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Energy gap of the ground state of CeNiSn caused by local and long-range magnetic-moment interactions

F. G. Aliev,* R. Villar, S. Vieira, and M. A. Lopez de la Torre†
Laboratorio de Bajas Temperaturas, Dpto. Fisica de la Materia Condensada, C-III, Universidad Autonoma de Madrid, Cantoblanco, 28049, Madrid, Spain

R. V. Scolozdra
Department of Chemistry, L'vov State University, 290022 L'vov, Ukraine

M. B. Maple
Department of Physics and Institute for Pure and Applied Physical Sciences, University of California at San Diego, La Jolla, California 92093

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We have studied the thermal expansion of the gapped intermetallic heavy-fermion compounds CeNiSn, $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$, and $\mathrm{Ce_{1-x}La_xNiSn}$ ($x = 0.03, 0.1$) between 0.5 K and 25 K; and the transport ($3 < T < 60$ K) and magnetic ($0.1 < T < 8$ K) properties of CeNiSn. The magnetic heavy-fermion compound $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ displays an antiferromagnetic (AF) transition at $T_{\mathrm{AF}} \sim 1.5$ K; CeNiSn exhibits a gapped ($E_g \sim 2-8$ K) and possibly "weakly" magnetic ground state $T < 0.5$ K; $\mathrm{Ce_{0.97}La_{0.03}NiSn}$ shows $T_{\mathrm{AF}} \sim 6$ K, and finally $\mathrm{Ce_{0.9}La_{0.1}NiSn}$ does not display heavy-fermion or gapped behavior. We have investigated the transition between the above regimes. The comparison between the thermal-expansion data of CeNiSn, $\mathrm{Ce_{0.97}La_{0.03}NiSn}$, and single-crystalline CeNiSn shows that gap formation may be unstable against the weak magnetic transitions with $T_{\mathrm{AF}} \sim 6$ K and $T_{\mathrm{AF}} \sim 2$ K. The anomalous negative thermal expansion of CeNiSn that is observed below 1 K allows us to propose a simple picture for the electron spectrum near the Fermi level.

INTRODUCTION

Intermetallic heavy-fermion systems (HFS) are usually characterized by a Fermi-liquid ground state.[1] But recently two HFS [CeNiSn (Refs. 2–4) and $\mathrm{Ce_3Bi_4Pt_3}$ (Ref. 5)] were unexpectedly found to show a gapped ground state. In the compound CeNiSn a small gap at the Fermi level (e.g., 6–10 K) within a many-body resonance (of width about 50 K) was found.[2-4] The main reasons for the gapping of the spectrum of CeNiSn, including the role of antiferromagnetic interactions, are still unclear. From the one side, NMR experiments showed the absence of any magnetic transition down to 0.1 K.[6] On the other hand, CeNiSn system is obviously near an antiferromagnetic (AF) instability, as was indicated by the magnetic properties of single-crystalline samples.[7] In this paper we present our results on temperature dependences of the thermal expansion for CeNiSn, $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ and $\mathrm{Ce_{1-x}La_xNiSn}$ ($x = 0.03$, 0.1) compounds ($0.5 < T < 25$ K), as well as of transport properties ($3 < T < 60$ K) and of the real χ and imaginary part χ'' of the ac magnetic susceptibility ($0.1 < T < 8$ K) for CeNiSn. We conclude that an important role in the gapping of the spectrum of CeNiSn is played by local antiferromagnetic Kondo-type correlations at temperatures about 2–8 K, and by long-range interactions of the Kondo suppressed Ce magnetic moments below 0.5 K. We propose a simple model for the electron density of states near the Fermi level, which allows a better understanding of the main low temperature properties of CeNiSn.

EXPERIMENT

All the polycrystalline samples studied in our work were characterized by a TiNiSn type crystal structure[8] with the following volumes of atomic cell: $V(\mathrm{CeNiSn}) \approx 263.33\,A^3$, $V(\mathrm{CeNi_{0.9}Cu_{0.1}Sn}) \approx 267.00\,A^3$, $V(\mathrm{Ce_{0.97}La_{0.03}NiSn}) \approx 263.54\,A^3$, and $V(\mathrm{Ce_{0.9}La_{0.1}NiSn}) \approx 263.97\,A^3$. The thermal expansion measurements were performed using the three terminal capacitance method.[9] The ac magnetic susceptibility χ_{ac} was measured in a dilution refrigerator. The resistivity ρ, Seebeck coefficient S, and thermal conductivity k, were studied simultaneously on small samples (about $4 \times 1 \times 1$ mm^3). Details of sample preparation as well as preliminary results on the thermal expansion of CeNiSn were reported previously.[10]

Figures 1(a) and 1(b) show the temperature dependences of the thermal expansion coefficient α and α/T for the CeNiSn and $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ samples. While for $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ an increase of the α/T term, indicating the formation of the heavy-fermion state, continues from about 12 K down to 2 K, for CeNiSn a weak maximum at about 7 K is seen. More interesting features were observed below 2 K: a maximum on the $\alpha(T)$ dependence ($T_{\max} \approx 1.3$ K) with an anomalous change to negative α values below 1 K for CeNiSn; and a sharp kink in $\alpha(T)$ near 1.5 K followed by a rapid decrease of α with temperature for $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$.

The temperature dependences of α and α/T for CeNiSn and $\mathrm{Ce_{1-x}La_xNiSn}$ ($x = 0.03, 0.1$) compounds are presented on Figs. 2(a) and 2(b). Substitution of 3%

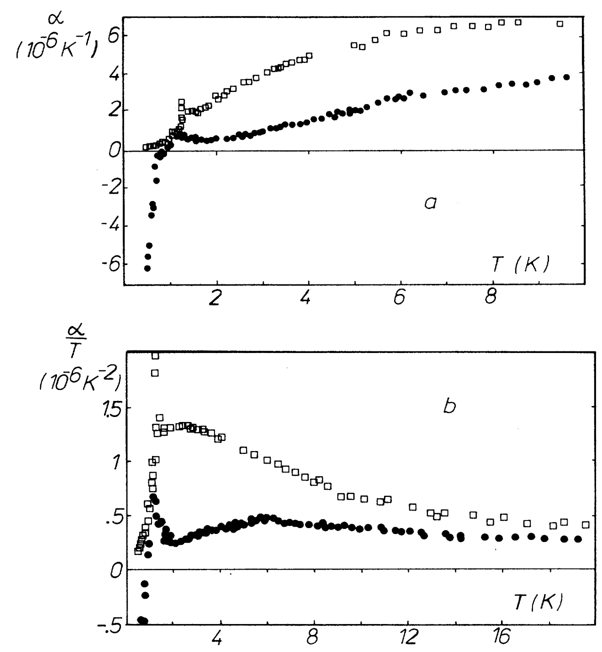

FIG. 1. Effect in the thermal expansion of CeNiSn of Ni substitution by Cu. (a) Temperature dependence of the coefficient of linear thermal expansion α for CeNiSn (●) and $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ (□), for $0 > T > 10$ K. (b) Same as above, but represented as α/T vs T up to 20 K, to show the behavior of the linear term in the thermal expansion.

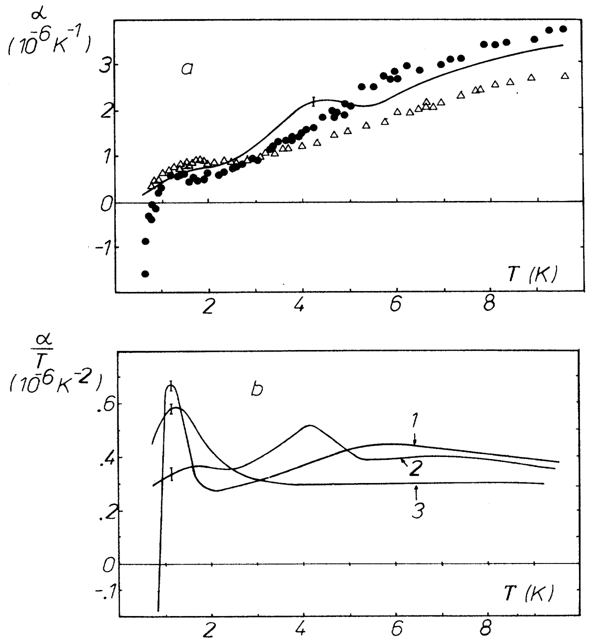

FIG. 2. Effect of Ce substitution by La in the thermal expansion of CeNiSn. (a) Thermal expansion vs temperature for CeNiSn (●), $\mathrm{Ce_{0.97}La_{0.03}NiSn}$ (line) and $\mathrm{Ce_{0.9}La_{0.1}NiSn}$ (△). (b) The same as above, but represented as α/T vs T. CeNiSn (curve 1), $\mathrm{Ce_{0.97}La_{0.03}NiSn}$ (2),and $\mathrm{Ce_{0.9}La_{0.1}NiSn}$ (3). The experimental points have been replaced by curves for clarity.

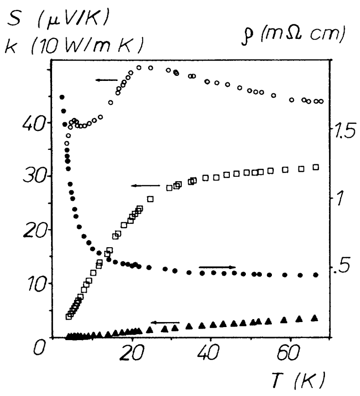

FIG. 3. Temperature dependence of the resistivity ρ(●), Seebeck coefficient S(○), thermal conductivity k(□), and upper limit of electron thermal conductivity k_e(▲) of CeNiSn.

of Ce atoms by La changes dramatically the low temperature behavior of $\alpha(T)$: the negative thermal expansion of CeNiSn transforms into a plateau, and a narrow maximum at $T\sim 5$ K in α/T appears instead. The $\mathrm{Ce_{0.9}La_{0.1}NiSn}$ compound is characterized by a nearly linear decrease of the thermal expansion with temperature for $3\ \mathrm{K} < T < 25$ K, followed by a wide maximum in the α/T ($T_{\mathrm{max}} \sim 1.5$ K) curve.

Figure 3 shows representative temperature dependences of resistivity, Seebeck coefficient, and thermal

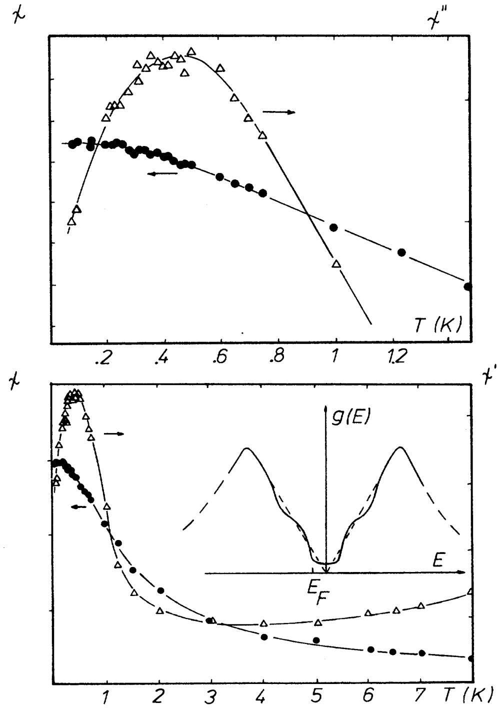

FIG. 4. Temperature dependences of the real (●) and imaginary (△) parts of the magnetic susceptibility (in arbitrary units) of CeNiSn. The inset shows schematically the dependence of the density of electron states $g(E)$ near E_F proposed for CeNiSn at $T = 0$.

conductivity for our polycrystalline CeNiSn samples. An estimation of the upper limit of the electron part of the thermal conductivity as $k_e \approx L_0 \times T/\rho$ ($L_0 = 2.45 \times 10^8 W\,\Omega\,\mathrm{K}^{-1}$) shows that the k_e/k relation is about 10% at 60 K and reduces below 0.5% in the gapped ($T < 4$ K) state (see Fig. 3). From thermoelectric properties a clear evidence of two maxima was seen: at about 20 K and 3–4 K. The thermal conductivity k, does not show any noticeable feature down to 4 K. This may be due to the fact that the main contribution to the heat transport is due to phonons, k_{ph}. At the same time a strong decrease of the electron part, k_e (of more tan one order of magnitude between 20 and 4 K) can be considered as an indirect evidence of the gapping of the spectrum.

The real and imaginary parts of the ac magnetic susceptibility of CeNiSn at ($0.1 \mathrm{~K} < T < 8$ K) are presented on Figs. 4(a) and 4(b). While no anomalies were found on the $\chi(T)$ behavior, below $T \sim 1$ K a rapid increase of the imaginary part χ'' followed by a maximum at about 0.5 K was observed.

DISCUSSION

From thermoelectric properties [of polycrystalline (Fig. 3) as well as of single crystalline[7] samples] and thermal expansion (Figs. 1 and 2) a clear evidence of the existence of two characteristic temperatures in the gapped ground state of CeNiSn at ($1 < T < 20$) K is seen. Another indication on the presence of a second transition in the gapped state is a maximum in the linear term of the heat capacity below 1.5 K,[11] which unfortunately was not discussed by the authors.

For a qualitative analysis of the $\alpha(T)$ behavior below 1 K we will use the theory of the negative thermal expansion in Kondo lattices.[12] This model, based on the two-component Fermi-liquid approximation, proposes a strong correlation between the existence of a pseudogap in the electron spectrum near the Fermi level and a negative α value at $T \rightarrow 0$. In fact, the gap (or pseudogap) at E_F exists in CeNiSn.[2–4] Moreover, modeling of the NMR data by different gap structures showed[13,14] the best correspondence of experimental data with a linear dependence of $g(E)$ with energy E (see dashed line in Fig. 4). Here we propose that this simple $g(E)$ dependence in the vicinity of E_F should be strongly modified due to at least two facts. The first is that recent NMR experiments revealed some deviation of the $1/T^1$ vs T dependence from the $g(E)$ fitting curve below 1.5 K, followed by quasisaturation of the $1/T^1$ signal at $T < 0.5$ K.[6] These data may be considered as an indication of a finite density of states $g(E_F)$ at $T \rightarrow 0$. The second reason is that neither a linear, nor a parabolic dependence of $g(E)$ near the Fermi energy can explain large negative values in the frame of the theory.[12] Both conditions can be satisfied using the model for density of states and position of the Fermi level, schematically presented in the inset to Fig. 4 by a solid line.

From the physical point of view the two-step $g(E)$ dependence inside the gap may originate from the fact that the strongly anisotropic CeNiSn crystal structure[8] with Ce atoms forming a system of (bc) planes, separated by planes containing Ni and Sn atoms results in the anisotropic parameter J, mirrored by the anisotropy of the magnetic and transport[7] properties. Along the "more magnetic" a direction, the transport gap is about 2–3 times lower than in the b-c plane. If now we try to draw schematically the character of the density of states discussed before, neglecting the possible anisotropy between b and c directions, then the effective density of states (see inset on Fig. 4) being the sum $g_{\mathrm{eff}}(E) = g_a(E) + g_{bc}(E)$ seems to be rather close to the one proposed to fit the NMR data[6] and at the same time will describe the negative thermal expansion coefficient at $T \rightarrow 0$ as well as the twofold anomalies in the gapped region observed in the temperature dependences of the thermal expansion, linear term of specific heat and of Seebeck coefficient.

The long-range coherent interaction of the Kondo-reduced magnetic Ce moments in CeNiSn possibly becomes important below 1 K. This tendency displayed by the thermal expansion does not affect strongly the magnetic susceptibility (only an increase of χ, followed by saturation below 0.5 K, was observed). In fact, in the HF compounds, for example UPt_3, $CeCu_2Si_2$, $CeAl_3$ and some other HFC, the weak magnetic transition is not seen in the magnetic susceptibility. On the other hand, the maximum of $\chi''(T)$ near 0.5 K (Fig. 4) may be considered as an indirect indication of the existence of this transition. More likely, the process of formation of the ground state is complete below $T = 0.5$ K. Recently, Kuogaki *et al.*,[15] based on NMR experiments carried out down to 0.08 K, also reported a magnetic instability in the gapped state of CeNiSn at very low temperatures: the development of static magnetic correlations inducing a "spin gap" of about 0.25 K was seen.[15]

In the electron spectrum proposed for CeNiSn, the nonsymmetry of the position of the Fermi level would reflect the degree of s-f hybridization.[12] At the same time the nonzero value of the density of states at E_F may be a consequence of energy transport through Ce atoms in the nonideal crystalline position where the phases of the coherent Kondo compensation should break.

Let us now analyze the influence of external factors, for example, change of composition or the effect of hydrostatic pressure[16] on the ground state of CeNiSn. The substitution of Ce by La, increasing the effective volume V according to the derivative $dV/dx \sim 7 A^3$, may result in a "negative pressure" effect. Even a 3% substitution of Ce by La changes the negative α value below 1 K to a positive one and results in the appearance of the maximum in the $\alpha(T)$ curve just below 5 K. It is interesting to note that the same type of anomaly near $T \sim 6$ K, possibly indicating the proximity of the ground state of CeNiSn to "weak" antiferromagnetism, was also recently deduced from the temperature dependences of volume thermal expansion[16] and thermal conductivity[17] of CeNiSn single crystals along the b direction.

On the other hand, another study of CeNiSn single crystals[18] did not show such strong anomalies on the volume thermal expansion in the gapped region. In our opinion this discrepancy should originate not from different crystalline morphologies, but from the extremely high volume dependence of α in CeNiSn. In fact, studies of thermal expansion of single crystalline CeNiSn under pressure[16] revealed that a hydrostatic pressure of about 8 kbars completely suppresses the AF instability at $T \sim 6$ K, reducing the absolute α values more than twice down to those corresponding to our data. Therefore we can conclude that, in comparison with single crystals,[7,16,17] the polycrystalline CeNiSn samples seem to be "pressed." In our opinion, the role of an external pressure of the order of a few kbars may be played by intercrystalline stresses. To our knowledge, no studies of the thermal expansion of single-crystalline CeNiSn samples under pressure have been performed below 4 K. Based on the analysis presented here, we believe that an anomalously strong effect will show up in the thermal expansion of CeNiSn at $T < 4$ K under a hydrostatic pressure of only a few kbars.

The substantial increase of the low temperature α/T values (as well as of the linear term in the heat capacity[12]) of $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$ very likely reflects the disappearance of the gap with the development of the magnetic ground state. The physical reason for the strengthening of magnetism in $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$, in comparison with CeNiSn, may be the decrease of the Kondo temperature, originated from the weakening of the s-f exchange due to substitution of the narrow Ni conduction electron zone by the wide Cu one.

CONCLUSIONS

The results on the transport and magnetic properties of CeNiSn and on the thermal expansion of CeNiSn, $\mathrm{CeNi_{0.9}Cu_{0.1}Sn}$, and $\mathrm{Ce_{1-x}La_xNiSn}$ ($x = 0.03, 0.1$) solid solutions presented here let us suppose the existence of four characteristic energies in the electron density of states near E_F: the highest is a Kondo temperature of about 50 K,[2–4] below which heavy-fermion behavior appears; two others due to anisotropic gapping of electron spectrum of about 2 and 6 K and the fourth one of about 0.5 K, possibly caused by "weak" magnetic ordering. The resulting low conducting and almost nonmagnetic ground state of CeNiSn is exceptionally unstable to external influences.

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[*] Also at: Low Temperature Physics Laboratory, Physics Department, Moscow State University, 119899, Moscow, Russia.

[†] Present address: Dpto. Fisica Aplicada, Universidad de Castilla la Mancha, Toledo, Spain.

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