Relativistic Stoner theory applied to $PuSn_3$

Olle Eriksson
Condensed Matter Theory Group, Institute of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden

M. S. S. Brooks
Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, Federal Republic of Germany

Börje Johansson
Condensed Matter Theory Group, Institute of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden
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Scalar relativistic and fully relativistic electronic-structure calculations are performed for some representative members of the ASn_3 series of compounds (A denotes actinide). It is found that the experimentally observed temperature-independent susceptibility for $PuSn_3$ can be explained by the spin-orbit splitting of the $5f$ states. A relativistic version of the Stoner criterion for the onset of ferromagnetism is presented.

I. INTRODUCTION

In the $CuAu_3$ isostructural ASn_3 (A=Th–Pu) series of compounds, the observed temperature-independent paramagnetism for $PuSn_3$ is highly anomalous.[1] For the other compounds in this series the physical properties can be summarized as follows: Although to our knowledge there are no magnetic data available for $ThSn_3$ one can safely assume that it does not order magnetically.[1] USn_3 is a typical narrow-band spin-fluctuating system[1] as concluded from the behavior of the low-temperature specific heat.[2] Furthermore, USn_3 displays a Curie-Weiss type of magnetic behavior above 20 K, while the susceptibility remains approximately constant below this temperature.[3–5] Also the x-ray photoelectron spectroscopy valence-band spectrum has been measured showing a peak at the Fermi level (E_F) that extends 2 eV below E_F.[6] The next system in the series, $NpSn_3$, orders antiferromagnetically.[7] The specific heat has an anomaly at 9.5 K (Ref. 1) and Mössbauer experiments show a small moment of $0.28\mu_B$ per neptunium atom at 4.2 K.[8] From this trend in the ASn_3 series one would expect $PuSn_3$ to show magnetic ordering as well, but surprisingly this is not the case and instead, as already mentioned, a temperature-independent paramagnetic behavior has been observed.[1] Therefore, we have undertaken a theoretical investigation of this anomaly in $PuSn_3$. This is done by means of electronic-structure calculations and a relativistic generalization of the Stoner theory for the onset of ferromagnetism. In the present work $ThSn_3$ and USn_3 are used as reference materials to get a better understanding of the trend of the electronic structure through the series. In earlier theoretical work on the ASn_3 series the electronic structure, density of states (DOS), and Fermi surface have been calculated for USn_3.[9,10] Furthermore, calculations of the magnetic moments for $NpSn_3$ have been published by Norman *et al.*[11]

II. RESULTS

First, we calculated the scalar-relativistic band structure for $ThSn_3$, USn_3, and $PuSn_3$, using the linear–muffin-tin-orbital technique,[12] and where the local-density approximation with the von Barth–Hedin parametrization was used for the exchange and correlation potential.[13] The densities of states from these calculations are presented in Fig. 1. For $PuSn_3$, it can be seen that the DOS is composed of a wide, tin sp band hybridizing with a 2-eV, broad plutonium $5f$ resonance. The Fermi level E_F lies in the middle of this resonance and the DOS at E_F is very high (Table I). Therefore, the calculated Stoner product is also high (=3.5) and from this we are led to the conclusion that $PuSn_3$ will order magnetically. This is, however, in total disagreement with the experimental data mentioned in the Introduction.

In order to relate the electronic properties of $PuSn_3$ to similar systems, we investigated $ThSn_3$ and USn_3. The scalar-relativistic DOS's for these two compounds are also plotted in Fig. 1. The partial occupation numbers and the value of the DOS at the Fermi energy are listed in Table I. In calculations of this kind one finds a broad $5f$ band above E_F in the Th metal as well as in its compounds and a more narrow $5f$ band pinned at E_F for the U and Pu metals and their compounds.[14,15] Our present results show no exception in this respect (Fig. 1) and also the calculated actinide $5f$ occupation numbers are very similar to what is found in other systems[14–16] (Table I). However, there is a fundamental difference between the electronic structure of Th, U, and Pu metals on one hand, and, on the other, the electronic structure for the corre-

TABLE I. Self-consistently (scalar-relativistic) calculated occupation numbers, density of states at the Fermi level (total, D_T, and $5f$ partial, D_f, both in units of states/Ry), and Stoner products, SP, for $ThSn_3$, USn_3, and $PuSn_3$. The calculated values are for a fixed volume of the unit cell (99.0 Å^3) for all three compounds.

	n_{Af}	n_{Sns}	n_{Snp}	D_T	D_f	SP
$ThSn_3$	0.53	1.62	2.29	32	5	0.4
USn_3	2.83	1.64	2.24	126	106	1.3
$PuSn_3$	5.26	1.64	2.17	259	245	3.5

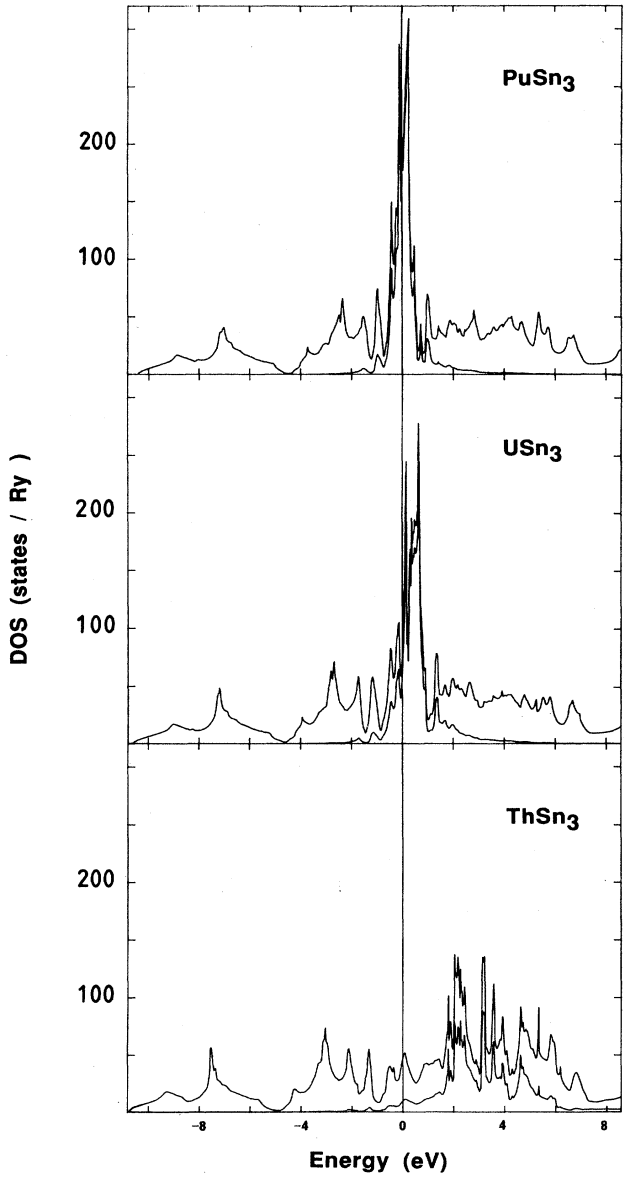

FIG. 1. Calculated (scalar-relativistic) DOS for $ThSn_3$, USn_3, and $PuSn_3$. The lower curve in each figure is the $5f$ partial DOS. The Fermi level is at zero energy.

sponding compounds with tin. For the latter, as in many other compounds,[17–19] it is the hybridization between the $5f$ states and the ligand states that is important for the width of the $5f$ band. For the USn_3-$PuSn_3$ compounds the $5f$ resonance lies in the middle of the tin p band and, accordingly, the A $5f$–Sn $5p$ hybridization is strong. For $ThSn_3$ the $5f$ resonance lies above the Fermi level and, therefore, the DOS at E_F is low resulting in a Stoner product considerably less than 1. Thus, as one would expect, $ThSn_3$ is far from showing magnetic ordering. On the other hand, USn_3 and $PuSn_3$ both have a quite large DOS at E_F, and hence their corresponding Stoner products are larger than 1. For USn_3, as well as for $PuSn_3$, we notice that the DOS at E_F is dominated by the $5f$ partial DOS and, therefore, we can to a good approximation omit the contribution from all the other partial waves in the calculation of the Stoner product. Then the Stoner product can be approximated by $I_f D_f/2$, where I_f is the exchange integral for the $5f$ states and D_f is the $5f$ partial DOS at the Fermi energy. From this we calculate the Stoner product to be 3.6 for $PuSn_3$, which compares favorably with the value obtained from the complete calculation (Table I).

In Fig. 2 we show the DOS for USn_3 and $PuSn_3$ obtained from a fully relativistic calculation. By "fully relativistic" we mean that the Dirac equation and the relativistic band-structure problem are solved self-consistently.[20,21] In USn_3 the self-consistently calculated spin-orbit splitting of the $5f$ states is 1.1 eV and in $PuSn_3$ it is 1.3 eV, i.e., values which are comparable to the $5f$ bandwidth obtained in the scalar-relativistic calculations. This splits the $5f$ band into two subbands, $5f_{5/2}$ and $5f_{7/2}$, which gives rise to a dramatic effect on the DOS. Integrated properties, however, such a partial occupation numbers, remain practically constant (Table II). The ratio R_2 between the partial occupation numbers for the $5f_{5/2}$ and the $5f_{7/2}$ subbands is very different from the statistical ratio 6:8 due to the appreciable spin-orbit splitting (Table II). In particular, the large value of R_2 for $PuSn_3$ implies that the $5f_{7/2}$ band is almost empty and the $5f_{5/2}$ band is nearly filled. From Table II it can be seen that Pu holds about two $5f$ electrons more than U, and that these two electrons indeed enter the $5f_{5/2}$ band while the $5f_{7/2}$ band remains almost empty. The Fermi level for $PuSn_3$ is found to be situated between the $5f_{5/2}$

TABLE II. Occupation numbers, density of states at the Fermi level (total, D_T, and $5f$ partial, D_f, both in units of states/Ry), and spin-orbit $\Delta_{s.o.}$ (in units of eV), from the fully relativistic, self-consistent calculation for USn_3 and $PuSn_3$. The volume was 99.0 Å^3 for both compounds.

	n_{Af}	$n_{Af_{5/2}}$	$n_{Af_{7/2}}$	D_T	D_f	R_2	$\Delta_{s.o.}$
USn_3	2.92	2.28	0.64	143	117	3.6	1.1
$PuSn_3$	5.19	4.61	0.58	27	16	7.9	1.3

and the $5f_{7/2}$ subbands in a "pseudogap" (Fig. 2). This is similar to what has been found earlier for the PuTe system, where the pseudogap actually developed into a real gap giving semiconducting behavior.[22] Thus in comparison to the scalar-relativistic calculations for $PuSn_3$, there is a most dramatic reduction of the DOS at the Fermi level caused by the spin-orbit splitting. Such a large reduction of the DOS at E_F is unique for $PuSn_3$ in the ASn_3 series, since here one encounters the appropriate number of $5f$ electrons needed to essentially fill the $5f_{5/2}$ band. For USn_3, on the other hand, the DOS at E_F is relatively little changed as compared to the scalar-relativistic calculations (Tables I and II). In this connection we would also like to point out the close similarity between our presently calculated scalar-relativistic DOS for USn_3 and earlier work.[9,10]

III. RELATIVISTIC STONER THEORY

Analogous to our previous work on δ-plutonium,[23] plutonium chalcogenides,[22] $PuCo_2$,[24] and $PuIr_2$,[25] we suggest that the spin-orbit-induced decrease of the DOS at E_F, together with the fact that the mixing between the $j=\frac{5}{2}$ and $\frac{7}{2}$ states is reduced to a minimum, is responsible for the paramagnetism of $PuSn_3$. In order to express this quantitatively, we have calculated the relativistic Stoner product[24] for $PuSn_3$ and found it to be as low as 0.2. This favors the paramagnetic ground state and is in agreement with the experimental observation. Similar to the procedure outlined in Ref. 24, the calculation of the relativistic Stoner product was performed by including a small uniform fictitious magnetic field H (only acting on the electron spin) to the paramagnetic solution to the self-consistent relativistic band-structure problem. Then a single iteration was done to obtain the induced magnetic moment m_{tl} on the tl orbital (t denotes atom type, l denotes orbital). From this we define a partial susceptibility $\chi^0_{tl}=m_{tl}/H$ and a uniform susceptibility

$$\chi^0=\sum_{t,l}\chi^0_{tl} \ . \tag{1}$$

The relativistic Stoner criterion for ferromagnetism can now be formulated as[24]

$$I\chi^0>1 \ , \tag{2}$$

where I is a generalized Stoner parameter

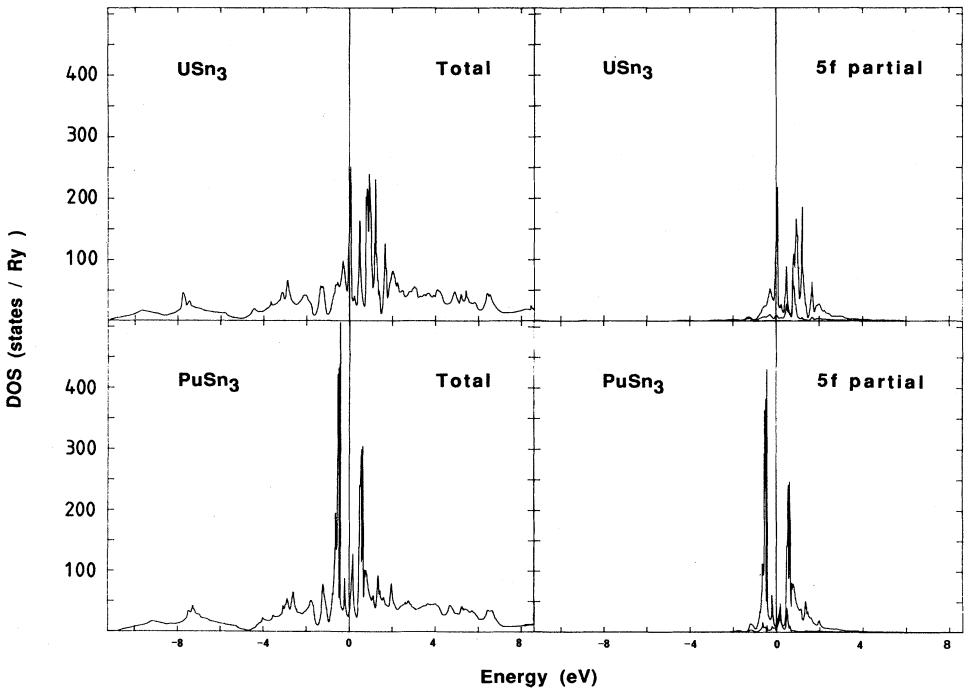

FIG. 2. Calculated (fully relativistic) total (to the left) and $5f$ partial (to the right) DOS's for USn_3 and $PuSn_3$. The $5f$ partial DOS has been divided into the $5f_{5/2}$ and $5f_{7/2}$ subband DOS's. The Fermi level is at zero energy.

$$I=\sum_{t,l} J_{tl}(\chi^0_{tl}/\chi^0)^2 , \tag{3}$$

and J_{tl} is the exchange integral for the tl orbital.[26]

The above procedure involves a band-structure calculation where the applied field H is included. Below we will show an approximate, but simple and analytic way to calculate the relativistic Stoner product. A full account of this derivation will be published elsewhere.[27]

Quite generally one can obtain the criterion for the onset of ferromagnetism for a system by considering the change of the total energy for an infinitesimal fictitious field H. In order to introduce the nomenclature we first derive the Stoner criterion for ferromagnetism for a system where the spin s_z is a good quantum number. The external field H induces a spin polarization which lowers the interaction energy of the system by the amount[26,28]

$$\Delta E_{\rm int}=-\sum_t n_t \sum_l J_{tl} m^2_{tl\frac{1}{4}}=-\sum_t n_t \sum_l J_{tl} D^2_{tl} H^2 . \tag{4}$$

Here D_{tl} is the tl partial DOS/spin at the Fermi energy and n_t is the number of t-type atoms in the Wigner-Seitz cell. At the same time there will also be an increase in the kinetic energy[28]

$$\Delta E_{\rm kin}=\sum_t n_t \sum_l D_{tl} H^2 . \tag{5}$$

Comparison between Eqs. (4) and (5) gives the normal multiband Stoner criterion[29]

$$ID_T=1 , \tag{6}$$

where D_T is the total DOS/spin of the system and I is

$$I=\sum_t n_t \sum_l \left[\frac{D_{tl}}{D_T}\right]^2 J_{tl} . \tag{7}$$

Equation (6) is the multiband Stoner criterion in the case where spin s_z is a good quantum number.

For the relativistic case j_z replaces s_z as the good quantum number. This is the case when the spin-orbit interaction is strong, as it is in transuranium systems. In the following we will derive an approximate, but analytic expression for the relativistic generalization of the Stoner theory. A few assumptions have to be made. First, we limit ourselves to an actinide compound, where for the second element we assume that the spin-orbit interaction is negligible. Second, we assume that the strong spin-orbit interaction of the transuranium atom reduces the mixing between the $j=\frac{5}{2}$ and $\frac{7}{2}$ states to a minimum, and it will be neglected. This assumption can be checked by inspection of the self-consistent band structure at different positions in the Brillouin zone and, for example, in $PuSn_3$ this is certainly a good approximation. With these assumptions we can write the gain in interaction energy due to the induced magnetic moment as

$$\Delta E_{\rm int}=-\left[\sum_t n_t \sum_l{}' J_{tl} m^2_{tl\frac{1}{4}}+n_A J_{Af} m^2_{Af\frac{1}{4}}\right] . \tag{8}$$

Here the prime indicates that we exclude the actinide $5f$ state in the summation. J_{Af} is the exchange integral, m_{Af} is the induced magnetic moment for the actinide $5f$ states, and n_A is the number of actinide atoms in the Wigner-Seitz cell. Equation (8) can be rewritten as

$$\Delta E_{\rm int}=-\left[\sum_t n_t \sum_l{}' J_{tl} D^2_{tl} H^2+n_A J_{Af} \times\left[\sum_j \sum_{mj<0} [(C^{j,mj}_+)^2-(C^{j,mj}_-)^2]^2 \times D_{j,mj}\right]^2 H^2\right] . \tag{9}$$

Here $C^{j,mj}_+$ and $C^{j,mj}_-$ are the Clebsch-Gordan coefficients and $D_{j,mj}$ is the j,mj-projected DOS for the $5f$ state. Similarly to Eq. (5) we can write the loss of kinetic energy as

$$\Delta E_{\rm kin}=\left[\sum_t n_t \sum_l{}' D_{tl} H^2 +n_A \sum_j \sum_{mj<0} [(C^{j,mj}_+)^2-(C^{j,mj}_-)^2]^2 \times D_{j,mj} H^2\right] . \tag{10}$$

Comparing Eqs. (9) and (10) gives the following critical condition for the onset of ferromagnetism:

$$ID^T_R=1 , \tag{11}$$

where

$$D^T_R=\sum_t n_t \sum_l{}' D_{tl}+n_A D_R , \tag{12}$$

and

$$D_R=\sum_j \sum_{mj<0} D_{j,mj}[(C^{j,mj}_+)^2-(C^{j,mj}_-)^2]^2 . \tag{13}$$

Finally, I is a generalized Stoner exchange parameter

$$I=\sum_t n_t \sum_l{}' \left[\frac{D_{tl}}{D^T_R}\right]^2 J_{tl}+n_A \left[\frac{D_R}{D^T_R}\right]^2 J_{Af} . \tag{14}$$

We have also calculated the product ID^T_R in Eq. (11) and found the same value as before for the Stoner product, namely 0.2. Hence, we conclude that $PuSn_3$ is far from a magnetic transition, in agreement with the experimental finding of a temperature-independent paramagnetism in this system. For USn_3 the relativistic Stoner product is calculated to be 0.98, which implies that also this compound is a paramagnet, although close to an instability. This neighborhood to an instability is also supported by the experimental observation of spin fluctuations in this system.[2]

IV. CONCLUSION

In conclusion we have shown that the temperature-independent paramagnetism of $PuSn_3$ can be understood from an itinerant picture of the Pu $5f$ electrons. However, this conclusion could only be obtained from a fully relativistic treatment of the electronic structure. The narrow delocalized $5f$ states in $PuSn_3$ should be possible to detect by means of x-ray photoelectron spectroscopy experiments. In contrast to USn_3 the $5f$ peak in $PuSn_3$ will be withdrawn from the Fermi energy and relatively

narrow. It also seems likely that for $PuSn_3$ there would appear a $5f$-valence-band satellite signal similar to the well-known 6-eV satellite in nickel metal. The temperature-independent paramagnetism in $PuSn_3$ is closely connected to the pseudogap of the $5f$ states originating from the spin-orbit splitting. In the ASn_3 series, $PuSn_3$ is unique in the sense that it is only for this compound that the $5f_{5/2}$ subband is nearly completely filled. This pseudogap located around the Fermi energy in $PuSn_3$ would also explain the observed[30] low-temperature electrical resistivity, $\rho \sim T^5$, a power-law behavior which indicates a dominance of s- and p-band electrons at the Fermi level. Finally, we have derived an expression for the relativistic generalization of the Stoner criterion for ferromagnetism and have shown that the Stoner product is less than 1 both for USn_3 and $PuSn_3$, in agreement with experiments. In the case of $PuSn_3$ this is in sharp contrast to what one would expect from the trends through the ASn_3 series of compounds.

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