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Plutonium chalcogenides: Intermediate valence and electronic structure

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The rocksalt-structure Pu chalcogenides show a series of puzzling physical properties that cannot be understood by an integer-valent $5f$ ground state of the Pu ion. However, a simple intermediate valent state between di- and trivalency seems to be ruled out by the lattice constant, which is less than that of the hypothetical Pu^{3+} or Pu^{2+} chalcogenides. We propose in this paper that the anomalous properties of the Pu chalcogenides can be consistently understood by taking the compounds as the high-pressure, collapsed intermediate valent phase of the corresponding Sm chalcogenides for which they have the same f occupation number. The temperature-independent magnetic susceptibility, the temperature dependence of the resistivity, the neutron scattering, the specific heat, and the compressibilities can thus be consistently explained.

INTRODUCTION

Uranium and neptunium chalcogenides and pnictides, in general, exhibit magnetic order.[1] The same is true for the plutonium pnictides,[1] but the Pu chalcogenides do not show magnetic order and, in general, behave anomalously.[1,2] Their magnetic susceptibility is, to a large extent, temperature independent, but rather high compared with a standard Pauli susceptibility.[3] The temperature dependence of the resistivity for the Pu chalcogenides is semiconductorlike with two apparent gaps of the order of 2 and 20 meV,[4] which seems to oppose the Pauli susceptibility typical for a metal. The γ value of the specific heat is, with a magnitude of some tens of $\mathrm{mJ\,mol^{-1}\,K^{-2}}$, rather typical for anomalous metals, although it does not have the size for heavy fermions.[5] Polarized-neutron experiments show that the orbital component of the magnetization density in PuTe is much reduced from that expected in a free Pu^{3+} ion.[2] This would be compatible with a wide-band-gap material. However, the temperature dependence of the resistivity—with the indication of an extremely small gap and the Fermi level being in this gap—again seems to oppose wide bands. The C_2 coefficient of the magnetic form factor would be 6 for a Pu^{3+} $5f^5$ state, but -1 for a Pu^{2+} $5f^6$ state. Experimentally, a C_2 value of $+1$ is observed[2] giving a vague clue that PuTe might be intermediate valent. These ideas, however, are always ruled out on the basis of simple lattice-constant measurements which show that the lattice constant of, e.g., PuTe, is 6.19 Å, less than the one of a trivalent or divalent Pu telluride.[6] There is, of course, the problem that only the trivalent Pu ionic radius with 1.07 Å is known,[7] whereas no divalent Pu compound exists. By comparison with the corresponding $4f^n$ Sm ionic radius of 1.04 Å for Sm^{3+} and 1.12 Å for Sm^{2+}, we estimate an ionic radius of 1.15 Å for the hypothetical Pu^{2+} ion. With the Te^{2-} radius of 2.21 Å,[7] we compute for rocksalt $Pu^{3+}Te$, 6.56 Å and for $Pu^{2+}Te$, 6.72 Å. Of course, this simple bookkeeping assumes mainly ionic bonding, which, however, is valid for the corresponding $4f^n$ SmTe, which has nearly these lattice constants.[8]

Another important contribution has been made by treating the Pu chalcogenides as relativistic semiconductors[9] that have two bands with $J=\frac{5}{2}$ and $\frac{7}{2}$ and the Fermi level right between them. Assuming hybridization and band formation, one was able to compute the existing lattice constants, but the calculated gap between the two bands was with about 200 meV for PuTe, at least 1 order of magnitude too large. However, the importance of f-d hybridization and the relativistic description of these compounds has been realized.

It is then obvious that no consistent description of the anomalous physical properties of the Pu chalcogenides has yet been given, so different aspects should be considered. We will show in the following that the Pu chalcogenides have intermediate valence in spite of what has been argued above. The discrepancy is solved by regarding the Pu chalcogenides as the high-pressure, collapsed phase of the corresponding Sm chalcogenides.[10] The reason that they are spontaneously in this collapsed phase is due to the larger radial extension of the $5f$ shell compared with the $4f$ shell.

INTERMEDIATE-VALENCE AND LATTICE PROPERTIES

Some principal properties of intermediate valence shall be recalled briefly. Generally speaking, this phenomenon has been observed only for lanthanides. It is still an open question whether USe and UTe, which both have a negative Poisson ratio, are intermediate valent because they show, in addition, ferromagnetic order at low temperatures, two features which so far are considered incompatible.[11] So, one typical feature for intermediate valence is a negative Poisson ratio. For the Pu chalcogenides this has not been measured. Another feature is a soft bulk modulus, which is less than the one of the corresponding di- and trivalent reference compounds.[12]

Compounds can be in the intermediate-valent state at ambient pressure like SmB_6,[13] YbB_{12},[14] or antiferromagnetic TmSe (Ref. 15), or they can be brought into this state from the divalent semiconducting form by the application of external pressure, as in SmS, SmSe, SmTe, or TmTe.[8] The selected examples by no means cover the vast amount of about 50 materials that are intermediate valent, but they all are examples of compounds which show hybridization gaps with the Fermi level being in this gap. The temperature dependence of the resistivity thus appears to be semiconductorlike with activation energies in the meV range.

The Tm chalcogenides represent an interesting example of how real pressure can be replaced by chemical pressure, i.e., substitution of ions with a smaller radius. TmTe is a divalent semiconductor, TmSe is intermediate valent, one can even produce any degree of valence mixing by alloying $TmSe_{1-x}Te_x$, and TmS is a trivalent metal. It would be very helpful if we could have similar conditions in the Pu chalcogenides, but they all seem to be in this anomalous state. There are especially no divalent reference compounds. However, is this really true? If we want a divalent Pu compound with the densely packed rocksalt structure, we should prepare a chalcogenide with an anion that has the largest possible radius—this is not Te but polonium Po. Thus, PuPo, plutonium polonide, has, in the authors' opinions, a high probability of being a divalent reference compound. On the other hand, PuO (not PuO_2) might be the trivalent reference compound and it probably must be prepared at high temperatures and high pressures just as is the case for GdO and SmO.[16]

From the position in the Periodic Table, the Pu chalcogenides are the actinide counterpart of the Sm chalcogenides. The latter exist at ambient conditions in the divalent, semiconducting form, but can be brought into the intermediate-valent and trivalent states by application of external pressure or chemical pressure by alloying with yttrium.[8] Since the Pu chalcogenides are neither divalent semiconductors (ruled out by the γ value of the specific heat and the optical plasma resonance of free carriers[17]) nor trivalent ($5f^5$) metals (ruled out by the nonmagnetic behavior), they must be intermediate valent, but have the high-pressure intermediate-valent state of the corresponding Sm chalcogenides.

Under the application of external pressure, a rocksalt divalent $4f$ compound will either change its electronic structure and become intermediate valent and eventually trivalent, or make a structural change towards a CsCl structure.[8] For most rocksalt actinides the transition to the CsCl structure has been established.[18] The transition pressure is usually above 100 kbar which, for typical deformation potentials, corresponds to about 1 eV. Thus, if the $4f^n$-$5d$ separation, the energy gap of a semiconductor, is larger than about 1 eV, at first one observes a transformation to the CsCl structure;[8] when the energy gap is less, the electronic transition towards intermediate valence comes first, followed by the CsCl structural change. As an example, for the Eu chalcogenides only EuO with a gap of 1.2 eV makes the electronic transition first; EuS, EuSe, and EuTe have larger gaps and make the structural change first. The Sm and Tm chalcogenides with very small energy gaps make the electronic transition first.[8] The reason for the small $4f^n$-$5d$ separation lies in the position in the Periodic Table which these rare-earth elements occupy. Divalent $4f^6$ and $4f^{13}$ rare earths are very unstable compared with the half-full or completely full neighboring $4f^7$ or $4f^{14}$ elements, thus their $4f$ ionization energy or $4f^n$-$5d$ transition energy is very small.[19] The divalent Pu chalcogenides would have the same f^6 configuration as the divalent Sm chalcogenides and their gap—obtainable with negative pressure—would be very small. In other words, at first they make the electronic-valence transition and at higher pressures, the structural transition.

Looking at the experimental volume-versus-pressure change of PuTe (Ref. 18), we observe the structural transition at 150 kbar. With the above reasoning, we would expect that the valence transition has occurred at lower pressures or even at ambient pressure. Comparing the bulk moduli of all measured actinide tellurides, it is remarkable that PuTe has, with 370 kbar, the smallest bulk modulus and is the softest material. It has, by an order of magnitude, the largest change in the bulk modulus $B_0' = 12$. These are indeed indications of intermediate valence. Here we want to remark that the bulk modulus of PuTe is even less than the one of UTe, which itself has a soft bulk modulus and a negative Poisson ratio.[11] PuSe has the softest bulk modulus of all transuranium selenides, but it is harder than USe,[11,20] which again has a negative Poisson ratio and is very soft. So, UTe and USe are not trivalent-actinide reference materials.

To make the matter more obvious we replot in Fig. 1 the volume-pressure curve of PuTe of Ref. 18. At 150 kbar we can safely assume that the compound is in its stable trivalent configuration, in fact, the bulk modulus is the same as in the trivalent neighbor compound NpTe. We thus can fit a Murnaghan equation at 150 kbar and below. However, we observe that the experimental PuTe curve, especially at low pressures, significantly deviates from theory, which has already been noted by the authors

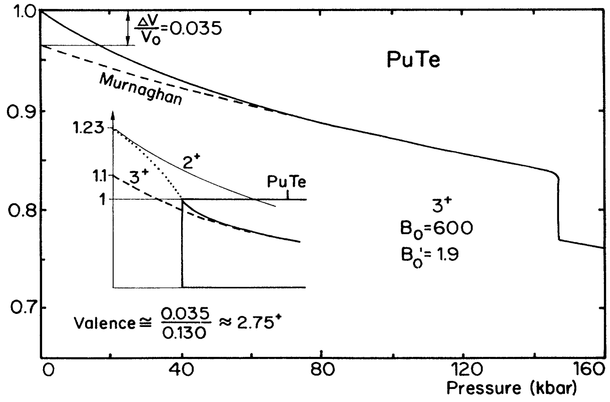

FIG. 1. Relative volume vs pressure of PuTe. Experimental values (solid curve) after Ref. 18. Dashed curve: trivalent Murnaghan equation with a fit at 140 kbar. Inset: relative volume vs pressure, same as the main figure but with an extension towards "negative" pressure and inclusion of a divalent Murnaghan equation.

of Ref. 18. The theory is, of course, only valid for an integer-valent compound, but if we discard physically unrealistic fits (such that with increasing pressure, PuTe transforms from a higher valence to a lower valence, i.e., a more voluminous configuration), we are left with the fit shown in Fig. 1 indicating trivalency at high pressure and intermediate valence between 2 and 3 at low pressures. In the inset of Fig. 1 we have continued the volume-pressure curves to negative pressures and we show the complete trivalent Murnaghan and also a divalent Murnaghan equation and, in addition, (dashed) the expected behavior of PuTe under expansion. The volume ratios larger than one are unusual, but this is caused by the experimental PuTe curve which has a value of one for an applied pressure of zero. We find, by linear interpolation between the divalent and the trivalent reference curves, that PuTe at ambient pressure has a valency of 2.75+.

We have already mentioned above that PuTe is the actinide counterpart of SmTe. We can thus take the experimental volume-pressure relation of SmTe (Ref. 8) and differentiate it to obtain the bulk moduli. This curve is shown in a relative-pressure scale (normalized with respect to the fcc-bcc transition pressure) in Fig. 2. In the same figure we plot the bulk moduli of PuTe (Ref. 18) also obtained by differentiating the volume-pressure experiment. It is obvious that the PuTe curve now falls exactly on the SmTe curve. The zero-pressure bulk modulus of PuTe is now, with 370 kbars, exactly the same as in SmTe under an applied pressure of 58 kbars. It is now indeed less than the one of a divalent (relative pressure 0) or a trivalent (relative pressure ~ 1) PuTe and thus typical for an intermediate-valence compound. In addition, the derivatives of the bulk moduli B' are the same for PuTe at zero pressure and SmTe at 58 kbars. Thus, it can be safely stated that PuTe at ambient pressure would be in the same condition as SmTe under an applied pressure of 58 kbars. Compared to the hypothetical divalent PuTe, real PuTe at ambient pressure has suffered a volume reduction V/V_0 of 0.81 (equal to 1/1.23 shown in the inset of Fig. 1). One-third of this value yields the change in the lattice constant. Starting from a lattice constant of 6.72 Å for the divalent PuTe, we obtain 6.29 Å for the lattice constant of PuTe at ambient pressure. This should be compared with the actually measured one of 6.19 Å, a difference of only 2%. In fact, this lattice constant is now less than the divalent one with 6.72 Å and the trivalent one with 6.56 Å calculated from the ionic radii of Pu and Te. It is exactly this point which has been constantly used as argument against the intermediate-valent nature of PuTe or the other Pu chalcogenides. The resolution of this problem is the evidence that the Pu chalcogenides are the high-pressure collapsed phase of the Sm chalcogenides.[10]

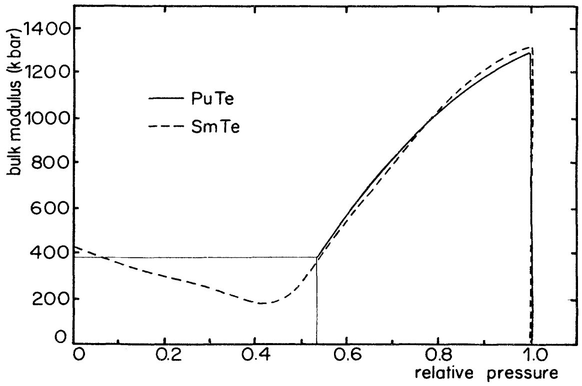

FIG. 2. Bulk moduli vs relative pressure of PuTe (solid curve) and SmTe (dashed curve) obtained by the differentiation of experimental volume vs pressure curves of Refs. 8 and 18. Both curves are matched at the fcc-bcc transition.

INTERMEDIATE-VALENCE AND ELECTRONIC STRUCTURE

The question remains to be answered of why the Pu chalcogenides represent the high-pressure phase of the Sm chalcogenides without using external or chemical pressure. To understand this we have to describe the essence of intermediate valence. It is basically given by the *f*-*d* hybridization between neighboring cations (on-site hybridization is forbidden due to opposite parity of the *f* and *d* wave functions).

An essential parameter in this hybridization is the separation in energy of the *f* and *d* states of semiconducting or insulating compounds. With partially occupied localized *f* states well below *d* bands (in the order of eV) as, e.g., in the Eu chalcogenides,[21] the *f*-*d* hybridization is small, thus the valence remains integral as verified by the Mössbauer effect.[22] But, since spins are involved, this so-called indirect cation-cation superexchange is nevertheless responsible for the magnetic properties. With the *f*-*d* separation reduced to a few tenths of an eV as in the nonmagnetic Sm chalcogenides[23] or in the magnetic $TmSe_{1-x}Te_x$,[12] the cations acquire various degrees of intermediate valence and the term "intermediate-valent semiconductors" has been coined.[12] Finally, with the application of pressure, the already present crystal-field splitting of the 5*d* band into t_{2g} and e_g subbands can be enhanced so much that the bottom of the 5*d* band enters the 4*f* state and the hybridizations augment significantly. We thus conclude that pressure only serves to increase the *f*-*d* hybridization in semiconducting materials.

If the Pu chalcogenides were divalent, they would be semiconductors with the $5f^6$ state a few tenths of an eV below the 6*d* band just as the semiconducting Sm chalcogenides are. However, the charge distribution of the 5*f* orbits extends outside the 4*f* orbitals, almost as far as to make a direct 5*f*-5*f* overlap, but not quite. The 5*f*-6*d* hybridization between neighboring cations thus is naturally much larger than the 4*f*-5*d* hybridization. Thus, comparing Sm and Pu chalcogenides, the latter do not need external or chemical pressures to arrive at the same degree of hybridization and intermediate valence as the former.

Once the *f* state is very close to (some tens of meV) or within the *d* band, due to the mixing of *f* and *d* wave functions, the *f* electrons have a certain probability to stay in the *d* band and the *f* state acquires a certain width—it becomes a narrow *f* band (some meV wide) but with an enormous density of states ($\cong 10^{26}/\text{cm}^3\,\text{eV}$). The total energy of all electrons can now be lowered by redistributing the electrons between *d* and *f* bands. Thus, the bottom of the *d* band undershoots the position of the *f* state appreciably as *f* electrons are pouring into the *d* band. The original occupation of the *f* state with six electrons in the divalent Sm or Pu chalcogenides will now be less than six, and since six electrons would correspond to divalency and five to trivalency, the condition of intermediate valence is obtained.

Where does this process terminate? It is well known that the ionic diameter of divalent rare-earth or actinide cations is about 10% larger than the one of a trivalent ion. In reducing the valence of a compound from divalent towards trivalent, the ionic diameter and the lattice constant shrink appreciably at the expense of the lattice energy—the repulsion term increases. It is thus obvious that the new equilibrium is found where the gain in electronic energy by lowering the Fermi level and the increase in lattice energy equal each other. This determines the degree of intermediate valence between 2 and 3.

For the theoretical description of the intermediate valence of a system of localized *f*- and *d*-band states, the Kondo effect has very often been invoked to describe the hybridization. In retrospect, this is basically unsatisfactory because, in rare-earth compounds, one does not have independent and dilute *f* impurities as in the true Kondo effect. The next variation, to use a so-called dense Kondo effect with the true density of *f* states, is also no progress because it does not contain the essence of the problem, namely, the periodicity of the *f* states. Thus, approaches using the periodic Kondo lattice or the periodic Anderson Hamiltonian are closer to reality.[24] This is not a criticism of these theories per se, but the result of the periodic models is qualitatively different compared to the nonperiodic models and it corresponds to experimental observation.

To illuminate this point, we show in Figs. 3(a) and 3(c) the dispersion of a localized periodic *f* state together with a classical band and their hybridization (dashed) and the resulting density of states in Figs. 3(b) and 3(d) with different Fermi energies E_F indicated. As soon as we treat the problem periodically, we obtain a double peak in the *f* quasiparticle density of states.[24,25] With a nonperiodic ansatz, we obtain only a single *f*-like density of states. We have to fill into this density of states the available number of electrons and find the Fermi level in the gap, or mostly pseudogap, or in one of the density-of-states peaks. The fact that one has a double-peak density of states with E_F in the gap has been experimentally verified on SmB_6, YbB_{12}, the high-pressure phase of SmS, and antiferromagnetic TmSe (e.g., Ref. 13) by an optical transition between the two density-of-states peaks. The above-mentioned materials are those for which the electrical resistivity indicates semiconducting behavior with gaps of a few meV. On the other hand, when the Fermi level is in one of the density-of-states peaks, the electrical resistivity indicates metallic behavior and the materials are heavy fermions. In most cases they are simultaneously intermediate valent, e.g., Ref. 26. Also, for these materials, optical transitions between the two density-of-states peaks have been observed.[26]

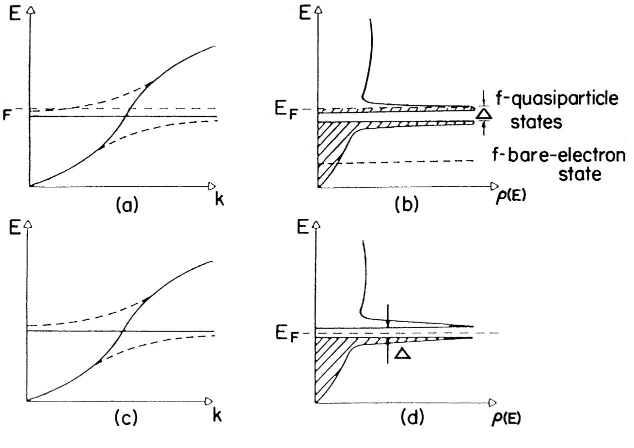

FIG. 3. Energy dispersion of a localized *f* state and a *d* band and their hybridization (a) and (c) and density of states of the two models (b) and (d).

THE MODEL

Once a double-peak structure of *f*-like quasiparticles superimposed with a more or less classical *d*-band density of states has been accepted, we can try to derive the electronic, magnetic, and thermodynamic properties of the material by using a renormalized Sommerfeld model of the quasiparticles which acquire heavy masses due to the high density of states (or narrow bands) of the *f* quasiparticle bands, which are not completely occupied. That the quasiparticles really are in a narrow band and acquire heavy effective masses can be derived from measurements of the de Haas–van Alphen effect which prove the existence of Fermi surfaces near E_F and effective masses of about 90 m.[27] This crude model has proven successful for practically all existing heavy fermions and some intermediate-valent compounds and has quantitatively described, with only one free adjustable parameter, the temperature dependence of the electrical conductivity, the specific heat, the temperature dependence of the γ value, and the temperature and field dependences of the magnetic susceptibility.[26,28–30] As experimental entities, the measured gap or pseudogap between the two quasiparticle bands and their bandwidth have been used besides the measured temperature dependence of conductivity, specific heat, and magnetic susceptibility. The two-band quasiparticle density of states has been modeled by two Gaussians; this choice is not important, but is convenient for the calculations. In the case of the Pu chalcogenides, or more specifically PuTe, measurements of gaps (meV) come from the temperature dependence of the conductivity,[4] the γ value from Ref. 5, and the magnetic susceptibility from Ref. 3.

We adopt, as a first approximation, a temperature-independent rigid-band model.[25] In this model, the main influence of temperature is to change the Fermi distribution function which, at room temperature, is much larger than the width of the whole double-peak electronic structure near E_F. Regarding the temperature dependence of the resistivity, we assume that heavy quasiparticles in the narrow subbands around E_F undergo collisions with other quasiparticles such as phonons or spin fluctuations. The latter will only be relevant at very low temperatures where the experimental conditions due to the self-heating of the material are not very precise. So, we concentrate on a temperature range above about 4 K. We also take into account thermal excitations of heavy electrons across the pseudogap, resulting in holes in the lower band and in additional electrons in the upper band. The sum of f and d electrons is six, the original occupation of the f state in divalent PuTe before the hybridization.

In principle, one wants to use the formula $\rho=1/\sigma=m^*/(ne^2\tau)$, where n and τ are temperature dependent. The effective masses of heavy electrons and holes are made equal $m^*=m_e^*=m_h^*$. The carrier concentration $n=n_{e_c}+n_c^{\text{exc}}+n_h$ and

$$n_{e_c}+n_c^{\text{exc}}=\int_{-\Delta/2}^{\infty}D(E)f(E-E_F(T),T)dE \ , \tag{1}$$

$$n_c^{\text{exc}}=n_h=\int_{-\infty}^{-\Delta/2}D(E)[1-f(E-E_F(T),T)]dE \ . \tag{2}$$

n_{e_c} is the carrier concentration at $T=0$ in the partially filled quasiparticle bands including the d electrons and Δ is the gap or pseudogap. $D(E)$ is the density of states (DOS) per cell and eV. By imposing $n_c^{\text{exc}}=n_h$, in order to keep the total number of heavy quasiparticles unchanged, we can determine the dependence of E_F on the temperature. With the experimentally determined gaps,[4] $E_F(T)$ changes very little with temperature. The important aspect is that one cannot approximate the Fermi function with an exponential as is usually done for semiconductors, since the standard condition that the Fermi energy is far away from the band edges is violated in this case. Also, one cannot put the Fermi function or its derivative in front of the integral as is usually done for larger bandwidth materials.

For the reciprocal scattering time we use, in a crude first approximation for $T>4$ K, a term linear in temperature, as is typical for electron-phonon scattering:[31]

$$\frac{m^*}{\tau}=\frac{\hbar k_F k\bar{\sigma}_a}{z^2}T\int_{-\infty}^{\infty}-\left[D(E)\frac{df(E)}{dE}dE\right] \tag{3}$$

where k_F is the Fermi vector, z the valence, and $\bar{\sigma}_a$ the average cross section for electron-phonon interaction. Using the latter as an adjustable parameter, we obtain, with the measured gap or pseudogap energies, a relatively good agreement of the temperature dependence of the resistivity with experiment.[26,28–30]

The next step is the computation of the specific heat and the γ value, the essential point being again that, with very narrow f-like subbands near and around E_F, the density of states $D(E)$ cannot be put in front of the integral of the total energy, as is done in the Sommerfeld theory. Thus,

$$c_v=\frac{dU}{dT}=\int_{+\infty}^{-\infty}E\,D(E)\frac{df(E-E_F(T))}{dT}dE \tag{4}$$

with $E_F(T)$ being the Fermi energy. We used, besides the gap and the double-Gaussian form of the density of states, the experimentally determined γ values and their temperature dependence.[26,28–30] It is obvious that, because of the very existence of a finite γ value, there is a certain density of states at the Fermi level, so if the latter falls into a gap it can only be a pseudogap. Then, in addition, in spite of seemingly semiconductorlike behavior of the electrical resistivity, it is clear that the resistivity for $T\to 0$ goes towards zero.

The large and mainly temperature-independent magnetic susceptibility of the Pu chalcogenides[3] prompts one to assume a Pauli susceptibility of heavy quasiparticles in narrow bands. A more or less large temperature region with relatively constant magnetic susceptibility, however, followed at higher temperatures by a Curie-like drop in the susceptibility is typical for intermediate-valent compounds[32,33] and heavy fermions.[26,28–30,34] For the Pu chalcogenides we assume, as a starting argument, that the experimentally observed rather constant susceptibility up to room temperature will be followed by the Curie-like drop above room temperature where no measurements exist. The temperature region of the Curie-like behavior commences when T is larger than the Fermi energy. That the latter can become very small for intermediate-valent and heavy-fermion materials can be simply visualized by using an adapted Sommerfeld model for heavy quasiparticles, namely,

$$E_F=(\hbar^2/2m^*)(3\pi^2n)^{2/3} \ .$$

With n, the carrier concentration, being about $10^{22}/\text{cm}^3$ and an effective mass in the order of 1000 m, we obtain E_F in the meV range.

To derive the Pauli magnetic susceptibility, we start with the total energy U in the following way:

$$U=\tfrac{1}{2}\int_{-\infty}^{+\infty}(E-\mu H)D(E)f(E-\mu H-E_F(T),T)dE$$
$$+\tfrac{1}{2}\int_{-\infty}^{+\infty}(E+\mu H)D(E)f(E+\mu H-E_F(T),T)dE \tag{5}$$

with $\mu=gJ\mu_0$ (g is the Landé factor, J is the quantum number of the momentum, μ_0 is the Bohr magneton), H is the magnetic field, $D(E)$ is the density of states, $f(E,T)$ is the Fermi distribution, and $E_F(T)$ is the Fermi energy which has been obtained from the condition that the total number of carriers is constant. Again, neglecting μH compared with the Fermi energy is not permitted, as is done in classical theory. Therefore, we obtain for the magnetization M and the susceptibility χ,[30]

$$M=\tfrac{1}{2}\mu\int_{-\infty}^{+\infty}D(E)[f(E-\mu H-E_F)$$
$$-f(E+\mu H-E_F)]dE \ , \tag{6}$$

$$\chi=\lim_{H\to 0}M(H)/H \ , \tag{7}$$

where the integral in Eq. (6) is the well-known expression of the Pauli magnetization.

COMPARISON WITH EXPERIMENT

The Pu chalcogenides offer severe experimental problems, mainly because of their high radioactivity (they are α emitters) which enforces a strict encapsulation of the crystals or measurements in clumsy glove boxes. In addition, the self-heating due to the radioactive decay makes measurements below about 4 K extremely difficult and undependable. For example, the specific heat has only been measured down to 10 K (Ref. 5) and then has been extrapolated towards zero temperature to obtain the γ value whereas in, e.g., $CeCu_2Si_2$, an upturn of the γ value by an order of magnitude only occurs well below 7 K.[34] Thus, in PuTe, a much more significant heavy-fermion behavior than suggested by the γ value remains an open question, although our model would rather exclude this. Another problem is the temperature dependence of the resistivity which yields two activation energies (2 and 20 meV),[4] obtained by an Arrhenius plot. This implies that the Fermi function can be replaced by the Boltzmann factor, an approximation that is only valid when the Fermi energy is far from the band edges, which is certainly not the case with such small gaps. The best method to measure directly the gaps or pseudogaps would be far-infrared optical spectroscopy at very low temperatures;[13,26,28–30] however, it will be a long time before such measurements can be performed on "hot" samples, although visible and near-infrared spectroscopy at room temperature has been performed recently for the first time on the Pu chalcogenides.[17]

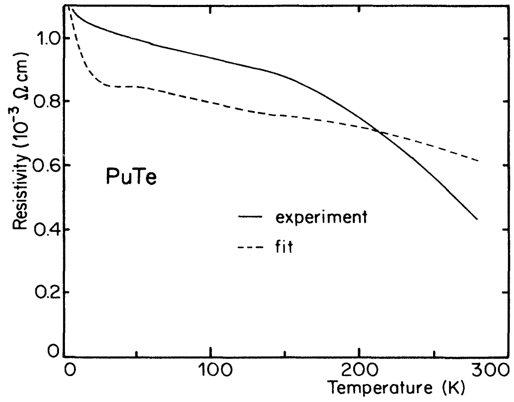

FIG. 5. Temperature dependence of the resistivity of PuTe. Experimental data after Ref. 4 (solid curve). Fit with the model, Eqs. (1)–(3).

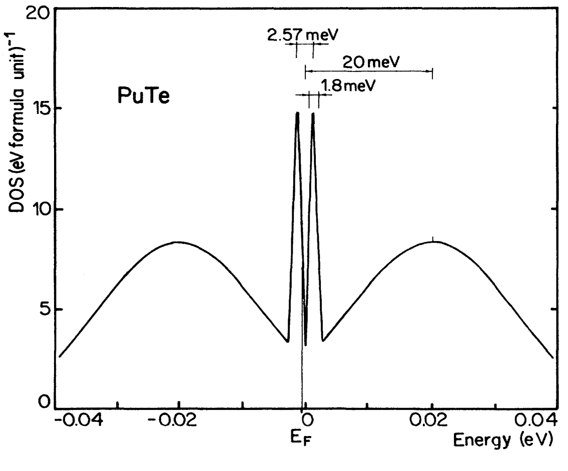

FIG. 4. Density of states per eV and formula unit of PuTe near E_F.

The two experimentally observed activation energies[4] prompted us to assume two Gaussian distributions for the density of states of the f-like quasiparticles as shown in Fig. 4. A multiple-peak density-of-states structure derived from far-infrared spectroscopy indeed is quite common in heavy-fermion compounds such as UPt_3 (Ref. 28) or $CeCu_6$.[35] We used a computer to make an optimal fit for the temperature dependence of the resistivity[4] and the magnetic susceptibility[3] using the equations mentioned above. The fits for each single physical property turned out to be rather good, with energies ranging within a factor of 2 of the values quoted in Fig. 4. We preferred, however, to choose energy values which remain the same for both physical properties mentioned above, namely, those shown in Fig. 4, and tolerate a less than optimal fit. Nevertheless, the gap values finally used and shown in Fig. 4 are very close to those measured experimentally.[4] The temperature dependence of the resistivity of PuTe is thus shown in Fig. 5 and that of the magnetic susceptibility is shown in Fig. 6. The inset of Fig. 6 exhibits the behavior of the susceptibility in that low-temperature range which is not accessible at the moment but can be reached with other Pu isotopes. It is remarkable that the theory reproduces the steep increase of the susceptibility below

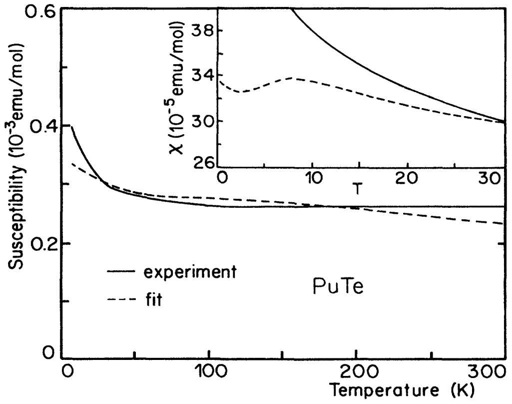

FIG. 6. Temperature dependence of the magnetic susceptibility of PuTe. Experimental data after Ref. 3 (solid curve), fit with the model, Eqs. (6) and (7). The inset shows a blown up extension towards lower temperatures.

about 30 K, but for the lowest temperatures turns into a flat maximum. In Fig. 7 we finally show how the susceptibility behaves for still higher temperatures than measured up to now. We indeed find the $1/T$ (or Curie-like) drop of the susceptibility commencing a little above room temperature. Of course, changes in the energy values of Fig. 4 within a factor of 2 also vary the onset temperatures of this drop within about a factor 2. The sum rule and the condition for the chemical potential, that the total number of the quasiparticles remains constant, served to fix the Fermi energy, which is also indicated in Fig. 4, and remarkably enough nearly falls into the pseudogap. This is the main reason why one observes an activated resistivity, but the fact that we have a pseudogap necessitates that the resistivity drops to very small values for extremely low temperatures. In fact, we believe that the resistivity behavior of PuTe is similar to the one of SmS under a pressure of 8 or 10 kbars.[36] Because of the higher pressures needed for SmTe, the real 4f counterpart of PuTe, a similar experiment is missing.

In spite of the fact that the Hall effect has been measured on PuTe,[37] no analysis of the carrier number has been given. However, it has been stated that the Hall resistivity is semiconductorlike with two gaps of the already mentioned magnitude. On solid solutions of $PuSb_{0.9}Te_{0.1}$ and $PuSb_{0.8}Te_{0.2}$, an analysis has been made and the carrier concentration was 0.15 and 0.13 per formula unit, respectively.[37] The trend is going in the direction that, for pure PuTe, the carrier concentration will be much less. Our model permits the calculation of the temperature dependence of the carrier concentration $n_c^{\text{exc}}+n_h$. At about 160 K we find 0.16, at 20 K, 0.024, and at 1 K, 0.005 carriers per formula unit, respectively. (Recall that the density of states is not zero at E_F.)

The specific heat can also be calculated from our model [Eq. (4)] or from the measured susceptibility. We obtain a γ value between 100 and 20 K of about 20 mJ/mol K^2, slightly increasing to 25 mJ/mol K^2 towards 0 K, similar to the temperature dependence of the magnetic susceptibility (Fig. 6). The Wilson ratio is an independent method to calculate the γ value from the susceptibility and it has proven to be valid in other heavy-fermion compounds.[28-30] We obtain 19 mJ/mol K^2 from the Wilson ratio.[38] This good agreement just shows the consistency of the models. However, the experimental γ value is, with 69 mJ/mol K^2, somewhat larger,[5] but we have pointed out above the experimental problems in obtaining this value. In addition, we expect another contribution to the specific heat which has not been taken into account at all,[5] namely, a Schottky-type anomaly caused by thermal excitations across the various density-of-states peaks shown in Fig. 4. To give a rough estimate of the temperatures where we expect such anomalies, we take the density-of-states peaks as sharp-level systems and calculate with the given energy separations of Fig. 4, 11, 80, and 230 K. Because we actually have a distribution of density of states, the peaks will not be as sharp as for classical Schottky anomalies. The one at 11 K certainly would severely affect an estimate of a γ value, and would lower it. The one at 230 K can possibly be associated with the observed peak at 260 K for which there is no explanation.[5] Schottky-type anomalies of the specific heat have been experimentally observed in heavy-fermion systems and we could quantitatively associate them with transitions between the density-of-states peaks.[29] Only when the specific heat of PuTe has really been measured down to at least 1 K, can an experimental confirmation be obtained.

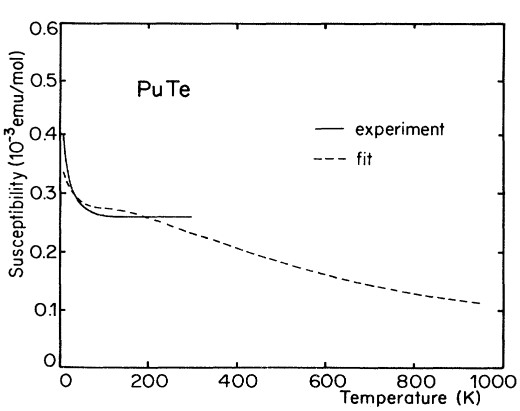

FIG. 7. Temperature dependence of the magnetic susceptibility of PuTe and an extension towards high temperatures.

Our model permits us to calculate from our γ value and the density of states at E_F the effective mass of the heavy quasiparticles. We obtain $m^*=65$ m, which is a "lightweight" heavy fermion,[38] though with intermediate valence.

CONCLUSION

We showed in this paper that the surprising and confusing experimental data on the Pu chalcogenides can be consistently explained with the assumption that the Pu chalcogenides represent the high-pressure intermediate-valent form of the isoelectronic Sm chalcogenides. Pressure in the divalent Sm chalcogenides serves only to enhance the f-d hybridization to achieve the intermediate-valent state, whereas in the Pu chalcogenides f-d hybridization is achieved without pressure due to the larger orbital extent of the 5f wave functions compared with the 4f wave functions. By comparing the pressure dependence of the bulk modulus of PuTe with the one of SmTe, an estimate of the degree of hybridization of PuTe under normal conditions could be obtained. PuTe under normal conditions is in the same state as SmTe under an applied pressure of 58 kbars and its degree of intermediate valence is 2.75+. Although in this paper we concentrate mostly on PuTe because most experimental data are available for this material, the resulting electronic structure would also be typical for the rest of the Pu chalcogenides.

For the electronic properties we use the model which has proved successful, for intermediate-valent and heavy-fermion compounds,[26,28-30] that the hybridization of f and d wave functions leads to (at least) a double peak in the density of states of renormalized heavy quasiparticles; the peaks are modeled by a Gaussian distribution. The width of these peaks and their separation in energy are then determined by fits of the temperature dependence of the resistivity, the specific heat, and the susceptibility using Eqs. (1)–(7). The essential point in using these equations is that, in all cases, the Fermi function or its derivative cannot be pulled in front of the integrals as is done in the usual theory because the Fermi function is strongly varying over the energy range of the density-of-states peaks. The position of the Fermi level, the carrier concentration, and the effective mass are then consequences of the calculation. It is remarkable that the Fermi level practically falls into the pseudogap of PuTe, which is the reason that one observes an activated conductivity and a small γ value of the specific heat.

Intermediate-valent materials, which have in common that the temperature dependence of the resistivity appears activated, have the Fermi level in the gap or pseudogap and, in addition, obey the Luttinger theorem.[39] This theorem states that, whenever the sum of f and d quasiparticles is even, the Fermi level is in the hybridization gap. An even sum is only obtained for Sm, Yb, Pu, and No chalcogenides (for the exception of antiferromagnetic TmSe, see Ref. 26). It is thus remarkable that the Fermi level of PuTe using our model falls about into the pseudogap without making use of the Luttinger theorem, but nevertheless obeys it.

Measurements that should be done in the future and might support this model are the growth of the Pu chalcogenides with other Pu isotopes which do not lead to a self-heating due to radioactive decay and thus permit measurements to lower temperatures. The measurement of the magnetic susceptibility should be carried to high enough temperatures above room temperature so as to permit the observation of the Curie-like decay of the susceptibility. The measurement of the L edge might permit the observation of two edges due to the intermediate valence. Such measurements are in progress.[40] The Mössbauer effect could possibly be measured and could become useful when a divalent Pu reference material is found. We propose the growth of PuPo single crystals. Finally, the elastic constants should be measured to verify a negative Poisson ratio in the Pu chalcogenides. Such experiments are in progress in our laboratory.

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