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Pressure driven collapse of the magnetism in the Kondo insulator UNiSn

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The effect of pressure on the electronic and magnetic properties of the antiferromagnetic ($T_N \sim 43$ K) narrow gap semiconductor UNiSn has been investigated by ^{119}Sn Mössbauer spectroscopy and nuclear forward scattering of synchrotron radiation, electrical resistance, and x-ray diffraction. We show that the decrease of the semiconducting gap which leads to a metallic state at $p \sim 9$ GPa is associated with an enhancement of T_N. At higher pressures, both T_N and the transferred magnetic hyperfine field decrease, with a collapse of magnetism at ~18.5 GPa. The results are explained by a volume-dependent competition between indirect Ruderman-Kittel-Kasuya-Yosida interaction and the 5*f*-ligand hybridization.

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The large variety of electronic and magnetic properties of strongly correlated 5*f* electron systems has motivated continuous experimental and theoretical efforts during the last decades. One of the central issues of actinides research is the question of the nature of the 5*f* electrons which behave, depending on the investigated compound, more localized or itinerantlike. There is now growing evidence that localized as well as delocalized 5*f* electrons can coexist in various actinide compounds.[1,2] This view, suggested by a large set of experiments, received recently strong theoretical support.[3] Besides this general topic, recent attention was focused on systems close to a magnetic instability because of the observation of unconventional superconductivity at the quantum critical point where magnetic order vanishes.[4] Various aspects of the electronic structure and magnetism of actinide compounds are intimately linked to the hybridization of the 5*f* orbitals either by direct 5*f*-5*f* interaction (interactinide distance below the Hill limit) or by overlap with the conduction-band electrons such as the actinide 6*d* and ligand *sp* or *d* electrons. An elegant way to tune the properties of a material is to reduce its interatomic distances and thus to increase the hybridization by applying an external pressure. Pressure experiments have recently produced a number of outstanding results as for instance the pressure induced enhancement of the tiny uranium moment in URu_2Si_2 (Ref. 5) or the appearance of superconductivity within the ferromagnetic phases of UGe_2 (Ref. 4) and UIr (Ref. 6).

UNiSn belongs to the class of so called Kondo insulators or narrow gap semiconductors and was extensively studied during the last two decades owing to its exceptional electronic and magnetic properties.[7] It crystallizes in a cubic structure (MgAgAs-type) and undergoes a first-order transition from a paramagnetic (P) semiconductor (S) to an antiferromagnetic (AF) metal (M) at $T_N \sim 43$ K (Ref. 8). Its magnetic structure determined by neutron diffraction was found to be of type I with ferromagnetic (001) planes stacked along the [001] axis in the sequence $+-+-$ (Ref. 9). The ordered U moment oriented along the [01] axis amounts to $\sim 1.55\ \mu_B$. Furthermore, it was shown that the S-M transition is accompanied by a concomitant tetragonal distortion and ferroquadrupolar (Q) order at $T_Q \approx T_{SM} \approx T_N$ (Ref. 10). This observation led to suggest that the ferroquadrupolar order is responsible for the change of electronic structure giving rise to metallic conduction below T_Q. The effect of pressure on the multiple phase transition is illustrated by the pressure-temperature dependence of the electrical resistivity $\rho(p,T)$ up to 8 GPa (Refs. 11–13). Below 3 GPa, the analysis of the $\rho(p,T)$ curves indicates that the semiconducting energy gap ($E_g \sim 64$ meV at $p=0$) decreases while T_N ($\equiv T_{SM}$ and T_Q) increases with applied pressure. The observation of two anomalies at 5 GPa led Akazawa *et al.*[13] to conclude that at that pressure the multiple transition is split, with T_N being shifted to lower temperature. At 8 GPa, the resistivity curve presents a metalliclike behavior above 100 K, i.e., the S-M transition has disappeared and the broad peak which shows up at ~55 K was attributed to the boundary between the paramagnetic and the antiferromagnetic quadrupolar metals.[13]

In this Communication we present high pressure results on UNiSn obtained in an extended pressure range using combined macroscopic [x-ray diffraction (XRD), electrical resistance $R(T,p)$] and microscopic [^{119}Sn nuclear forward scattering (NFS) of synchrotron radiation and Mössbauer spectroscopy (MS)] techniques in a diamond anvil cell (DAC). This allowed us to determine the volume dependence of the electronic and magnetic properties of UNiSn from the pressure induced variation of the Néel temperature and the transferred magnetic hyperfine field at the ^{119}Sn nuclei and from the evolution of the $R(T,p)$ resistance curves.

Polycrystalline samples of UNiSn were prepared following methods described in Ref. 11. For the ^{119}Sn NFS experiments the sample was isotopically enriched to 90% in ^{119}Sn. The same sample was also used for the $R(T,p)$ measure-

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ments. High pressure was applied using either modified Merril-Basset[14] (M-B) DACs [for the MS and $R(T,p)$ measurements] or piston-cylinder[15] (PC) DACs (for the NFS measurements) and was determined by the ruby fluorescence method at room temperature. In the M-B cell usually only a slight increase of the pressure is detected at low temperatures (4.2 K) and the pressure values given below are those measured at room temperature. A larger increase of the pressure at low temperature, but decreasing with increasing pressure, was determined on the PC DAC ($\sim$15% and $\sim$4% at 10 and 21 GPa, respectively) with a calibration run where the pressure was determined both at room temperature (ruby fluorescence) and below 10 K (Pb manometer). The pressure values for the NFS measurements have been corrected according to this calibration. In order to reduce the risk of dispersion of uranium dust in case of breakage of the pressure cell, the sample was mixed with epoxy which also acted as a pressure-transmitting medium. The ^{119}Sn NFS experiments were carried out at the undulator beamline ID18 (Ref. 16) of the ESRF in Grenoble. A more detailed description of the ESRF experimental set up can be found in Ref. 17. The measured NFS patterns were analyzed with the programs CONUSS (Ref. 18) and MOTIF.[19] The energy dispersive XRD measurements were performed at the beamline F3 at HASYLAB in Hamburg.

The XRD patterns recorded at 300 K up to 25 GPa indicate that UNiSn retains the cubic MgAgAs-type structure in the whole investigated pressure range. In addition, we find within the accuracy of the measurements no discontinuity in the pressure dependence of the unit-cell volume. We obtain a value for the ambient pressure bulk modulus of $B_0 = 168(10)$ GPa and for its pressure derivative $B_0' \approx 1.4$. The ^{119}Sn Mössbauer spectra recorded at ambient pressure in the 4.2-300 K temperature range agree well with those published in the literature.[8,20] At 4.2 K, in the magnetically ordered state, the spectrum consists of a superposition of a pure magnetically split sextet [with a transferred magnetic hyperfine field $B_{\mathrm{thf}} = 7.2(1)$ T] and a single line (about 15% of the spectral area). The observation of a sextet is expected owing to the fact that each Sn atom, according to the known magnetic structure, is surrounded by six U nearest neighbors with four spins up and two spins down.[9] The nonmagnetic contribution (single line) is tentatively ascribed to Sn atoms occupying the Ni site.[8]

^{119}Sn Mössbauer spectra have been recorded at 4.2 K for pressures up to 10 GPa. The pressure range has been extended up to above 20 GPa by ^{119}Sn NFS at temperatures between 3 and 200 K. Figure 1(a) presents some selected ^{119}Sn NFS patterns obtained at 3 K and various pressures up to 21.4 GPa. At high temperatures and for all pressures the NFS spectra are characteristic of unsplit nuclear levels, as expected for Sn atoms in the absence of magnetic order and in an environment of cubic symmetry. Magnetically split sextets are observed in all Mössbauer spectra recorded at pressures up to 10 GPa at 4.2 K, while clear quantum beat patterns appear at low temperatures in the NFS spectra for pressures less than 18.5 GPa. Above 18.5 GPa the quantum beat pattern disappears indicating that B_{thf} and thereby the magnetic state have collapsed.

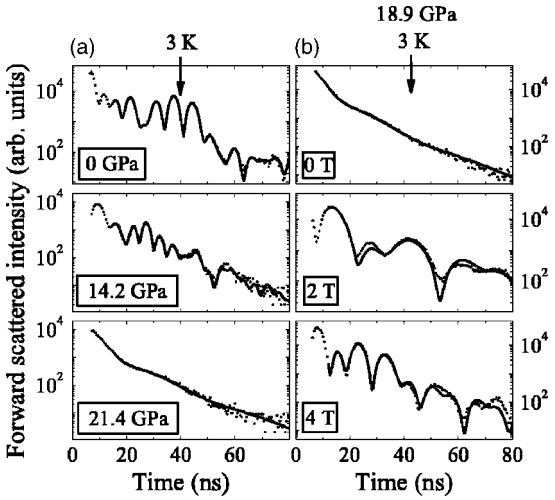

FIG. 1. ^{119}Sn NFS spectra of UNiSn (a) at $T = 3$ K for some selected pressures and (b) at $T = 3$ K and $p = 18.9$ GPa for different applied magnetic fields. The dots represent experimental data points, while the lines are fits.

The pressure-volume dependence of the transferred magnetic hyperfine field B_{thf} is illustrated in Fig. 2. The origin of B_{thf} at the Sn nucleus is twofold: an indirect polarization of the conduction electrons by localized 5f moments, mediated by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, is combined with the direct polarization of the outer 5sp electrons of the Sn atoms due to their overlap with the U-5f electrons.[21] To a first approximation B_{thf} is proportional to: (i) a hyperfine coupling constant A which depends on the electronic structure of the material, (ii) the magnitude of the U magnetic moment, (iii) the weighted vector sum of the U magnetic moments in the immediate vicinity of the Sn atom (which equals 2 for a type I antiferromagnetic structure as found in UNiSn at $p = 0$). Figure 2 shows that B_{thf} increases almost linearly from 7.2(1) T at $p = 0$ to 9.4(1) T at $p = 7.5$ GPa. A less steep increase of B_{thf} is then observed up to 16.5 GPa where $B_{\mathrm{thf}} = 9.9(2)$ T. Above that pressure it drops dramatically and at 18.9 GPa ($\Delta V/V \sim 10\%$) B_{thf} is found to vanish to zero.

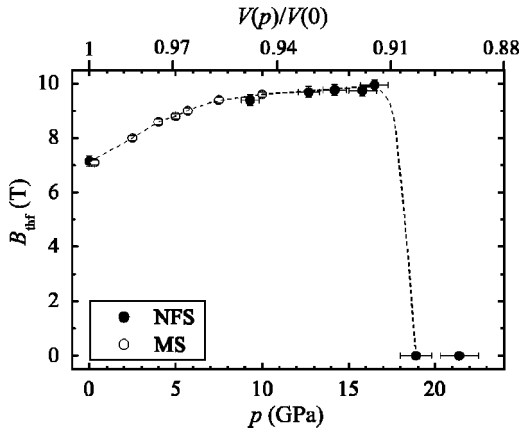

FIG. 2. Dependence on pressure and reduced volume of the transferred hyperfine field B_{thf} (measured at low temperature $T \leq 4.2$ K) for UNiSn. The dashed line is a guide to the eye.

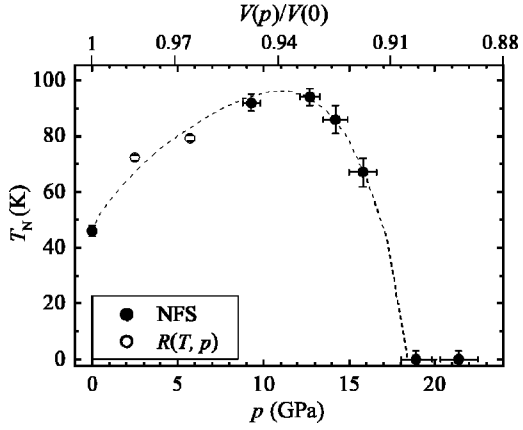

FIG. 3. Dependence on pressure and reduced volume of the Néel temperature T_N for UNiSn. The dashed line is a guide to the eye. The $R(T,p)$ measurements are considered only for $p < 8.1$ GPa.

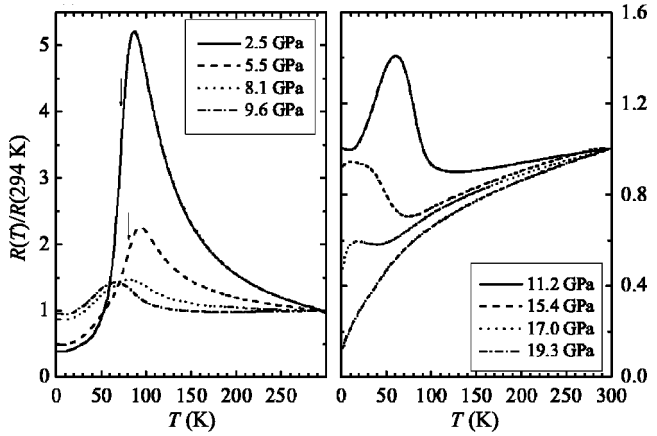

FIG. 4. Temperature dependence of the normalized electrical resistance, $R(T,p)/R(294\ \mathrm{K},p)$, of UNiSn at some selected pressure values. Note the different scales for the normalized resistance in panels (a) and (b). The arrows indicate the position of T_N.

Figure 3 illustrates the pressure-volume dependence of the Néel temperature as determined from the temperature variation of the NFS spectra and the analysis of the resistance $R(T,p)$ data (see below). $T_N(p)$ first increases with pressure, in agreement with previous results,[11–13] reaches a maximum value of about 95 K at $p \approx 13$ GPa, and then starts to decrease. At 18.9 GPa no transition was observed down to the lowest measuring temperatures [3 and 1.8 K for NFS and $R(T,p)$ measurements, respectively]. This clearly indicates the collapse of the magnetism at 18.9 GPa. To gain information on the nature of this nonmagnetic state, we have measured ^{119}Sn NFS spectra in applied magnetic fields (B_{app}) at 3 K [see Fig. 1(b)]. Their analysis gives values of the induced fields (B_{ind}) of 0.4(2) T and 0.6(2) T for $B_{app}=2$ and 4 T, respectively. The observation of such sizable values of B_{ind}, which correspond to a Knight shift (B_{ind}/B_{app}) of $\approx$15%, clearly indicates the existence of rapidly fluctuating U moments in the pressure induced nonmagnetic state.[22]

In the following we discuss the mechanism underlying the delocalization of the U-5f moments in UNiSn at high pressure. Because of the greater spatial extent of the 5f wave functions as compared to the 4f ones, a pressure induced demagnetization process is often driven by the transition from a local to an itinerant (bandlike) state rather than by the Kondo effect (which is, for example, the typical cause of the disappearance of the 4f magnetic moment in Ce compounds). According to Sheng and Cooper,[23] the decrease of the interatomic distances caused by pressure induces the 5f wave functions to diffuse more outside the core region, enhancing the 5f-ligand hybridization and causing a gradual washout of the ordered U moment and the consequent suppression of ordered magnetism. On the other hand, the increased overlap between the 5f and ligand orbitals enhances the exchange integrals and this can cause a strengthening of the magnetic order and thus an increase of the ordering temperature. Although initially this latter mechanism may prevail, the moment reduction is always predominant at higher pressures. This model has been succesfully applied to describe the pressure dependence of the ordering temperature of U monochalcogenides[23–25] and UPtAl and UNiAl.[26] The same model could explain the pressure dependence of T_N in UGa_3 (Ref. 27) and in UPb_3 (Ref. 28). The results of our measurements as shown in Figs. 2 and 3 can be interpreted in terms of the model mentioned above. The initial increase with pressure of both T_N and B_{thf} suggests that, at least up to $p \sim 13$ GPa, the U magnetic moments are localized. This suggestion is consistent with the observation of crystal field excitations by neutron scattering experiments on UNiSn at ambient pressure.[29] However, fully localized f moment compounds were shown to exhibit a quadratic increase of T_N with pressure.[30,31] Thus, UNiSn should rather be regarded as a nearly localized system. The monotonic increase of B_{thf} is ascribed to the strengthening of the hyperfine coupling constant rather than to an increase of the U moment which is expected to remain constant as long as it may be considered (nearly) localized. On the other hand, we do not observe any steplike anomaly in the pressure dependence of T_N which could be attributed to a sudden change of the magnetic structure. Thus, one can conclude that for pressures below $\sim$13 GPa the RKKY exchange interaction prevails over the mechanisms which tend to weaken or destroy the magnetic order, whereas at higher pressures the latter dominate. In fact for $p \geqslant 13$ GPa the ordering temperature starts to decrease rapidly and a nonmagnetic state is reached at $\sim$18.5 GPa, where the magnetic hyperfine field also vanishes. This suggests that the 5f-ligand(spd) hybridization, as a consequence of the increasing 5f bandwidth with increasing pressure, drives UNiSn from the magnetic to a nonmagnetic state.

Finally, we discuss the effect of pressure on the temperature induced S-M transition and its possible connection to magnetic order in UNiSn. Figures 4(a) and 4(b) display the temperature dependence of the electrical resistance $R(T,p)$ normalized to its room-temperature value $R(294\ \mathrm{K},p)$ for some selected pressures up to 19.3 GPa. The behavior observed at ambient pressure remains visible up to 8.1 GPa. At high temperature the resistance increases exponentially with decreasing temperature, as expected for a semiconductor, following the law $R(T,p) = R_0(p)\exp[E_g(p)/(2k_BT)]$. As pressure increases the resis-

tance maximum shifts towards higher temperatures, while the semiconducting gap E_g decreases approximately linearly at a rate of ~ -7 meV/GPa and closes at a pressure of ~ 9 GPa. Up to 5.5 GPa, below the maximum $R(T,p)/R(294\ \mathrm{K},p)$ drops rapidly indicating a metallic behavior which is associated with the AF ordering at T_N defined by the maximum of the temperature derivative of the resistance (e.g., $T_N \approx 80$ K at $p=5.5$ GPa, see Fig. 3). At 8.1 GPa, the shape below the maximum of the resistance curve starts to be modified with the appearance of a shoulder at about 70 K. By increasing further the pressure to 9.6 GPa the resistance curve exhibits a broad maximum at about 65 K and a metalliclike behavior above 150 K. A crossover between two regimes was already observed by Akazawa *et al.*,[13] but at a somewhat lower pressure. Our NFS data combined with the resistance measurements, however, show unambiguously that the crossover is accompanied by a further shift of T_N to higher temperature contrary to the interpretation of those authors.[13] The amplitude of the broad bump observed at 9.6 GPa decreases progressively at higher pressures and vanishes at 19.3 GPa reflecting the disappearance of magnetic ordering (see NFS data in Fig. 3).

In conclusion, using high-pressure electrical resistance measurements, ^{119}Sn nuclear forward scattering, and Mössbauer spectroscopy, we were able to show that pressure has a dramatic effect on the multiple phase transition behavior of UNiSn at 43 K at ambient pressure. We find that the decrease of the semiconducting gap and the pressure induced semiconductor to metal transition at $p \sim 9$ GPa is accompanied by an enhancement of T_N. Such an increase of T_N with a maximum at ~ 13 GPa suggests a nearly localized behavior of the $5f$ electrons. This finding and the observed collapse of the magnetic state at a critical pressure of ~ 18.5 GPa can be well explained by an interplay between the indirect RKKY interaction and the hybridization between the U-$5f$ and the ligand-*spd* electrons.

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