increasing of the moment-jump transition temperature. The magnetic structure transforms from the antiferromagnetic type I to the type Ia, and by further addition of sulfur new long-period magnetic structures appear sequentially in the intermediate composition region. Finally, the ferromagnetic structure appears at about 25% of US content. In the ferromagnetic region, the Curie temperature increases gently with increasing amount of sulfur. The magnetic moments in US below T_c are aligned along the [111] direction[32], inducing the large rhombohedral distortion[33].

The present results suggest the existence of a phase boundary in the ferromagnetic region as indicated in Fig. 4. The reasons are as follows: Firstly, UP0.4S0.6 exhibits an extra, small heat capacity anomaly at 86 K; this is consistent with the observation by Kamimoto et al. [27] that the corresponding change occurs in the shape of the electrical resistivity of UP0.4S0.6 at this temperature. Secondly, Counsell et al. [12] also observed a similar anomaly in UP_{0.25}S_{0.75} at about 45 K. Furthermore, the variation in the shape of the anomalous heat capacity around the Curie temperature is seen across the ferromagnetic region; the present results, together with those of Counsell et al. [12], show that the US-rich samples (x = 0.6, 0.75, 0.8, 1.0) exhibit a λ -type anomaly, whereas the other ferromagnetic samples (x = 0.4, 0.5) show an unusually humped anomaly, as shown in Figs. 2 and 5. The crystallographic investigations [34] on $UP_{1-x}S_x$ also revealed the variation in the ferromagnetic region. Allbutt et al. observed that UP0.25S0.75 exhibits rhombohedral distortion below the Curie temperature (173 K) as US does [33] and below 50 K it disappears suddenly. They observed furthermore that UP0.5S0.5 becomes ferromagnetic without distortion of the NaCl-type structure. These features of the crystallographic distortion are precisely correlated with those of the heat capacity. This leads, as indicated by Marple et al. [35], to the suggestion that the phase boundary determined above seems to correspond to the moment-rotation transition from the [111] direction in the US-rich phase to the [001] direction



Fig. 5. Excess heat capacities. (a) Excess heat capacities in the vicinity of the magnetically ordering temperatures. Three curves correspond to three different magnetic structures shown in Fig. 4. (b) The maximum heat capacities at $T_{c,n}$ included the results of Westrum *et al.*[11], \Box , and of Counsell *et al.*[10, 12], Δ . Solid symbols are the values after subtracting the lattice contribution.

in the other phase. It can be seen that the transition is not accompanied with the abrupt change in magnitude of the moments in view of the very small heat of transition observed.

On the other hand, UP exhibits a sharp increase of the heat capacity with approaching the Néel temperature; this is consistent with the sharp drop of the ordered magnetic moments[31] and NMR frequency[36]. When the amount of sulfur in $UP_{1-x}S_x$ is increased, the peak of the heat capacity at the Néel temperature decreases quite rapidly as presented in Fig. 5(a). Slight broadening of the anomaly with increasing sulfur content could be ascribed in part to the inhomogeniety of composition in the solid solution samples; similar effects due to the inhomogeniety were detected in other physical properties such as X-ray or neutron diffractometric traces and patterns [25]. Nevertheless, the shape of the anomaly remains still sharp as compared with that of the ferromagnetic transition. This sharpness suggests the corresponding sharp drop of the magnetic moment at the Néel temperature in the intermediate composition up to x = 0.2.

Differences in the features of the heat capacity between the ferromagnetic and the antiferromagnetic transitions can be also detected over a wide temperature range fairly below and above the transition. Figure 5(b) shows that the antiferromagnetic compounds have a small excess heat capacity below T_N and a large one above T_N , in contrast to the ferromagnetic compounds. This seems to correspond to the features of the electrical resistivity [27] that the antiferromagnetic compounds exhibit an unusual negative slope above the transition temperature. In the UP-rich region, therefore, the large fluctuation of the magnetic moments would stabilize the paramagnetic phase even at low temperatures, causing the magnetically ordering transition to be of first order.

(c) Analysis in the paramagnetic region

From the viewpoint of the itinerant model[3], the density of states at the Fermi level, obtained by band calculation, should be compared with the electronic heatcapacity coefficient in the parmagnetic region, γ_p , rather than that in the low temperature limit, since the density of states would be modified by the appearance of the new magnetic Brillioun zone corresponding to the long period magnetic structure, or since the electron mass would be enhanced at low temperatures through the many-body interactions [37-39]. On the other hand, from the viewpoint of the localized model [2, 4], analysis of the heat capacity should be made over a wide temperature range in order to detect the Schottky anomaly, because the crystal field [4] in the NaCl-type actinide compounds is recognized to be very strong as compared with the corresponding lanthanide compounds [40], in which the Schottky anomaly is usually detected below 300 K.

The high temperature heat capacity of $UP_{1-x}S_x$ is analyzed by examining the temperature dependence of C_1 , C_{e1} and C_{mag} , which are summerized as follows:

(1) The lattice entropy expression derived from the harmonic approximation is proven to be correct to the first order of the anhormonicity [41]. The lattice entropy is

then differentiated to give the lattice heat capacity at constant pressure;

$$C_1 = T\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_p = 6R\left[1 - \frac{1}{20}\left(\frac{\theta_{\mathrm{ee}}}{T}\right)^2\right] + A_p T, \qquad (1)$$

where the first term represents the usual harmonic contribution characterized in terms of the Debye temperature in the high temperature limit, θ_{∞} , and the second term is the combined contribution of dilation and explicit anharmonicity, resulting from the temperature dependence of the phonon frequencies at constant pressure.

(2) The heat capacity of the conduction electrons is expressed by:

$$C_{el} = \gamma_p T. \tag{2}$$

Here γ_p can be regarded to be independent of temperature as a first approximation.

(3) The magnetic heat capacity above the transition temperature can be represented by

$$C_{\rm mag} = aT^{-2} + bT^{-3} + \dots \tag{3}$$

The gross heat capacity at high temperatures, being combined all these contributions, can be represented as follows;

$$C_p = 6R + (A_p + \gamma_p)T - \left(\frac{6R}{20}\theta_{\infty}^2 - a_{mag}\right)T^{-2}.$$
 (4)

Rearranging the eqn (4), one can obtain

$$(C_p - 6R)T^{-1} = (A_p + \gamma_p) - (B_p - a_{mag})T^{-3}, \quad (5)$$



Fig. 6. High temperature heat capacities plotted as $(C_p - 6R)T^{-1}$ vs T^{-3} plot.

where $B_p = (6R/20)\theta_m^2$. When the heat capacity is plotted as $(C_p - 6R)T^{-1}$ vs T^{-3} , the slope provides the information on the Debye temperature and the magnetic term, and the intersection a combined term $(A_p + \gamma_p)$. Figure 6 shows the results of this plot for the heat capacities of $UP_{1-x}S_x$ together with that of ThS. It should be noted that all samples exhibit a linear relation in this plot including $UP_{0.4}S_{0.6}$ which has particularly small heat-capacity values in the paramagnetic region. Thus, the heat capacity of $UP_{1-x}S_x$ in the paramagnetic region, namely above 220 K, can be well represented as the sum of three terms:

$$C_{\rm P} = 6R + AT - BT^{-2}.$$
 (6)

A slight upward deviation in US in the low temperature region may be ascribed to the increasing magnetic term with approaching the Curie temperature, 180 K.

The lattice contribution to the linear and the T^{-2} terms, A_p and $B_{p'}$ can be estimated from the corresponding coefficients of ThS resulting in the values of $A_p = 2.7 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $B_p = 432 \text{ kJ mol}^{-1}$. Then the values of γ_p and a_{mag} are calculated by subtracting these lattice contributions and are presented in Table 3.

(d) Magnetic heat capacity in the paramagnetic region

The magnetic term arises from the energy of the interaction between the magnetic ions:

$$H = \sum_{ij} J_{ij} S_i S_j \tag{7}$$

where S_i is the localized moment at the atomic site 1.

One can thus obtain the magnetic term coefficient, a_{mag} , in the high temperature approximation as follows [42]:

$$a_{\text{mag}} = \sum_{ij} J_{ij}^2 \frac{[S(S+1)]^2}{3k_B}$$
$$= \frac{R}{6} \sum_{j} [(J_j k_B)^2 (g_J - 1)^4 [J(J+1)]^2] \qquad (8)$$

where k_B is the Boltzmann constant, R being the gas constant; the factor [S(S+1)] was replaced by $(g_J - 1)^2[J(J+1)]$, J and g_J being the total angular moment and its Lande factor. In the same approximation as eqn (8), one can also obtain the expression for the paramagnetic effective magnetic moment, μ_{eff} ;

$$\mu_{eff}/\mu_B \equiv P = g_J \sqrt{(J(J+1))}, \qquad (9)$$

where μ_B is the Bohr magneton.

In the UP-US system, the magnetic susceptibility measurements (25, 26, 34) established the Curie-Weiss' behavior in a wide temperature region throughout the series, and the present analysis successfully provided the magnetic T^{-2} term throughout the series. This makes it possible to evaluate the value of the exchange interaction, $\langle J \rangle = [\sum_{I} (J_{I}/k_{B})^{2}]^{1/2}$, by combining both results through eqns (8) and (9), although the total angular moment, J, in the UP-US system has not yet been established exactly because of the ambiguity in the valence state of the uranium ions in the solid solution. The evaluated values are given in Table 4; the results of Allbutt *et al.* [34] for μ_{em} were adopted by suitable interpolation, and the g_{J} was assumed to be 8/11, the weak-

Table 3. Results of the high temperature heat-capacity analysis on $UP_{1-x}S_x$: The coefficients A and B were obtained by fitting the experimental data to the form of $C_p = 6R + AT - BT^{-2}$

x	0.0	0.1	0.2	0.4	0.6	0.8	1.0
A / mJ K ⁻² mol ⁻¹	10.1	10.9	11.6	10.9	7.5	10.8	10.7
B / kJ K mol ⁻¹	248	267	270	279	279	285	271
$\gamma_p / mJ K^{-2} mol^{-1}$	7.4	8.2	8.9	8.2	4.8	8.1	8.0
a _{mag} / kJ K mol ⁻¹	184	165	162	153	153	147	161

Table 4. Physical properties in the UP-US system derived from the heat-capacity analysis

x	$\frac{\mu_{eff}(34)}{\mu_{B}}$	$\left(\frac{g_{J}^{-1}}{g_{J}}\right)^{2} = \frac{\langle J \rangle}{\kappa}^{(a)}$) _{<j></j>} (b) К	<u>т_{с, N}</u> к	< <u>J></u> ^T C,N	electrons eV ⁻¹ atom ⁻¹
0.0	3.19	35.8	254	120.8	2.10	3.1
0.1	3.10	35.9	255	95.6	2.67	3.5
0.2	2.95	39.5	279	84.2	3.31	3.8
0.4	2.78	43.0	306	131	2.34	3.4
0.6	2.68	46.3	329	156	2.11	2.0
0.8	2.48	53.8	383	170	2,25	3.4
1.0	2.25	67.4	479	130	2.66	3.4

(a) <J> is given in unit of Kelvin.

(b) This values were evaluated under the assumption of $q_1 = 8/11$.

crystal-field value for the 3+ valence state, throughout the series for convenience. This simple assumption on g_J seems to give rise to the uncertainty in magnitude on $\langle J \rangle$ by a factor of 2-10, because $\langle J \rangle$ is sensitive to g_J in the above derivation. Nevertheless, the derived values of $\langle J \rangle$ have nearly the same magnitude as the magnetically ordering temperature. This confirms reasonably the assumption in the present analysis that the excess T^{-2} term is of the magnetic origin.

The composition dependence in $\langle J \rangle$ is of quite interest in the light of the magnetically ordering properties. The value of $\langle J \rangle$ does not show the similar composition dependence to the magnetically ordering temperature, but increases monotonically with increasing sulfur content; an upward change in slope of the $\langle J \rangle$ vs x curve can be seen at about x = 0.6, where the magnetic moments in the order state rotate from the [001] to the [111] direction. Although the magnetically ordering temperature is depressed in the antiferromagnetic-ferromagnetic transition region, the quantity, $\langle J \rangle$, shows no significant change in that composition region. The difference between $T_{C,N}$ and $\langle J \rangle$ can become clearer when the value of $\langle J \rangle$ is reduced by $T_{C,N}$ throughout the series; the derived quantity, $\langle J \rangle / T_{C,N}$, has the maximum value at x = 0.2 and around x = 0.6, a broad bottom.

The difference in composition dependence between the quantity, $\langle J \rangle$, and the magnetically ordering temperature can be interpreted reasonably as follows; the value of $\langle J \rangle$ is related to the energy of the paramagnetic fluctuation of the moments corresponding to all possible magnetic structures, whereas the magnetically ordering temperature is a measure of the stabilized energy of one particular magnetic structure to be established at low temperatures. One can thus expect the depression of $T_{C,N}$ despite no drastic change of $\langle J \rangle$ in the intermediate composition region where the ferromagnetic and the antiferromagnetic interactions compete with each other. Furthermore, it seems to be reasonable that the composition dependence of $\langle J \rangle$ changes not in the composition region where the long range magnetic ordering changes, but in the region where the direction of the moments changes; the fluctuation of the moments can be regarded to be of short range fairly above the ordering temperature and its energy seems to depend rather on the direction around which the moments fluctuate.

(e) Electronic heat capacity in the paramagnetic region

The linear term after subtracting the anharmonic contribution can be considered to be due to the conduction electrons. Since the magnetic contribution due to the 5felectrons is assumed to be the T^{-2} term alone in the above estimation, the present estimates for γ_p give the value of upper limit in this calormetric determination. The corresponding density of states presented in Table 4 was derived under the assumption that any enhancement would not occur in the paramagnetic state. It is of quite interest to point out that the change in the slope of γ_p vs x curve closely corresponds to the change of the magnetically ordering properties from the antiferromagnetic to two ferromagnetic phases, in a similar manner to the value of $\langle J \rangle/T_{C,N}$. Especially, the composition dependence of $\gamma_{\rm p}$ in the UP-rich region, showing the initial increase to the maximum at x = 0.2 and the subsequential gentle decrease with increasing sulfur content, can be confirmed by the analytical results by Fradin [42]. He made analysis on the magnetic and the NMR properties of $UP_{1-x}S_x$ with the emphasis on the interaction between the conduction electrons and the magnetic ions, and derived the density of states with essentially the same composition dependence as the present one. It seems to be resonable that the magnitude, in addition to the composition dependence, of his results agrees roughly with the present ones, in spite that the magnitude of his values, ranging 1.6-2.4 electrons eV^{-1} atom⁻¹, is sensitive to the treatment for the 5f electron. The present electronic heat capacity coefficients determined in the paramagnetic region are lower throughout the series than those in the lowest temperature limit [10-12] and are only twice of those of ThS[5], leading to the expection that the derived density of states in this analysis would not contain virtually the 5f contribution.

On the other hand, the present density of states shows a good agreement with the band calculational results of Davis[3], ranging from 1.4 to 3.0 electrons eV^{-1} atom⁻¹. Although the band calculational results show the density of states near the Fermi level being essentially of the f-d like character, this agreement cannot seem to lead directly to the evidence of the itinerancy of the 5f electron. From the photoemission experiment on US, Eastman and Kuznietz[43] also derived the "optical" density of states, which has the same magnitude as the present one. However, care must be taken in comparing the two values. The "optical" density of states was derived to be of the higher l character, l being the orbital quantum number, whereas the present one is considered to be of the lower l character excluding the 5f states as mentioned above. In addition, the differences are in the excitation process of the electron system as well as the method of deriving the density of states.

5. **DISCUSSION**

(a) Band structure and its relation with magnetic structures

The UP-US system provides many interesting features of the magnetic properties such as the sequential change of the magnetic structure and the abrupt change in magnitude and direction of the moments. The present study on the electronic structure has proven that such magnetic properties are strongly correlated with the rather sharp structure of the conduction bands. When the density of states approaches the maximum with increasing sulfur content, the ferromagnetic interactions become stronger than the antiferromagnetic ones. Furthermore, the moment-rotation transition in the ferromagnetic region occurs in the vicinity of the minimum of the density of states.

The latter observation is of quite interest in view of the experimental fact that the moment-rotation transition is accompanied with the change of the magnetically induced distortion. Recently, Chan[44] studied on the magnetically ordering properties through the group theory and concluded that the direction of the moments in the ferromagnets with octahedral symmetry is determined in terms of the elastic properties; that is, if the elastic constant C_{44} is harder than the constant (C_{11} - C_{12}), the [100] direction is favored, whereas if C_{44} is softer, the [111] is favored. This means that in the UP-US system, the softening of the constant C_{44} will cause the moments to rotate from the [100] direction to the [111] direction with increasing temperature and/or sulfur content. The sharp structure of the conduction bands suggests that the probable softening of the elastic constant C_{44} would be ascribable to the increasing anisotropy in the Fermi surface along to the [111] direction. It is of interest to point out that such features of the Fermi surface can be derived from the free-electron-like rigid band model proposed by Grunzweig-Genossar and Cahn [45]. They discussed the appearance of the longperiod magnetic structures in the UP-rich region in terms of the instability of the Fermi surface. According to their model, as x is increased, the Fermi surface will extend and touch firstly at the point I, of the Brillouin zone at about x = 0.35. In the US-rich region, consequently, the Fermi surface will become to have a large anisotropy. When electrons are further increased, the Fermi surface might form the holes centered at x. If the additional electrons would start to occupy the states in the next Brillouin zone, the minimum point in the density of states at x = 0.6 might correspond to the overlapping region of two conduction bands.

Such speculation for the band surface is consistent with the thermoelectrical observation of Tetenbaum [46]. Recently, Kamimoto *et al.* [27] have observed that the lattice thermal conductivity of UP is higher than that of US. This difference might be explicable in terms of the difference in the Fermi level in the rigid bands described above.

(b) On the nature of the 5f electron

The present study has been started to detect the Schottky heat capacity or to derive the electronic heat capacity coefficient in the paramagnetic region. The latter attempt successfully provided the reasonable values of the density of states in the light of the current understanding on the electronic structure in the actinide compounds. It was, however, failed to detect such Schottky heat capacity anamaly as would be predicted by the strong crystal field theory [4, 28, 47] which shows the energyseparation scheme for the crystal field states being in an order of 10²-10³ K and very sensitive to the magnitude of the crystal field parameters, especially of the sixth parameter, A_6 . This failure corresponds to the results of neutron scattering experiment [24] that also failed to detect the transition between the crystal field states. Instead of the information of the Schottky heat capacity, the present analysis provided the considerable interesting features in the magnetic T^{-2} term as well as the linear term strongly related with the magnetic ordering and the paramagnetic properties such as the magnetic susceptibility and the NMR properties. Furthermore, the correlation between the magnetic term and the conduction electron term suggests the importance of the interaction between two particles in order to understand the magnetic and related properties. In this meaning, it is worthwhile noticing that the results of Fradin[42] are essentially consistant with the present results, though some respects remain uncertain concerning the nature of the 5f-states. The theory of Robinson and Erdos[48] is also of interest, but the emphasis is placed on the ordered state. In order further to clarify the nature of the 5felectrons calorimetrically, it needs to examine the excess thermodynamic properties in the ordered state. Unfortunately, this is beyond the present study for lack of the lower temperature data of heat capacity.

Acknowledgement—The authors wish to thank Mr. K. Tanaka of the Central Laboratory of Mitsubishi Metal Co. Ltd. for the preparation of the samples.

REFERENCES

- Freeman A. J. and Darby J. B., Jr. (Editors), The Actinide: Electronic Structure and Related Properties. Academic Press, New York (1974).
- Grunzweig-Genosser J., Kuznietz M. and Friedman F., Phys. Rev. 173, 562 (1968).
- 3. Davis H. L., In Rare Earths and Actinides (Conference Digest No. 3), p. 129. Institute of Physics, London (1971): idem, In Ref. [1], Vol. II, p. 1.
- 4. Chan S. K. and Lam D. L., In Ref. [1], Vol. I, p. 1.
- Flotow H. E., Osborne D. W. and Walters R. R., J. Chem. Phys. 55, 880 (1971).
- 6. Danan J., CER-R-4453 (1973).
- 7. Grunzweig-Genossar J., Solid State Commun. 8, 1673 (1970).
- Yokokawa H., Takahashi, Y. and Mukaibo T., In Thermodynamics of Nuclear Materials 1974 (Proceedings of a symposium, Oct. 1974), Vol. II, p. 419. IAEA, Vienna (1975).
- de Novion C. H. and Costa P. C., C. R. Held. Seanc. Acad. Sci. Paris 270B, 1415 (1970).
- Counsell J. F., Dell R. M., Junkison A. R. and Martin J. F., Trans. Faraday Soc. 63, 72 (1967).
- Westrum E. F. Jr., Walters R. R., Flotow H. E. and Osborne D. W., J. Chem. Phys. 48, 155 (1968).
- Counsell J. F., Dell R. M., Junkison A. R. and Martin J. F., In *Thermodynamics of Nuclear Materials* 1967 (Proceedings of a symposium, Oct. 1967), p. 385. IAEA, Vienna (1968).
- 13. Adachi H. and Imoto S., J. Nucl. Sci. Technol. 6, 371 (1969).
- 14. Fisk Z. and Coles B. R., J. Phys. C3, L104 (1970).
- Takahashi Y., Yokokawa H., Sekine Y., Kadokura H. and Mukaibo T., J. Chem. Thermodynamics, to be published.
- Yokoawa H. and Takahashi Y., J. Chem. Thermodynamics, to be published.
- Takahashi Y. and Westrum E. F. Jr., J. Chem. Thermodynamics 2, 847 (1970).
- Kadokura H., Yokokawa H. and Takahashi Y., Netsusokutei (Calorimetry and Thermal Analysis) 4, 52 (1977).
- A list of numerical values for the experimental heat capacity data is available on request.
- Nakai E., Ono F., Takahashi Y. and Mukaibo T., J. Nucl. Sci. Technol. 7, 41 (1970).
- Murabayashi M., Takahashi Y. and Mukaibo T., J. Nucl. Mater. 40, 353 (1971).
- 22. Moser J. B. and Kruger O. L., J. Appl. Phys. 38, 3215 (1967).
- 23. MacLeod A. C., J. Inorg. Nucl. Chem. 33, 2419 (1971).
- 24. Wedgewood F. A., J. Phys. C7, 3203 (1974).
- Kuznietz M., Lander G. M. and Baskin Y., J. Appl. Phys. 40, 1130 (1969): Kuznietz M., Compos F. P. and Baskin Y., *ibid.* 40, 3621 (1969): Kuznietz M. and Cox D. E., Phys. Rev. 188, 963 (1969): Maglic R. C., Lander G. H., Mueller M. H., Crangle J. and William G. S., *ibid.* B10, 1943 (1974): Kuznietz M. and Baskin Y., Solid State Commun. 6, 877 (1968).
- Trzebiatowski W. and Polewski T., Phys. Status Solidi 34, K51, (1969).
- Kamimoto M., Takahashi Y. and Mukaibo T., J. Nucl. Mater. 59, 149 (1976); J. Phys. Chem. Solids 37, 719 (1976).

- 28. Tróc R. and Lam D. J., Phys. Status Solidi (b) 65, 317 (1974).
- 29. Gulick J. M. and Moulton G., Phys. Lett. A35, 429 (1971).
- 30. Lander G. H. and Mueller M. H., Phys. Rev. B10, 1994 (1974).
- 31. Sidhu S. S., Volgelsang W. and Anderson K. D., J. Phys. Chem. Solids 27, 1197 (1966).
- 32. Wedgewood F. A., J. Phys. C5, 2427 (1972).
- 33. Marples J. A., J. Phys. Chem. Solids 31, 2431 (1970).
- 34. Allbutt M., Dell D. M., Junkison A. R. and Marples J. A., J. Inorg. Nucl. Chem. 32, 2159 (1970).
- 35. Marples J. A., Sampson C. F., Wedgewood F. A. and Kuznietz M., J. Phys. C8, 708 (1975). 36. Carr S. L., Long C., Moulton W. C. and Kuznietz M., Phys.
- Rev. Lett. 23, 786 (1969). 37. Grimvall G., J. Phys. Chem. Solids 29, 1221 (1968).
- 38. Berk S. and Schrieffer J. R., Phys. Rev. Lett. 17, 433 (1966).

- 39. Doniach S. and Engelsberg S., Phys. Rev. Lett. 17, 750 (1966).
- 40. Birgeneau R. J., Bucher E., Maita J. P., Passell L. and Turberfield K. C., Phys. Rev. B8, 5345 (1973).
- 41. Hui J. L. K. and Allen P. B., J. Phys. C8, 2923 (1975).
- 42. Fradin F. Y., J. Phys. Chem. Solids 31, 2715 (1970); see also, Ref. [1], Vol. 1, p. 181.
- 43. Eastman D. E. and Kuznietz M., J. Appl. Phys. 42, 1396 (1971).
- 44. Chan S. K., In Plutonium 1975 and Other Actinides (Edited by H. Blank and R. Linder), p. 575. American Elsvier, North-Holland, New York (1976).
- 45. Grunzweig-Genossar J. and Cahn J. M., Int. J. Magnetism 4, 193 (1973).
- 46. Tetenbaum M., J. Appl. Phys. 35, 2468 (1974).
- 47. Lam D. J. and Fradin F. Y., Phys. Rev. B9, 238 (1974).
- 48. Robinson J. M. and Erodös P., Phys. Rev. B8, 4333 (1973); **B9**, 2187 (1974).