Theory of the anomalous magnetic phase transition in UNiSn

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(Received 6 May 1996; revised manuscript received 28 May 1996)

The anomalous magnetic phase transition in UNiSn is explained on the basis of electronic-structure calculations. The energy band approach in which the local density Hamiltonian is generalized with an additional on-site Coulomb interaction U provides a fully satisfactory picture of both the metallic antiferromagnetic ground state and the paramagnetic semiconducting state, with a band gap of 0.12 eV, as well as a total energy difference of the correct magnitude as compared to the Néel temperature. [S0163-1829(96)51230-0]

UNiSn displays one of the most peculiar phase transitions: it is a *semiconducting* paramagnet at higher temperatures, but becomes a *metallic* antiferromagnet at temperatures below the Néel temperature $T_N \approx 45$ K.[1–3] This anomalous phase transition has drawn considerable attention, as it is typically not a Mott-Hubbard-type metal-insulator transition. More appropriately, it is an *inverse* metal-insulator transition, since at temperatures above T_N a band gap is not closed, but rather opened. In spite of it being thoroughly investigated, the underlying mechanism has still not been explained. Experimental investigations showed that UNiSn has the Heusler C_{1_b} (i.e., MgAgAs-type) structure, within the type I antiferromagnetic (AF) phase a magnetic uranium moment of about $(1.55 \pm 0.10)\mu_B$.[4] In the semiconducting state, UNiSn is reported to have an intrinsic band gap of approximately 0.105–0.12 eV.[1,3] The metal-insulator transition, furthermore, takes place almost without any significant lattice deformation.[2] Generally it is assumed that the inverse metal-insulator transition is due to a unique behavior of the uranium $5f$ electrons.[4,5] These are undoubtebly correlated, but there is no indication of heavy electron behavior, as the specific heat coefficient of UNiSn is quite modest, $\gamma \approx 18$–28 mJ/mol K^2.[1,5] In this paper, we present a theoretical explanation of the anomalous phase transition. We adopt as a *model* approach a band-structure description based on the local density approximation (LDA) of density functional theory generalized with an on-site Coulomb correlation U (LDA$+U$), and show that this model approach correctly describes *a whole group of materials* including UNiSn.

Previous theoretical studies of UNiSn were based on electronic structure calculations within the LDA as well as including orbital polarization (OP).[6,7] Scalar-relativistic LDA calculations predicted UNiSn to be a half-metallic ferromagnet,[6] i.e., metallic for majority, but semiconducting for minority spin electrons (see also Ref. 8). Although at first sight the predicted half-metallicity seems to be close to the observed semiconducting state, ''half-metallic'' really means metallic, and ferromagnetic ordering was never confirmed. Also, the large spin-orbit interaction (SOI) of uranium should not be neglected (cf. Ref. 9). Other relativistic band-structure calculations, which took SOI and OP into account, gave a reasonable value of the magnetic moment in the AF state.[7] However, on the basis of these electronic-structure calculations the anomalous phase transition could not be explained. Another, quite different attempt to approach its mechanism has been made through studying a model Hamiltonian.[10] The thus obtained information might be useful, however, it depends on the choice of the model Hamiltonian, which was chosen to match the fictitous half-metallic ferromagnetic state.[10]

In studying UNiSn, it is important to note that it belongs to a group of closely related ternary actinide compounds.[1–3] None of these, however, shows the exceptional behavior of UNiSn. An explanation of the phase transition in UNiSn would be of no value, if one cannot at the same time understand why these related compounds exhibit a different behavior. For this reason, we have also investigated two other compounds, ThNiSn and UPtSn, which also crystallize in the MgAgAs structure.[1] ThNiSn is a suitable reference compound, because it has no occupied $5f$ electrons. It does not undergo a metal-insulator transition, so that it remains a paramagnetic (PM) semiconductor down to zero temperature.[1–3] UPtSn, on the other hand, undergoes a PM to AF phase transition at approximately 75 K, but remains semiconducting at all temperatures.[1] Contrary to UNiSn, the band gap in UPtSn is thus not closed by the magnetic ordering. It is, however, difficult to make good quality samples of UPtSn, therefore its physical properties are less well established (see, e.g., Ref. 11).

The application of plain LDA calculations to f-electron systems meets problems in most cases, because of the correlated nature of the f shells. Applied to UNiSn, the LDA yields a strong f hybridization of states at the Fermi energy E_F, while photoemission experiments locate the $5f$ states about 0.55 eV below E_F for UNiSn and about 0.75 eV for UPtSn.[12] To account better for the on-site f-electron correlations, we have chosen the LDA$+U$ approach,[13] using the von Barth–Hedin exchange-correlation parametrization,[14] together with a fixed $U = 2$ eV, which is applicable for uranium.[15] The Hubbard-like U acts in this approach naturally only on the correlated f electrons. ThNiSn has no occupied f electrons, wherefore no U is to be applied. Within this well defined model approach, all ground state properties are derived from total energy minimization.[16] The band-structure calculations were performed using the fully relativistic linear muffin-tin orbital method with combined corrections.[17] The band gaps computed in this way can depend on the particular atomic sphere radii. To eliminate this

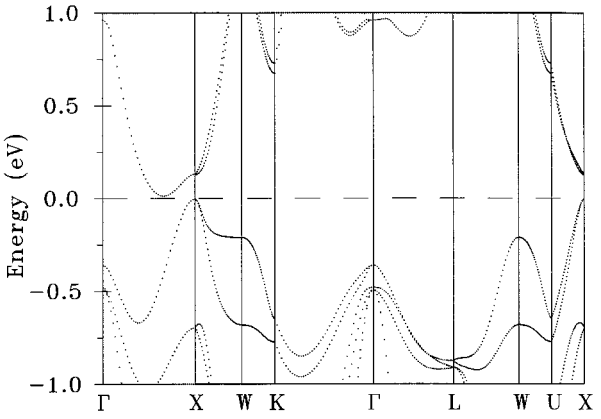

FIG. 1. Band structure of PM ThNiSn, calculated for the single unit cell of the MgAgAs structure.

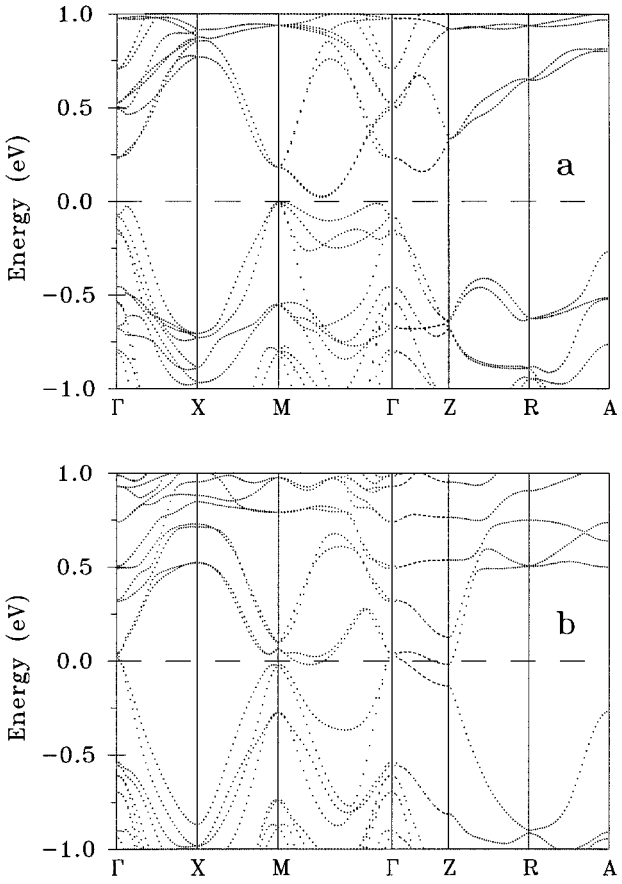

FIG. 2. Band structure of UNiSn in the PM phase (a), and (b) in the AF phase ($m=-3,\ -2$ configuration; see text), as calculated with the LDA+U method. Both band structures are shown in the double (i.e., AF) unit cell for comparison.

dependence we calculated the atomic sphere radii by minimizing the Hartree energy.

Using this model approach, we carried out self-consistent calculations in the single and double (i.e., AF) unit cell, with restricting the spin polarization to the PM, AF, and ferromagnetic state, respectively. For uranium we adopted a $5f^2$ occupation, which is in accordance with susceptibility measurements.[5] Total energy differences of all candidate ground states were considered to find the lowest energy state. Furthermore, we analyzed the relationship between magnetic ordering and the band structure near E_F, considering the occurrence of an excitation gap as a ground state property.

The numerical results we obtained with this approach completely correctly describe the different physical behavior of ThNiSn, UNiSn, and UPtSn: ThNiSn is found to be a PM semiconductor, with an indirect band gap of 0.03 eV and a direct gap of 0.13 eV (see Fig. 1), which is in accord with the measured gap of 0.066–0.149 eV,[2,3] and a recent scalar-relativistic calculation.[18] For UNiSn and UPtSn we obtain an AF ground state, which is *metallic* in UNiSn, but *semiconducting* in UPtSn. Next in energy above the ground state, a *semiconducting* PM state is found for both UNiSn and UPtSn. For PM UPtSn an excitation gap of 0.21 eV is obtained, while for PM UNiSn a smaller gap is obtained, with a direct value of 0.12 eV and an indirect value of 0.04 eV. These gaps are close to those found experimentally in the PM phases.[1–3] The calculated band structures of UNiSn and UPtSn in the PM and AF phase are shown in Figs. 2 and 3.

The metal-insulator transition due to the onset of antiferromagnetism in UNiSn is precisely reproduced when explicit on-site Coulomb interactions are added to the LDA Hamiltonian. Even the subtle difference in the behavior of the isoelectronic compound UPtSn, which does not become metallic, is described. In the present work we are not concerned with discussing the merits of LDA+U, but with the physics of the inverse metal-insulator transition. However, before we can analyze the origin of the inverse metal-insulator transition in UNiSn, and of the striking difference between UNiSn and UPtSn, some remarks about the LDA+U method and other physical quantities are to be made.

First, it should be mentioned that LDA+U is a crude correction to LDA, but it nevertheless captures the basic physics. The Coulomb repulsion brings two occupied f states down by $U/2$, while the unoccupied ones are shifted up by $U/2$. This physically motivated correction yields state dependent potentials. The down-shifted states are, notably, *not strictly localized*, but they hybridize, and together with all other electrons relax to self-consistency. In effect, the $5f$ density of states has a broad shape, with its maximum at 0.57 eV below E_F for PM UNiSn, and at 0.85 eV for PM UPtSn. This is in close agreement with photoemission spectroscopy, which places the $5f$'s 0.55 eV, 0.75 eV below E_F for UNiSn, UPtSn, respectively.[12] Another quantity to be discussed is the magnetic moment, which depends particularly on the orbital occupations. In the LDA+U approach one has to determine via the LDA+U prescription and the total energy those states out of the seven angular momentum states per spin that are to be occupied. For the PM phase it is natural to populate $m=0$ for both spin directions. In the AF phase we find that the configuration with $m=-3$ and $m=-2$ states of one spin direction occupied gives the lowest total energy. Second in energy above the $m=-3,\ -2$ configuration is the configuration with the $m=-3,\ -1$ states of one spin populated. The spin moment is in both configurations $-2\ \mu_B$, but the resulting total uranium moment is 2.48 μ_B for the $m=-3$,

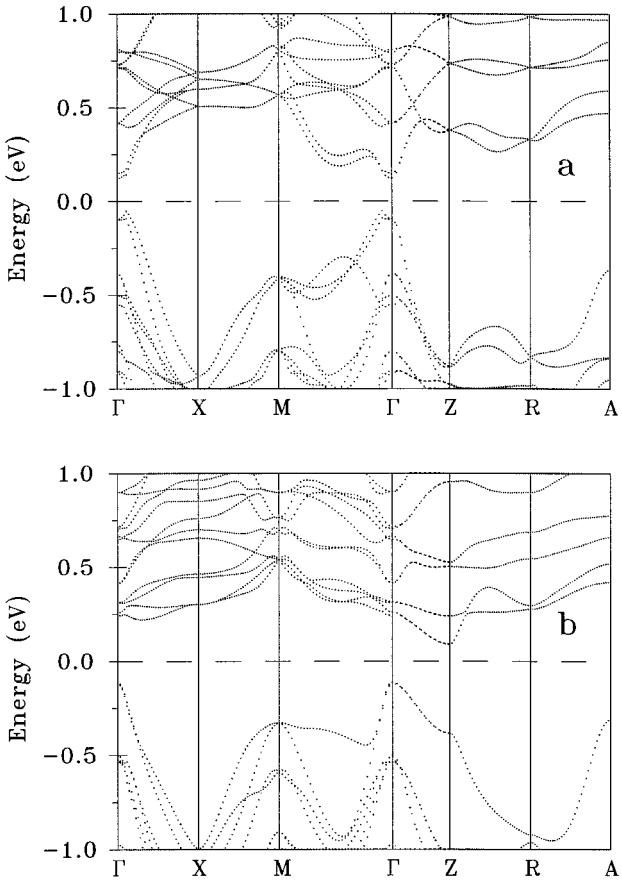

FIG. 3. As Fig. 2, but for UPtSn.

-2 configuration, while that of the $m=-3,\ -1$ configuration is $1.61\mu_B$. The later moment is closer to the experimental value of $(1.55\pm 0.10)\ \mu_B$.[4] Due to spin fluctuations, a mixing of these two m configurations can occur, which would lead to a reduction of the ground state moment. We note, however, that although the magnetic moment depends on the configuration of m states, the physics of the metal-insulator transition does not depend on it: *Both* the $m=-3,\ -2$ and the $m=-3,\ -1$ configuration give metallic behavior for AF UNiSn, and semiconducting behavior for AF UPtSn. Moreover, we find that the metallic/insulating behavior in these compounds does also not depend on the precise value of U.

Second, we consider the energy scales on which the magnetic phase transition takes place. For UNiSn we find a total energy difference between the PM and AF state (with $m=-3,\ -2$) of about 160 K per electron, while for UPtSn we obtain about 360 K per electron. These values compare quite well with the experimental Néel temperatures of about 45 K for UNiSn and 75 K for UPtSn,[1] when one takes into account that we neglect spin fluctuations. These energy differences are, on the other hand, much smaller than the gap energies, which correspond to about 1300 K for UNiSn, and 2400 K for UPtSn.

The main questions, which are to be addressed now, are what is the origin of the metal-insulator transition in UNiSn, and why is the behavior of UNiSn so different from that of UPtSn? To start with, we find that the degree of localization of the ''semilocalized'' $5f$ electrons differs in the two compounds. It is important to note, that although the same U is applied in both cases, already in the PM phase the occupied f electrons in UPtSn relax to a 0.28 eV deeper position. This is caused by the different crystal potentials, which are in turn due to the larger lattice constant of UPtSn [6.617 Å versus 6.385 Å for UNiSn (Ref. 1)], the different SOI of Ni and Pt, and the position of the Pt d states, which are energetically much lower than the Ni d states. This explains the already larger band gap of UPtSn in the PM phase, since in these compounds Ni and Pt like to have a full d shell (d^{10}). As for the metal-insulator transition, we find that in going from the PM to the AF configuration, a complete energy band reconstruction takes place, in which the connectivities of the bands change (see Figs. 2 and 3). We furthermore find that in the AF phase the occupied $5f$ states relax farther in both compounds by about 0.6 eV to a position *deeper* below E_F. Major band-structure rearrangements do thus occur upon AF ordering. The important bands for the metal-insulator transition are the hybridized bands near E_F, which are not of f character, but more free electron like, e.g., Sn(p), U(d), and Ni(d) or Pt(d). These bands become rearranged in the AF phase, because the corresponding orbitals strongly interact with the asymmetric, spin and orbitally polarized $5f$ states through polarization dependent exchange interaction. This reconstruction of the energy bands in UNiSn is large enough to close the already rather small gap in PM UNiSn (see Fig. 2). In UPtSn also a reconstruction of the energy bands near E_F occurs, but the gap in PM UPtSn is larger than that in UNiSn, and the reconstruction of the hybridized bands is not big enough to close the gap, leading thereby to a completely different physical behavior from UNiSn.

With regard to the combination metal-insulator, AF-PM phase transition, we expect another type of highly correlated mechanism, because spin fluctuations are strongly coupled to charge fluctuations through SOI. A local spin excitation in the PM state can obviously locally close the gap for charge excitations. Many-body techniques are needed to investigate this mechanism. In an applied magnetic field pronounced changed of the resistivity can be expected, as witnessed by the observed giant magnetoresistance $[(\rho(0)-\rho(B))/\rho(B)\approx 600\%]$ near T_N.[3]

In conclusion, electronic-structure calculations which take strong on-site Coulomb interactions of the $5f$ electrons into account quantitatively explain the exceptional behavior of UNiSn, as compared to ThNiSn and UPtSn. The inverse metal-insulator transition in UNiSn is found to be due to a reconstruction of the bands caused by the polarization dependent exchange interaction of the valence orbitals with the semilocalized, spin and orbitally polarized $5f$ states. This is an as yet unprecedented mechanism for a metal-insulator transition. We propose that the theory given here can be verified experimentally by photoemission spectroscopy on UNiSn and UPtSn in the AF phase. Also it would be of urgent interest to investigate experimentally the possibility of a pressure induced inverse metal-insulator transition in UPtSn.

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