Low-temperature specific heat of uranium monopnictides and monochalcogenides

H. Rudigier, H. R. Ott, and O. Vogt

*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, ETH-Hönggerberg,
CH-8093 Zürich, Switzerland*

We present a systematic investigation of the low-temperature specific heat of single-crystalline NaCl-type UX compounds ($X=$N, P, As, Sb, S, Se, Te) at temperatures between 0.12 and 12 K. It is primarily intended to determine the low-temperature electronic specific heats $C_e = \gamma T$ of these materials. From our experiments, γ increases from UN (25.8 mJ/mole K^2) to UAs by a factor of about 2, but is an order of magnitude smaller in USb. For the chalcogenides, a decreasing electronic specific heat with increasing anion size is observed. The measurements at the lowest temperatures reveal the onset of a nuclear Schottky anomaly, from which we derive magnetic hyperfine fields and obtain good agreement with published values from Mössbauer experiments for UP and USb. Except for USb, the nuclear heat capacity is negligible at temperatures above 1.5 K.

I. INTRODUCTION

The NaCl-type uranium monopnictides and monochalcogenides exhibit a great variety of interesting physical properties associated with the presence of $5f$ electrons in these materials. In particular, the pnictides order antiferromagnetically with a Néel temperature T_N varying between 53 K (UN) and 213 K (USb),[1] revealing unusual structures in the ordered state. Single-k structure for UN, double-k structure for UP and UAs, and a triple-k structure for USb were claimed from neutron experiments,[2] and large magnetic anisotropies were indicated from magnetization measurements.[3] The chalcogenides all undergo a transition to a ferromagnetically ordered state at temperatures between 180 K (US) and 104 (UTe), with the [111] direction as the easy-magnetization axis and anisotropy fields of the order of 1 MOe.[3]

In contrast to their $4f$ counterparts of the rare-earth (RE) elements, the wave functions of the $5f$ electrons are spatially much more extended and the corresponding states energetically less stable, at least for the light actinides. Consequently, this results, also for our substances, in a rather complex electronic structure in the vicinity of the Fermi energy E_F as itinerant electronic states with f and d symmetry interact considerably. Another detail of the electronic structure, namely a mixing between cation f and anion p states, which are situated several eV below E_F,[4] was suggested to explain the variation of the lattice constant with increasing anion size.[5] Obviously, the knowledge of the electronic structure, and, in particular, the degree of localization of the $5f$ electrons, provides the key for an understanding of the physical properties of these materials.

Experimentally, numerous photoemission investigations favor a picture of a narrow f band, hybridized with d states, at the Fermi level.[6-8] Magneto-optical[9] studies were interpreted in terms of an increasing localization of bandlike f states with increasing anion size. This is supported by neutron-scattering experiments, revealing features characteristic for localized f electrons for the compounds with the largest lattice spacing. Distinct magnon branches,[10,11] and probably excitations between crystalline-electric-field (CEF) -split energy levels of the $5f$-electron ground state, were observed in USb,[10] but have not been found, e.g., in UN and US. Finally, from the occurrence of $5f^2$ final-state effects, a quasilocalized $5f^3$ ionic configuration was deduced from resonant photoemission experiments for UAs, USb, USe, and UTe.[12]

In order to obtain further information on the electronic spectrum of these compounds and, in particular, about the density of states (DOS) at E_F, $N(E_F)$, and its variation through the series, we measured the specific heat at low temperatures and derived the electronic heat capacity C_e, from which, in principle, $N(E_F)$ can be calculated. Another reason for this work was given by the fact that published specific-heat measurements on these materials have mostly been done on powdered samples with relatively large amounts of material and have often given controversial results. Our experiments were made on single pieces of small single crystals and, for an unambiguous determination of C_e, the measurements were extended to below 1 K.

II. APPARATUS AND SAMPLES

The experiments on single-crystalline specimens of about 80—200 mg were performed either in a conventionally pumped ^{4}He cryostat or in a ^{3}He-^{4}He dilution refrigerator, thus covering the temperature range from 0.12 to 11 K (26 K in the case of UP). The preparation of the samples is described in Ref. 13.

The precision of our calorimeter, whose mode of operation was based on a thermal relaxation method, was checked by comparing experimental results of a copper sample with the "copper reference equation,"[14] which is commonly used for interlaboratory comparisons. Our coefficient, γ, of the electronic specific heat of Cu is within 1.5% of the value given in Ref. 14, for the measurements below and above 1 K. The lattice contribution approximated simply with a cubic term above 1.5 K devi-

ates less than 4.5% from the value at 15 K cited in Ref. 14.

The radioactive self-heating of the U samples, though small in these compounds, poses severe problems at the lowest temperatures, and it was, with our particular setup, not possible to cool the specimens to below 0.12 K. Therefore, for temperatures below 0.8 K a correction to the sample temperature had to be applied, whereas above 0.8 K the temperature difference between the sample and the thermal bath was less than 0.5 mK and was therefore neglected.

III. RESULTS AND ANALYSIS OF THE DATA

A. $X = $N,P,As,S,Se,Te

In Fig. 1 we show the results of our experiments at temperatures above 1.5 K in the usual form, i.e., as a C_p/T-versus-T^2 plot. In order to determine the lattice (C_L) and the electronic contribution ($C_e = \gamma T$), we fitted the data to

$$C_p = C_e + C_L = \gamma T + \beta T^3 , \qquad (1)$$

where the electronic specific-heat coefficient γ is given by

$$\gamma = \tfrac{1}{3}\pi^2 k_B^2 N_{BS}(E_F)(1+\lambda) , \qquad (2)$$

where $N_{BS}(E_F)$ is the band-structure density of electronic states at the Fermi level, and $1 + \lambda$ is an, in most cases unknown, enhancement factor due to electron-lattice and electron-electron interactions. $C_L = \beta T^3$ is the low-temperature phonon contribution in the Debye approximation. The relation between the Debye temperature Θ_D and β (in units of J/mol K^4) is given by

$$\Theta_D = (1944r/\beta)^{1/3} , \qquad (3)$$

where r denotes the number of atoms per molecule. Assuming that the relative errors are approximately independent of temperature, the fitting procedure is chosen such as to minimize
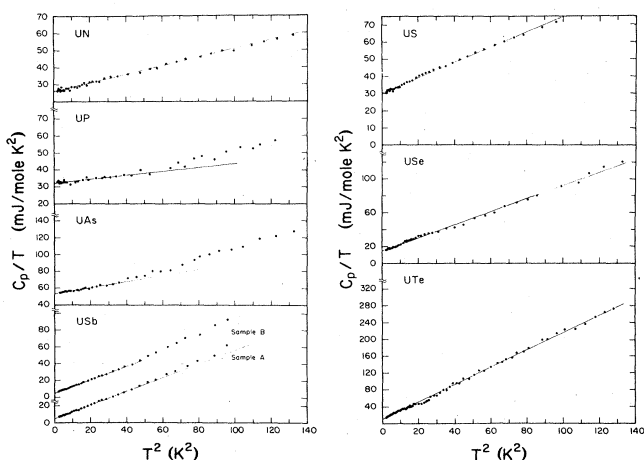
$$Q = \sum_i [(C_p^i - C_p)/C_p^i]^2 , \qquad (4)$$

where C_p^i is the measured value at T_i, and C_p is the corresponding fit value.

In our analysis of the data we have neglected the difference between the specific heat at constant volume, C_V, and at constant pressure, C_p, which for UP we estimate to be $\simeq 0.8\%$ of the total heat capacity at 19 K. Furthermore, we have not taken into account any contributions from excited electronic energy levels within the 5f-electron Hund's-rule ground state, as they, if they exist at all, are probably at too high energies to give sizable contributions to the heat capacity in the temperature range of our measurements. The only experimental evidence for such a level was reported for USb with an excitation energy of approximately $290 k_B$.[15]

The optical-phonon modes of all UX compounds investigated were found to lie above 220 K.[11,15,16] Hence, within the Einstein approximation ($h\nu_E = 220 k_B$ K) these modes contribute less than 3 μJ/mol K to the heat capacity at 10 K, and therefore have been neglected.

Using the simple form of Eq. (1), all data points above 1.5 K for UN and the chalcogenides could be fitted within a rms deviation $(Q/N)^{1/2}$ of 3%. This was not possible for UP and UAs, as in the C_p/T-versus-T^2 plot a weak kink occurs at $T^2 \simeq 60$ K^2 for UP and at $T^2 \simeq 40$ K^2 for UAs. Therefore, for a reasonable determination of γ and β of these compounds from the data above 1.5 K, it was necessary to limit the temperature range in which Eq. (1) could be used. Addition of a δT^5 term to Eq. (1) to account for the enhanced increase of C_p above the kink temperature changes β up to a factor of 3 (1.5) in the case of UP (UAs). Hence only a better mathematical representa-
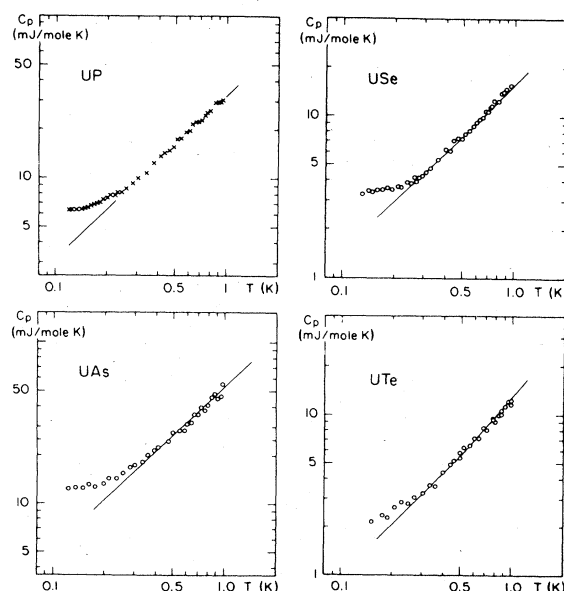

FIG. 1. C_p/T vs T^2 for the UX compounds investigated in the temperature range $1.5 < T < 12$ K. For USb, two different specimens (A and B) have been measured. The solid lines indicate a least-squares fit according to Eq. (1).

FIG. 2. Specific heat for UX ($X = $P,As,Se,Te) at temperatures below 1 K. The solid lines are calculated using Eq. (1), taking the parameters γ and β (Table I) from the experiments above 1.5 K. The deviations at the lowest temperatures are due to a nuclear Schottky anomaly.

TABLE I. Electronic specific-heat coefficient γ (mJ/mol K^2) and Debye temperatures Θ_D (K) for the U monopnictides and mono-chalcogenides. Θ_D is calculated from Eq. (3) using $r = 2$. The values for the distance between the U atoms, $d_{U\text{-}U}$, was calculated from the lattice constants given in Ref. 1. For the cited values of γ and Θ_D from previous work, we also quote the temperature range they have been derived from.

UX	$d_{U\text{-}U}$	γ	Θ_D (K)	Temperature range (K)	References
UN	3.46	25.8±0.5	249±3		This work
		49.6	324	$1.3 < T < 4.6$	26
		46	289	$5 < T < 23$	30
		34	276	$T > 11$	31
UP	3.95	32.1±1.1	319±4		This work
		9.6	224	$10 < T < 20$	32
UAs	4.08	53.2±1.5	221±2		This work
		53		$T > 5$	34
USb A	4.38	4.36±0.25	168±2.5		This work
USb B		4.56±0.25	169±2.5		This work
US	3.88	30.0±1	205±2.5		This work
		23.3	239	$1.5 < T < 9$	28
USe	4.06	14.7±0.6	172±2.3		This work
		86.8		$T > 5$	35
UTe	4.35	10.3±0.4	124±2.5		This work

tion of the data would be achieved at the cost of physically meaningless coefficients β and δ. The results of our analysis of the data above 1.5 K are summarized in Table I.

As it becomes evident from Fig. 1, an unequivocal determination of γ and β, especially for UP and UAs, calls for extending the experiments to temperatures below 1 K. These data are shown in Fig. 2 (the upturn of C_p at the lowest temperatures is discussed below). In Fig. 2 we also have indicated the extrapolations of the high-temperature data using Eq. (1) and the parameters of Table I by solid lines. Above 0.3 K they obviously fit the data quite accurately in all cases, providing further confidence in the value listed in Table I.

B. $X = \text{Sb}$

In our first experiment on USb (henceforth denoted as sample 0) (Ref. 17), deviations from Eq. (1) occurring in the temperature interval between 0.3 and 4 K were attributed to an impurity effect, and thus the γ value could only be obtained from the data above 4 K. We therefore investigated two more single-crystalline samples grown from different melts (Fig. 1, samples A and B). From the experimental data, γ and β were determined by fitting $C_p - C_N$ to Eq. (1), where $C_N = 1.44 \times 10^{-3}/T^2$ (J/mol K) is a contribution to C_p originating from a nuclear Schottky anomaly, as discussed below and which was derived from the data of sample 0 below 0.3 K (see Fig. 3). For USb, C_N/C_p(total) amounts to $(6.8 \pm 0.1) \times 10^{-2}$ at 1.5 K, thus being 2 orders of magnitude larger than for the other UX compounds investigated below 1 K (Table

II). Again, for the same reasons as in the case of UP and UAs, the parameters γ and β were determined from data points in the temperature interval between 1.5 and 7 K, although in this case the extension of Eq. (1), including a δT^5 term, to all data points above 1.5 K, would alter these parameters only within the errors given in Table I.
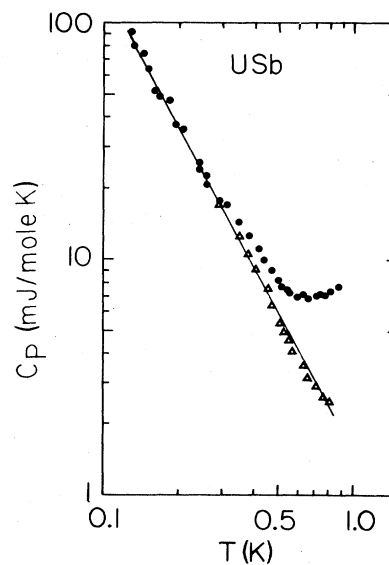

FIG. 3. Heat capacity of USb below 1 K. The dots are the experimental data; above 0.3 K the nuclear heat capacity C_N is calculated as explained in the text and shown as open triangles.

TABLE II. Hyperfine fields (in kOe) of the uranium and anion nuclei. a_2^{expt} is the coefficient of the T^{-2} term of C_N [Eq. (7)] obtained from our experiments. a_2^{calc} denotes the calculated value from published data of Mössbauer experiments. a_2 is given in units of J K/mol.

	UP	UAs	USb	USe	UTe
$H_{\text{eff}}(U)$	3600[a]		4500[a]	3200±400	1850±600
$H_{\text{eff}}(X)$	27.3[b]	68±5	170[c]		130[d]
a_2^{expt}	4×10^{-5}	9×10^{-5}	1.44×10^{-3}	2.5×10^{-5}	2×10^{-5}
a_2^{calc}	4.08×10^{-5}		1.38×10^{-3}		

[a]Reference 11.
[b]Reference 12.
[c]Reference 13.
[d]Reference 14.

C. Nuclear heat capacity C_N

As already mentioned above, the increase of C_p at the lowest temperatures (Fig. 2) originates from a nuclear Schottky anomaly due to the hyperfine-split ground states of both the anion and the cation nuclei. The cation contribution is only due to ^{235}U nuclei with a concentration of less than 0.7% in the starting material. For the anions, some of the stable isotopes have a nuclear spin $I \neq 0$. C_N was determined by subtracting from the experimental data the lattice and electronic contribution as shown in Table I. The remaining heat capacity was plotted on a log-log scale and this is shown in Fig. 3 for USb (triangles) and in Fig. 4 for the other compounds.

As the maximum of C_N occurs below 0.1 K in these compounds, it is sufficient for an analysis of C_N to expand the general expression for a Schottky anomaly[18] in inverse powers of T to obtain

$$C_N = a_2 T^{-2} + \cdots . \tag{5}$$

Neglecting quadrupole interactions, the coefficient a_2 of the leading term is given by[18]

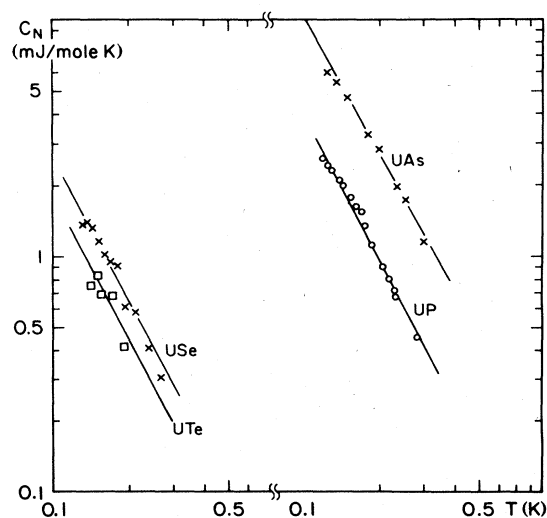$$a_2/R = \tfrac{1}{3}(\mu_N H_{\text{eff}}/k_B)^2 I(I+1)/I^2 , \tag{6}$$

FIG. 4. Nuclear heat capacity of UP, UAs, USe, and UTe. The T^{-2} behavior is shown by the solid line. Note the order-of-magnitude difference to USb (Fig. 3).

where R denotes the gas constant, μ_N the nuclear magnetic moment, k_B Boltzmann's constant, I the nuclear spin, and H_{eff} the effective magnetic field at the nucleus. From Figs. 3 and 4, C_N obeys a T^{-2} law in all cases (solid lines), indicating that higher-order terms in the expression of C_N [Eq. (5)] are negligible in our temperature range. Taking into account that all the various isotopes with $I \neq 0$ of both the cation and the anion contribute to C_N, Eq. (6) is generalized to

$$a_2/R = \alpha_U \nu_U H_{\text{eff}}^2(U) + \left[\sum_i \nu_X^i \alpha_X^i \right] H_{\text{eff}}^2(X) . \tag{7}$$

In Eq. (7), ν_X^i is the percentage of the abundance of the isotope i of the element X, and $\alpha_X^i = (a_2^i/R)H_{\text{eff}}^{-2}(X)$. For USb and UP the agreement between the calculated values of a_2, inserting published values for H_{eff} of U (Refs. 19 and 20), P (Ref. 21) and Sb (Ref. 19) into Eq. (7), and the experimental value a_2^{expt}, is within 2% for UP and 4.3% for USb (see Table II).

For UAs, an evaluation of Eq. (7), using the experimental value of a_2 and taking $H_{\text{eff}}(U) = 3700$ kOe from the linear relationship between $H_{\text{eff}}(U)$ and the magnetic moment μ_n in the ordered state,[20] yields $H_{\text{eff}}(As) = 68 \pm 5$ kOe. This value is clearly only weakly influenced by the value of $H_{\text{eff}}(U)$ because $\nu_{As} \gg \nu_U$. For UTe and USe, however, the total natural abundance of the ^{123}Te and ^{125}Te isotopes together of only 7.87% and 7.58% for ^{77}Se make the coefficient a_2 more sensitive to the U hyperfine (hf) field. For UTe we obtain $H_{\text{eff}}(U) = 1850 \pm 600$ kOe using Eq. (7) and taking $H_{\text{eff}}(Te) = 130$ kOe from Ref. 22. Assuming that a similar relation as

$$H_{\text{eff}}(Sb)/\mu_n = H_{\text{eff}}(Te)/\mu_n \approx 60 \text{ kOe}/\mu_B \tag{8}$$

also holds for the combination USe-UAs, we calculate $H_{\text{eff}}(Se) = 61$ kOe and $H_{\text{eff}}(U) = 3200 \pm 400$ kOe for USe.

We have listed all relevant parameters for the analysis of our data below 1 K in Table II, including some hf fields from the literature cited above. From this table it is evident that C_N is negligible for temperatures above 1.5 K in all UX compounds except USb.

D. Contributions to C_p in a magnetically ordered state

Because of the magnetic ordering in all UX compounds, it may be expected that at low temperatures the thermal excitation of spin waves contributes to the heat capacity

(C_M). From theory, the low-temperature behavior of C_M for a three-dimensional system is expected to obey a $T^{3/n}$ law,[23] where n is the exponent of the spin-wave dispersion relation $\omega \propto q^n$. For antiferromagnets, $n=1$ and thus C_M is, without applying a magnetic field, indistinguishable from the lattice contribution. For ferromagnetic magnons, $n=2$. In the presence of a gap Δ in the excitation spectrum due to magnetic anisotropy, the temperature dependence of C_M is influenced by the usual Boltzmann distribution; hence[24]

$$C_M = f(T)\exp(-\Delta/T) \ . \tag{9}$$

For USb and UTe, well-defined spin-wave branches were observed by neutron-scattering experiments, revealing large gap values of 74 K for USb (Ref. 10) and 165 K for UTe (Ref. 11), respectively. For UN the inelastic magnetic response consists of a broad featureless spectrum with a gap value of 170 K.[11] No neutron-scattering experiments have been reported for USe; however, from resistivity measurements, $\Delta = 135$ K was deduced, assuming $\omega \propto q^2$.[25] We note that for USb and UTe the Δ values from resistivity data are roughly 50% lower than those obtained from neutron-scattering experiments.

From these large anisotropy gaps for UN, USb, USe, and UTe we conclude that the thermal activation of magnetic excitations is substantially suppressed at low temperatures in these compounds and, therefore, C_M is negligible in the low-temperature range $(T < 7$ K) of our experiments. Collective spin-wave excitations have not been observed in the case of UAs,[27] although magnetic inelastic scattering intensity is present over the whole range of accessible energy transfers in neutron scattering. Therefore we have no reason to expect a contribution $C_M \approx T^3$ to C_p for UAs in our temperature range. Moreover, for UAs it seems very unlikely that magnetic contributions to C_p obeying a temperature dependence different from $C_M \approx T^3$ are concealed behind an almost perfect linear C_p/T-versus-T^2 behavior over a temperature range of more than an order of magnitude at low temperatures $(T^2 < 40$ K$^2)$, as may been seen from Figs. 1 and 2. We therefore conclude that our values for γ and Θ_D (Table I), which have been deduced from the data obtained at temperatures below ≈ 7 K, do not contain any magnetic contributions.

The situation is less clear for UP because (i) no information on the magnetic excitation spectrum is presently available, and (ii) a phase transition from a collinear to a double-k antiferromagnetic structure occurs at (for our sample) $T_{N_2} = 22.1 \pm 0.2$ K and therefore the data at higher temperatures $(T > 7$ K$)$ may be affected by some magnetic contribution. Therefore we decided to extend the experiments up to 27 K, and we show the result in Fig. 5. Obviously, above 7 K, C_p increases more rapidly than might be expected from the behavior of C_p below that temperature, and between 11 and 18 K the data may be represented by Eq. (1), taking $\gamma = 8.2$ mJ/mol K^2 and $\Theta_D = 224$ K. We note that these parameters γ and Θ_D are quite different from those given in Table I, but are close to those reported by Counsell et al.[32] (see Table I), which were evaluated from data between 10 and 20 K. The ad-
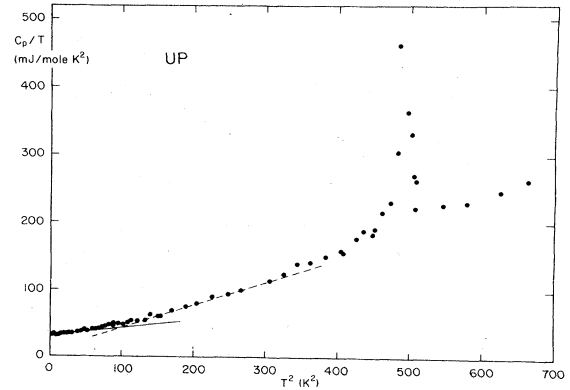

FIG. 5. C_p/T vs T^2 for UP $(1.5 < T < 26$ K$)$. The anomaly at 22.1 K is due to a change in the magnetic structure (see text). The solid line indicates a fit according to Eq. (1) for $1.5 < T < 7$ K, whereas the dashed lines represent a fit in the temperature interval $11 < T < 18$ K, from which Counsell et al. (Ref. 32) have deduced γ and β, respectively.

ditional contribution to C_p probably originates from magnetic excitations or, alternatively, is partly due to lattice contributions beyond the Debye approximation. However, from Fig. 1 it obviously is negligible at temperatures below 7 K and therefore does not affect the analysis of the data below 7 K. As a by-product, our measurements on UP above 10 K corroborate the first-order nature of the phase transition at T_{N_2} (Ref. 33) by the observation of a latent heat and a corresponding entropy change of 1.77 ± 0.06 J/mol K which is within 11% of the value cited in Ref. 32.

Finally, for ferromagnetic US, we find no reason to include magnetic contributions in our analysis because of the clear-cut linear C_p/T-versus-T^2 behavior shown in Fig. 1. Nevertheless, we have performed the same analysis as that reported in Ref. 28 and subtracted a calculated magnon contribution $C_M = 0.0011 T^{3/2}$ J/mol K (Refs. 28 and 29) from the experimental data. Without magnetic contribution, we obtain $\gamma = 28.02$ mJ/mol K^2 and $\beta = 0.435$ mJ/mol K^4, whereas fitting the data to $C_p = \gamma T + \beta T^3 + \delta T^{3/2}$ yields $\gamma = 21.4$ mJ/mol K^2, $\beta = 0.33$ mJ/mol K^4, and $\delta = 5.67$ mJ/mol K$^{5/2}$ with a rms deviation slightly lower than that obtained from a fit using Eq. (1), and which we believe to be solely due to the additional parameter.

IV. DISCUSSION

To allow for a comparison we also cited published values for γ and Θ_D in Table I, as well as the temperature range they have been derived from. We believe that our values are the most reliable for several reasons. First, the measurements were done on single crystals of the same quality as those used in neutron-scattering experiments,[2,10,11,13,15,27] and by using a well-calibrated calorimeter (see Sec. II). Moreover, we extended the experiments to lower temperatures for at least an order of magnitude, thus giving more confidence to the values obtained by the fitting procedures. Finally, we note that these fitting pro-

cedures result in values of magnetic hyperfine fields that are in excellent agreement with those obtained previously with more direct methods.[19,21]

The electronic specific-heat coefficient γ is defined in Eq. (2) of Sec. III. In order to obtain an estimate for the magnitude of λ in these compounds, we have calculated γ for UN from $N_{BS}(E_F) = 72$ states/Ry U-atom, as stated in Ref. 5, where unfortunately only the f density of states for the paramagnetic phase is given. By comparison with the γ value from our experiment, we conclude $\lambda \simeq 1$. For US we find $\lambda = 0.78$ when inserting $N_{BS}(E_F) = 100$ states/Ry U-atom from Ref. 36 into Eq. (2).

For comparisons with band-structure calculations, it should be kept in mind that our γ values are obtained in magnetically ordered states for which the density of states at E_F may differ from the value in the paramagnetic phase. In particular, for the pnictides, the antiferromagnetic ordering may produce gaps in the excitation spectrum, causing different γ values above and below the transition temperature. This has been observed, for instance, in U_2Zn_{17},[37] $NpSn_3$,[38] and UCd_{11}.[39] Exchange splitting of the energy bands in the ferromagnetic state may cause problems when comparing experiments and calculations for the U monochalcogenides.

A. Pnictides

From a comparison of the γ values for UN, UP, and UAs (Table I) with those of the corresponding LaX [with γ values of the order of 1 mJ/mol K^2 (Ref. 40)] and ThX compounds [$\gamma \approx 3-5$ mJ/mol K^2 (Refs. 34 and 41)], where the f states are unoccupied, one might conclude that in these compounds $N_{BS}(E_F)$ is almost entirely due to the presence of f states at E_F.

To shed some light on the variation of the electronic specific-heat coefficient γ within a series, we also have listed in Table I the separation of the U atoms d_{U-U}, which certainly influences the direct overlap of $5f$ wave functions of adjacent U atoms. Provided that λ is roughly constant, the increasing γ from UN to UAs indicates an increasing $N_{BS}(E_F)$ due to the narrowing of the f-d− hybridized band-structure profile in the vicinity of E_F as a consequence of the increasing lattice parameter. Focusing on the pnictides, the most intriguing feature of Table I, however, is the dramatic drop of the γ value by a factor of $\simeq 12$ upon going from UAs to USb. Referring to the low γ value of LaSb [0.8 mJ/mol K^2 (Ref. 40)], we deduce a small but probably nonvanishing f density of states at E_F for USb, indicating substantially but not strictly localized $5f$ electrons.

With the exception of UN, the large separation of the U atoms in these compounds (Table I) precludes any appreciable amount of direct overlap of the $5f$-electron wave functions. Consequently, the particular variation of γ with d_{U-U} as evidenced by Table I seems to indicate the sensitivity of the electronic structure and thus of the DOS in the vicinity of E_F to interactions (mixing) between U $5f$ and pnictogen p as well as U d states.

B. Chalcogenides

As in the case of the pnictides, the presence of f states at the Fermi level may be deduced by considering the much lower γ values (in mJ/mol K^2) of both the La and Th chalcogenides [LaS, 3.28; LaSe, 3.77; LaTe, 4.65 (Ref. 42); ThS, 3.8 (Ref. 43); ThSe, 4.82 (Ref. 44)], especially when taking into account the excess of one d electron in Th. For the U monochalcogenides, a decrease of f DOS at E_F upon going from US to UTe is indicated by the values of γ in Table I. We note that the existence of d states at E_F has experimentally been proven by spin-polarized photoemission.[8]

Although the variation of γ with d_{U-U} is apparently quite different from that observed for the pnictides, it may have the same physical origin in both cases, namely a suppression of the itineracy of electronic states with f symmetry with increasing separation of the U atoms. Again, this is corroborated by the increase of the ordered magnetic moment with increasing d_{U-U}, the sharp magnon branches in UTe,[11] and by results of magneto-optic investigations.[9] From Table I we also obtain evidence for the crucial role of the d electrons in the chalcogenides as pointed out before by Reihl and co-workers.[12] While in US the γ value is comparable to that of UP and therefore also dominated by electronic states with f symmetry, the same comparison for USe and UAs reveals the fading of the f-electron contribution in the chalcogenide or, in other words, the increasing relative contribution due to electronic states with d symmetry. The same trend holds for UTe. It seems, however, difficult to reconcile our γ value for UTe with a strict localization of the f electrons in this compound, as was inferred from photoemission valence-band spectra.[12]

C. Comparison with band-structure calculations

As far as band-structure calculations are concerned, we believe that it makes little sense to compare numerical values of a calculated DOS [$N_{BS}(E_F)$] with the experimental electronic specific heat for one particular compound alone because of the uncertainties involved with the enhancement parameter λ. Rather, one should compare the tendencies of the γ values with calculated DOS within a series. For the UX compounds, no available systematic band-structure calculation predicts similar variations of $N_{BS}(E_F)$ as we observe for γ. For example, we note that Brooks,[45] neglecting spin-orbit coupling, has found the same trend for $N_{BS}(E_F)$ in the paramagnetic phase for both the chalcogenides and the pnictides, namely an increasing DOS at E_F with increasing anion size. Possibly these calculations predict the correct contribution of the $5f$ electrons to bonding as the anion changes; however, a proper description of the variation of γ through a series certainly demands a fully relativistic spin-polarized calculation. It should be mentioned that a relativistic band-structure calculation for UBi and UTe (Ref. 46) qualitatively predicts a considerable amount of d character for the electronic states close to E_F in UTe.

D. Lattice contribution C_L

From the Debye temperatures of Table I, which are valid for $T \rightarrow 0$ K, one recognizes (i) a smooth variation of Θ_D for the chalcogenide series in contrast to the pnictides, and (ii) the generally much lower Θ_D for the chalcogenides. The low Θ_D of UN is possibly due to a large metallic f-f bonding as suggested by a calculated unhybridized bandwidth roughly twice that of UP (Ref. 47) and, correspondingly, a much smaller lattice constant in contrast to the more covalent UP. Interestingly, this stiffening of the lattice occurs upon going from the alledged itinerant-electron antiferromagnet UN (Ref. 48) to the more localized $5f$ electrons in UP. The large difference in the lattice contribution to C_p between the pnictides and the chalcogenides (see Table I and Fig. 1) obviously arises from the metallic softening of the lattice due to the additional electron, and is most pronounced for the compounds investigated with the largest lattice spacing. The low Θ_D of UTe is certainly correlated with the anomalous phonon spectrum of this compound,[49] which is similar to that of intermediate-valence SmY_xS_{1-x},[50] and also with the negative elastic constant C_{12} as revealed by ultrasonic measurements,[51] suggesting a rather large electron-lattice interaction.

E. Hyperfine fields

Here we do not discuss the hf fields at the U nuclei in the pnictides, as the values of Table II were cited from literature. For the chalcogenides the large error given for $H_{eff}(U)$ is due to the small contribution of C_N to C_p in the temperature range of our measurements. Therefore, before ascribing any physical meaning to them, our values of $H_{eff}(U)$ have to await further support from Mössbauer experiments.

The increase of the anion hf fields in the pnictides has, without knowledge of $H_{eff}(As)$, which was not determined previously, been ascribed[19] to the increasing atomic hf fields as the number of core shells increases. From our results on UAs and the published values (Table II) of $H_{eff}(X)$, we have found a remarkable correlation between the anion hf fields and the paramagnetic Curie temperature Θ_p in these compounds as evaluated from measurements of the magnetic susceptibility. This interdependence is shown in Fig. 6. Possibly, this can be regarded as an indication of an anisotropic superexchange mechanism due to f-p hybridization [in addition to a long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction], as proposed by Rossat-Mignot and co-workers[2] to account for the complicated magnetic structures in the pnictides.
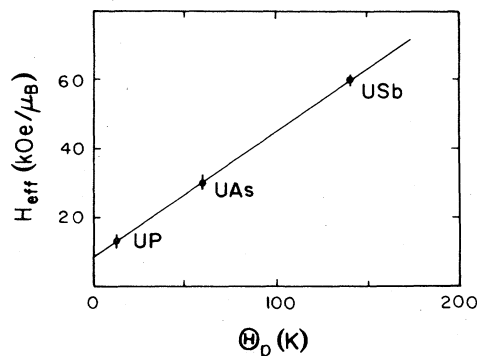

FIG. 6. Dependence of the anion hyperfine fields of the U pnictides on the paramagnetic Curie temperature Θ_p.

V. CONCLUSION

We have shown that an unambiguous evaluation of the electronic specific heat $C_e = \gamma T$ of the UX compounds ($X =$ N,P,As,Sb,S,Se,Te) demands experiments to be carried out below 1 K. From our data the increasing γ values from UN to UAs reflect a narrowing of the predominantly U-derived band-structure in the vicinity of E_F, whereas the low γ value of USb certainly points to rather localized $5f$ electrons. For the chalcogenides our experimental results indicate a similar tendency towards localization as in the pnictides. In both series, however, a complete or strict localization of the f electrons is not achieved even in the compounds with the largest U-U separation. The low Debye temperature of UTe points to large electron-lattice interaction effects. From the onset of a nuclear Schottky anomaly below 1 K we deduce the hitherto unpublished values for the hyperfine fields at the U nuclei in UTe and the anion nuclei of UAs and find compatibility with previously published Mössbauer data for UP and USb. It is found that in the pnictides the anion hf fields scale with the paramagnetic Curie temperature, suggesting that the anions play a crucial role in the exchange mechanism in these materials.

ACKNOWLEDGMENTS

[1]P. Erdös and J. M. Robinson, in *The Physics of Actinide Compounds* (Plenum, New York, 1983), p. 14.

[2]J. Rossat-Mignod, P. Burlet, S. Quezel, and O. Vogt, Physica (Utrecht) **102B**, 237 (1980).

[3]O. Vogt, Physica (Utrecht) **102B**, 206 (1980).

[4]J. Schoenes, Phys. Rep. **66**, 187 (1980).

[5]M. S. S. Brooks, J. Phys. F **14**, 857 (1984).

[6]Y. Baer, Physica (Utrecht) **102B**, 104 (1980).

[7]R. Baptiste, M. Belakhorsky, M. S. S. Brooks, R. Pinchaux, Y. Baer, and O. Vogt, Physica (Utrecht) **102B**, 63 (1980).

[8]M. Erbudak and F. Meier, Physica (Utrecht) **102B**, 134 (1980).

[9]W. Reim, J. Schoenes, and O. Vogt, J. Appl. Phys. **55**, 1853 (1984).

[10]G. H. Lander, W. G. Stirling, and O. Vogt, Phys. Rev. Lett.

42, 260 (1979).

[11]W. J. L. Buyers, A. F. Murray, T. M. Holden, E. C. Svensson, P. de V. DuPlessis, G. H. Lander, and O. Vogt, Physica (Utrecht) **102B**, 291 (1980).

[12]B. Reihl, N. Mårtensson, and O. Vogt, J. Appl. Phys. **53**, 2008 (1982).

[13]G. H. Lander, M. H. Mueller, D. M. Sparlin, and O. Vogt, Phys. Rev. B **14**, 5035 (1976).

[14]D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instrum. **38**, 159 (1967).

[15]W. G. Stirling, G. H. Lander, and O. Vogt, Physica (Utrecht) **102B**, 249 (1980). See also Ref. 10.

[16]F. A. Wedgwood, J. Phys. C **7**, 3203 (1974).

[17]H. Rudigier, Ch. Fierz, H. R. Ott, and O. Vogt, Solid State Commun. **47**, 803 (1983).

[18]O. V. Lounasmaa, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frenkel (Academic, New York, 1967), p. 467.

[19]G. K. Shenoy, G. M. Kalvius, S. L. Ruby, B. D. Dunlap, M. Kuznietz, and F. P. Campos, Int. J. Magn. **1**, 23 (1970).

[20]G. K. Shenoy, M. Kuznietz, B. D. Dunlap, and G. M. Kalvius, Phys. Lett. **42A**, 61 (1972).

[21]C. L. Carr, C. Long, W. G. Wedgwood, and M. Kuznietz, Phys. Rev. Lett. **23**, 786 (1969).

[22]G. Longworth, F. A. Wedgwood, and M. Kuznietz, J. Phys. C **6**, 1652 (1973).

[23]See, e.g., L. J. de Jongh and A. R. Miedema, in *Experiments on Simple Magnetic Model Systems* (Taylor and Francis, London, 1974), p. 176.

[24]See, e.g., B. Coqblin, *The Electronic Structure of Rare Earth Metals and Alloys: The Magnetic Heavy Rare Earths* (Pergamon, London, 1977), p. 271.

[25]J. Schoenes, B. Frick, and O. Vogt, Phys. Rev. B **30**, 6578 (1984).

[26]J. O. Scarbrough, H. L. Davies, W. Fulkerson, and J. O. Betterton, Jr., Phys. Rev. **176**, 666 (1968).

[27]T. M. Holden, W. J. L. Buyers, E. C. Svensson, J. A. Jackman, A. F. Murray, O. Vogt, and P. de V. DuPlessis, J. Appl. Phys. **53**, 1967 (1982).

[28]E. F. Westrum, Jr., R. R. Walters, H. E. Flotow, and D. W. Osborne, J. Chem. Phys. **48**, 155 (1968).

[29]F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

[30]E. F. Westrum, Jr. and C. M. Barber, J. Chem. Phys. **45**, 635 (1966).

[31]J. F. Counsell, R. M. Dell, and J. F. Martin, Trans. Faraday

Soc. **62**, 1736 (1966).

[32]J. F. Counsell, R. M. Dell, A. R. Junkison, and J. F. Martin, Trans. Faraday Soc. **63**, 72 (1967).

[33]M. Steinitz and J. Grunzweig-Genossar, J. Phys. (Paris) Colloq. **40**, C4-34 (1979).

[34]A. Blaise, R. Troc, R. Lagnier, and M. J. Mortimer, J. Low Temp. Phys. **38**, 79 (1980).

[35]Y. Takahashi and E. F. Westrum, Jr., J. Phys. Chem. **69**, 3618 (1965).

[36]M. S. S. Brooks and D. Glötzel, J. Magn. Magn. Mater. **15-18**, 873 (1980).

[37]H. R. Ott, H. Rudigier, P. Delsing, and Z. Fisk, Phys. Rev. Lett. **52**, 1551 (1984).

[38]R. J. Trainor, M. B. Brodsky, B. D. Dunlap, and G. K. Shenoy, Phys. Rev. Lett. **37**, 1511 (1976).

[39]Z. Fisk, G. R. Stewart, J. O. Willis, H. R. Ott, and F. Hulliger, Phys. Rev. B **30**, 6360 (1984).

[40]F. Hulliger, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam, 1979).

[41]V. Maurice, J. L. Boutard, and D. Abbe, J. Phys. (Paris) Colloq. **40**, C4-140 (1979).

[42]E. Bucher, K. Andres, F. J. DiSalvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and C. W. Hull, Jr., Phys. Rev. B **11**, 500 (1975).

[43]H. E. Flotow, D. W. Osborne, and R. R. Walters, J. Chem. Phys. **55**, 880 (1971).

[44]H. Haessler, M. Mortimer, and C. H. de Novion, J. Phys. C **16**, 1487 (1983).

[45]M. S. S. Brooks, J. Phys. F **14**, 653 (1984).

[46]P. Weinberger, R. Podloucky, and A. Neckel, J. Magn. Magn. Mater. **29**, 247 (1982).

[47]M. S. S. Brooks and D. Glötzel, Physica (Utrecht) **102B**, 51 (1980).

[48]B. Reihl, G. Hollinger, and F. J. Himpsel, Phys. Rev. B **28**, 1490 (1983).

[49]W. J. L. Buyers, A. F. Murray, J. A. Jackman, T. M. Holden, P. de V. DuPlessis, and O. Vogt, J. Appl. Phys. **52**, 2222 (1981).

[50]H. A. Mook and R. M. Nicklow, Phys. Rev. B **20**, 1556 (1979).

[51]J. Neuenschwander, H. Boppard, J. Schoenes, E. Voit, O. Vogt, and P. Wachter in Proc. 14èmes Journées des Actinides, Davos 1984, edited by J. Schoenes (unpublished), p. 30.