Electronic properties of the half-metallic ferromagnetic NiUSn

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The electronic structure of NiUSn was obtained using a spin-polarized scalar relativistic linear muffin-tin orbital (LMTO) method. The self-consistent calculations were performed at the observed experimental lattice constant for the cubic MgAgAs crystal structure. Because of the open nature of this crystal structure the LMTO combined correction terms as well as additional empty spheres were used. Like transition-metal analogs (NiMnSb, for example) NiUSn is found to be a half-metallic magnet, with a semiconducting gap in the minority-spin bands and metallic behavior for the majority-spin bands. The calculated magnetic moment ($1.99\mu_B$) was found to be about $\frac{2}{3}$ of the experimental high-temperature value ($3.08\mu_B$).

INTRODUCTION

Uranium (U) intermetallic compounds have many unusual superconducting, magnetic, and transport properties that are believed to be due to the U $5f$ electron states. The list of anomalous behavior includes high specific-heat coefficients (γ) at low temperatures (heavy-electron systems),[1] unusual temperature-dependent susceptibilities (spin fluctuators),[2] extra peaks in valence x-ray photoemission and bremstrahlen isochromat spectroscopy XPS/BIS data (Kondo effects),[3] and high resistivities with unusual temperature dependence.

The TUSn and TUSb series, where T is a transition-metal atom, have recently been found to have unusual resistivity properties.[4] The compounds with the highest resistivities show a low-temperature maximum followed by an exponential decrease. These systems are also characterized by rather modest γ values so that their unusual resistivities are not thought to be associated with heavy-electron behavior. Gaps on the order[4] of 0.1–0.5 eV result from fitting the high-temperature resistivity data with a gap equation ($\rho \sim \exp[-E_{\rm gap}/2k_BT]$). Of these compounds NiUSn has the most pronounced peak at low temperatures.[4] The XPS spectra of some of these U compounds forming in the MgAgAs structure have also recently been obtained.[5] For NiUSn, resonant spectra suggests itinerant U $5f$ states with a peak 0.5 eV below the Fermi energy (E_F).

These and similar thorium (Th) compounds form in three different crystal structures: the cubic MgAgAs, the hexagonal Fe_2P, and the $CaIn_2$ structures.[6] NiUSn, which is the focus of this paper, crystallizes in the fcc-based cubic structure (space group $F43m$). This structure is closely related to the Heusler alloys of type $L2_1$, and can be described as four interpenetrating fcc lattices. For the MgAgAs structure there are atoms at positions Y (0,0,0), Z ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$), and X_2 ($\frac{3}{4},\frac{3}{4},\frac{3}{4}$). The difference between the $L2_1$ and the $C1_b$ (MgAgAs) structures is that the former has atoms at X_1 ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$) while the latter does not. So NiUSn has the same crystal structure as NiMnSb, whose electronic structure has been reported in Ref. 7.

The electronic-structure calculations found NiMnSb to be a half-metallic ferromagnet.[7] By that it is meant that for the two sets of bands with different spins, the majority spin bands intersect the Fermi energy (E_F) (metallic behavior) while the minority-spin bands have a gap at E_F (semiconductor behavior). In NiMnSb it was found that the Ni d bands through hybridization play only a small role in the half-metallic behavior and that it is the strong exchange splitting of the Mn d bands coupled with the loss of inversion symmetry that creates this electronic structure[7] and the large itinerant magnetic moment. Because NiUSn has this same crystal structure and exhibits both an unusual magnetic and resitivity behavior, we were motivated to consider its electronic structure. We were particularly interested in effects generated by the $5f$ states of the U atom.

METHOD

The electronic structure of compounds with actinide components is complicated by simultaneous, large spin-orbit and spin-polarization components.[8] While the theory for performing spin-polarized Dirac calculations within the local-density approximation (LDA) has been developed[9] and some calculations have been performed,[10] this approach has not yet developed to the point of being used routinely or self-consistently for such compounds. Since the interest in NiUSn is also in its magnetic properties we have performed self-consistent-field scalar relativistic spin-polarized calculations. The effect of spin-orbit coupling in the valence states will be considered in the future as this is the mechanism for generating large magneto-optical effects. The present calculations were carried out using the LMTO method with the combined correlation terms included.[11] The von Barth–Hedin exchange-correlation potential was used.[12] The electronic structure was converged using 95 **k** points in the irreducible wedge of the MgAgAs Brillouin zone. The calculations were performed in the Cl_b crystal structure with empty spheres at the X_1 ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$) position. The density-of-states (DOS) functions were obtained using the tetrahedron method.[13] Spin-orbit coupling was included in the core states, which were held fixed during the self-consistent iterations of the valence states. The experimental lattice constant [12.065 a.u. (Ref. 6)] was used.

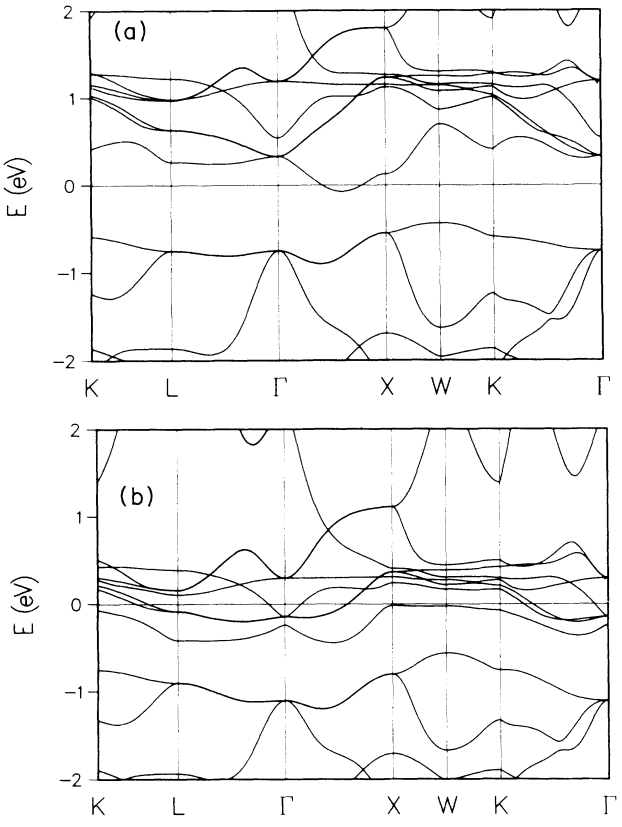

FIG. 1. Electronic structure of NiUSn along symmetry directions for (a) the minority-spin bands and (b) the majority-spin bands.

RESULTS AND DISCUSSION

In Fig. 1 the bands for (a) the minority and (b) majority spins are given along the high-symmetry directions of the fcc Brillouin zone. The unusual feature seen in the NiMnSb band structure, namely, a semiconducting gap in the minority-spin bands with the majority-spin bands cutting E_F, is also seen in this compound. The position

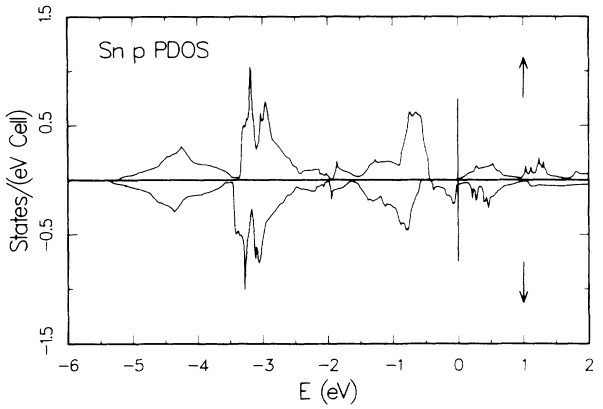

FIG. 3. The partial DOS function for the $l=1$ (p) spin-up and spin-down states around the Sn sites. E_F is at zero.

of E_F is determined by the majority bands so that in our calculation it unfortunately comes at the top of the gap in the minority bands instead of being in the gap itself. Because we have neglected important spin-orbit effects in these calculations we have not felt that it was worthwhile to play with the exchange-correlation potential or other refinements in order to slightly shift E_F into the minority-spin gap, which is in accord with the experimental results. In Fig. 2 the total majority (spin-down) and minority (spin-up) DOS functions are presented. The extent of the exchange splitting of the bands is seen in the difference between the spin-up and spin-down DOS functions. To understand this structure the partial DOS functions for the Sn p states, the Ni d states Ni, and the U f states, which are the dominant states near E_F, are given in Figs. 3–5. These show the gap in the minority-spin states at E_F, that the exchange splitting is largest (1.5 eV) for the U $l=3$ states, and that these states give the dominant contribution to the metallic behavior. The exchange splitting of the Ni d states is much less (0.1 eV), but there are differences in these spin-up and spin-down states near E_F. The p states on the Sn sites have almost no shift of the spin-up and

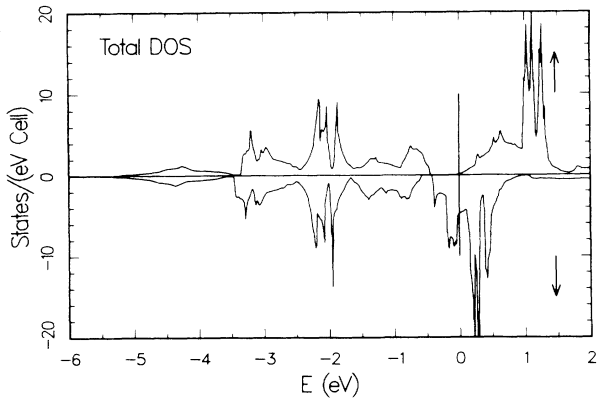

FIG. 2. The total DOS functions for the spin-up and spin-down states. E_F is at zero.

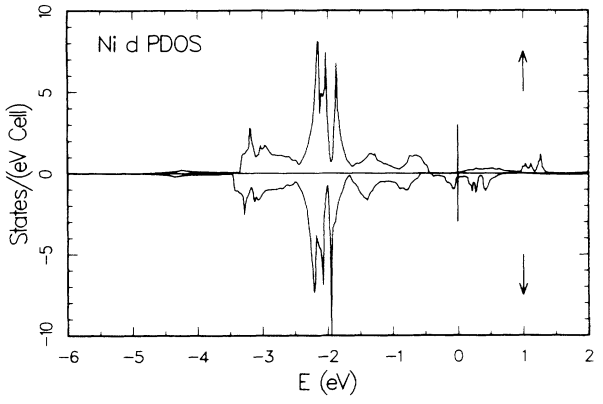

FIG. 4. The partial DOS functions for the $l=2$ (d) spin-up and spin-down states around the Ni sites. E_f is at zero.

TABLE I. Charge-density analysis in terms of spin-up and spin-down densities around each site. Also given is the charge transfer and spin moment around each site.

	Ni site				U site			
l character	s	p	d	f	s	p	d	f
Spin down	0.460	0.537	4.481	0.051	0.122	0.112	0.615	2.108
Spin up	0.441	0.532	4.482	0.031	0.120	0.112	0.555	0.368
Sum	0.901	1.069	8.963	0.082	0.242	0.224	1.170	2.476
Difference	0.019	0.005	−0.001	0.020	0.002	0.000	0.065	1.740
Charge transfer per site			+1.01				−1.88	
Site moment			0.04				1.80	
	Empty site				Sn site			
l character	s	p	d	f	s	p	d	f
Spin down	0.319	0.289	0.141	0.049	0.648	0.929	0.115	0.017
Spin up	0.240	0.248	0.130	0.042	0.656	0.945	0.090	0.016
Sum	0.559	0.537	0.271	0.091	1.304	1.874	20.5	0.033
Difference	0.079	0.041	0.011	0.007	−0.008	−0.016	+0.025	0.001
Charge transfer per site			+1.45				−0.59	
Site moment			0.14				0.001	

spin-down bands relative to each other, although there are also differences near E_F. From these results we conclude that the exchange splitting of the U f ($l=3$) states dominate the electronic structure near E_F and that differences in the other bands are due to hybridization with these $5f$ states. Comparing these results to NiMnSb, in both systems the Ni d states play no real role in the half-metallic behavior and it is the exchange splitting of the U or Mn states which is the most important feature. The major difference between these systems is that for NiMnSb the hybridization between the Mn t_{2g} and Sb p states requires a broken inversion symmetry, whereas for NiUSn the U f states can hybridize with the Sn p states whether or not there is broken inversion symmetry.

In Table I a charge-density analysis is given along with the calculated site moments in NiUSn. This shows charge transfer onto the Ni site and hence a filled d band (less than 10 d electrons are found for this band due to hybridization with other bands). The empty sphere ends up with about 1.5 electrons and there is charge transfer away from the U sites (about 1.9 electrons) and from the Sn sites (about 0.6 electrons). It is also seen that almost all the spin moment is on the U sites and due to the $5f$ electrons. The total calculated moment per formula unit is $1.98\mu_B$ compared to the experimental high-temperature value[6] of $3.08\mu_B$.

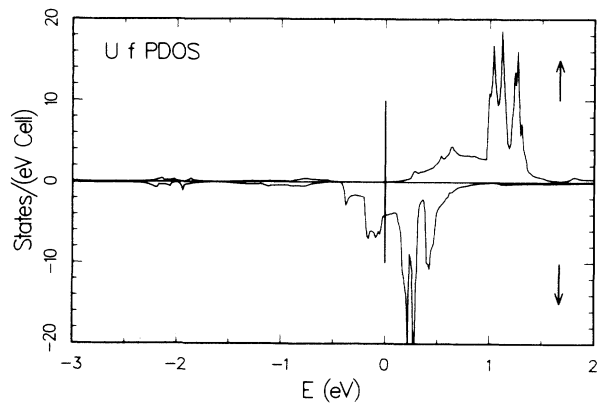

FIG. 5. The partial DOS functions for the $l=3$ (f) spin-up and spin-down states around the U sites. E_f is at zero.

CONCLUSIONS

We have presented the electronic structure of NiUSn and have shown that it is a half-metallic magnet, which is due to the itinerant $5f$ states of uranium. The magnetic $3d$ metal atom plays almost no role in the magnetic properties. The calculated direct gaps in the minority-spin bands along high-symmetry directions are much larger ($\sim$0.5–1.0 eV) than that used (0.12 eV) to fit the resistivity data. However, the minority-spin DOS functions (which include both direct and indirect points and lower-symmetry directions) shows a gap of about 0.2 eV. A better test of the size of this gap could be given by performing optical or photoemission experiments on this material. We do not believe that the existence of the gap itself is in doubt, only the exact size. Our calculated magnetic moment of $1.99\mu_B$ should probably not be compared to the high-temperature value ($3.08\mu_B$), so we can not determine by such a comparison whether or not there is the large orbital contribution seen in other actinide compounds.[8] Unlike the case of NiMnSb where it is known that only spin-polarization effects are large—in NiUSn we believe that spin-orbit coupling is important and should lead to a large magneto-optical polar Kerr effect. We are working on a scheme to perform the Kerr-angle calculation and will report on this aspect shortly. In this paper we have shown that a spin-polarized calculation leads to half-metallic behavior in this compound.

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