Role of Conduction Electrons in Valence Fluctuations

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We report magnetic susceptibility results for the valence fluctuation system $CeIn_{3-x}Sn_x$. In the intermediate-valence regime the characteristic energy of spin fluctuations does not vary monotonically with solute e/a ratio, but oscillates with x in the same manner as the conduction-electron density of states. This provides experimental evidence for the role played by the conduction electrons in controlling the spin fluctuation energy.

An important characteristic of valence-fluctuation materials[1] is that the $4f$ electrons demagnetize at low temperatures, i.e., the magnetic susceptibility evolves from Curie-Weiss–like behavior to a temperature-independent value as the temperature is lowered, indicating a loss of moment. An implicit assumption in most theories is that the $4f$ electrons are coupled to the band electrons by a hybridization interaction which broadens the level to a width $\Delta = V_{kf}^2 N(\epsilon_F)$, in traditional Friedel-Anderson notation. Although this view, taken over from the theory of dilute magnetic alloys, is widely held, we are unaware of any experiment which clearly proves its validity for the nondilute intermediate-valence materials.

In this Letter we report experimental evidence which supports the notion that the conduction electrons play a key role in the process of demagnetization. The experiment involves studies of the valence-fluctuation intermetallic alloy $CeIn_{3-x}Sn_x$. In $CeIn_3$ the cerium ions are trivalent[2]; it orders magnetically at low temperature and its anomalous Curie-Weiss susceptibility[3] and resistance minimum[3] suggest that it is a "Kondo metal."[1] $CeSn_3$ possesses a lattice-constant anomaly[2] and susceptibility maximum[3] suggestive of weakly-temperature-dependent intermediate valence. Both materials exhibit the cubic $AuCu_3$ crystal structure; earlier studies[4] indicate complete miscibility in the alloy system. We analyze our magnetic susceptibility results in terms of the concept of a characteristic energy for spin fluctuations,[5] $T_{SF}(x)$, and show that T_{SF} varies proportionally to the conduction-electron density of states $N(\epsilon_F; x)$, whose behavior can be inferred from work on related materials.[6] We conclude with a discussion of the microscopic origin of the observed characteristic energy behavior.

Polycrystalline alloys were prepared by arc melting the purest commercially available starting materials; the assay indicated the main magnetic impurity was iron to a level of 20 ppm. We analyzed our samples utilizing a metallurgical microscope, an x-ray powder diffractometer, and a scanning electron microscope with fluorescence attachment. For all concentrations x, the samples were essentially single phase (we observed 2–3% indium and/or tin in the grain boundaries[2]), exhibited the $AuCu_3$ structure, and were basically homogeneous (stoichiometry variations across the sample surface were several percent). Crystallites were irregularly shaped with typical linear dimensions 30–50 μm.[2] We made duplicate samples at several concentrations; the lattice constants and susceptibility were reproducible. For $x \geq 1.0$, an extrinsic nonreproducible impurity contribution A/T was observed in the susceptibility below about 10 K (Fig. 1). We have left this in the data as it has only a negligible effect on our main results (Fig. 2). High-temperature annealing increased A by an order of magnitude, whereas the lattice constant remained unaltered. The Curie-Weiss parameters $\Theta(x)$ were obtained by linear fits to χ^{-1} for $T > 2.5\,\Theta(x)$. We intend to report on these matters in detail in a forthcoming publication.
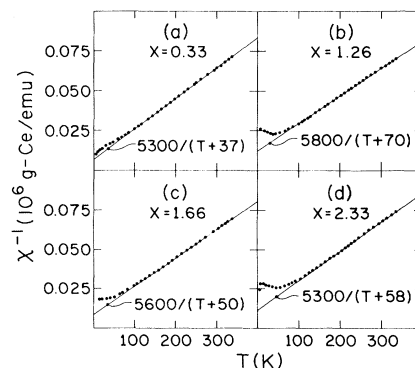

FIG. 1. Inverse magnetic susceptibility $\chi^{-1}(x; T)$ for four representative concentrations x in the system $CeIn_{3-x}Sn_x$. The solid lines represent Curie-Weiss–like behavior, $C/(T + \theta)$ with the parameters as specified, where the units of C are 10^{-6} emu K (g Ce)$^{-1}$.
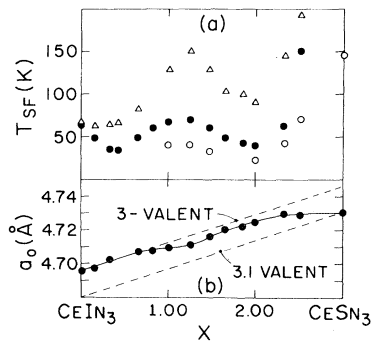
FIG. 2. (a) Three estimates of the characteristic temperature T_{SF} for $CeIn_{3-x}Sn_x$—the Curie-Weiss parameter $\Theta(x)$ (closed circles), the temperature of the maximum in the susceptibility $T_{max}(x)$ (open circles), and the inverse low-temperature susceptibility C/χ (10 K) (triangles). (b) Room-temperature lattice constants vs x. The dashed lines represent Vegard's-law behavior (Ref. 15). Note the oscillatory deviation from Vegard's law.

The susceptibilities of four representative samples are shown in Fig. 1. We note the following features: At high temperatures, Curie-Weiss–like behavior is observed for all x. For $x \geqslant 1.0$ the susceptibility either exhibits a maximum or for $1.6 \leqslant x \leqslant 1.9$ approaches $T = 0$ with zero slope. For $x \leqslant 0.6$, the susceptibility behaves qualitatively differently, namely it continues to increase strongly to the lowest temperature studied (4.2 K). For $CeIn_3$ magnetic order occurs below $T_{mag} = 9.5$ K; preliminary studies indicate that the ordered state does not occur for x larger than about 0.4.

The demagnetization of intermediate-valence materials can be discussed in terms of relaxational spin dynamics involving a characteristic energy for spin fluctuations, kT_{SF}. This behavior has been substantiated by inelastic neutron scattering experiments and susceptibility measurements in $Ce_{1-x}Th_x$[5,7] and $CePd_3$.[8] The spin excitation spectrum is found to be Lorentzian:

$$\text{Im}\chi(Q, \omega) = B\,\Gamma\omega/(\Gamma^2 + \omega^2) \tag{1}$$

and kT_{SF} can be defined as $\hbar\Gamma$. It seems that the following is generally true: For $T \gg T_{SF}$ the dc susceptibility is Curie-Weiss–like,

$$\chi(T) = m_1 C/(T + \Theta)\,, \tag{2}$$

where $\Theta = m_2 T_{SF}$; for $T \ll T_{SF}$ the system demagnetizes and the susceptibility approaches a finite value

$$\chi(T = 0) = m_3 C/T_{SF}; \tag{3}$$

the crossover occurring in the vicinity of T_{SF}

often takes the form of a maximum in the susceptibility,[9] at a temperature $T_{max} = m_4 T_{SF}$. Here C is the free-ion Curie constant (for cerium with $J = \frac{5}{2}$, $C = 5760 \times 10^{-6}$ emu K (g Ce)$^{-1}$ and the m_i are dimensionless constants of order unity. We thus have three independent order-of-magnitude estimates of the characteristic energy, namely $\Theta(x)$, $C/\chi(x; T = 0)$, and $T_{max}(x)$.

The data of Fig. 1 demonstrate that the high-temperature behavior is indeed Curie-Weiss–like, and is consistent with $m_1 = 1$. In Fig. 2(a) we plot $\Theta(x)$, $T_{max}(x)$, and $C/\chi(x; 10$ K) for all samples studied. [We use the value of χ at 10 K because it adequately represents $\chi(0)$ and because at this temperature the impurity contribution A/T is negligible.] For $x \geqslant 1.0$ there exists a rough proportionality amongst these parameters, viz., $C/\chi(0) \approx 2\theta$ and $T_{max} \approx \theta/2$. Similar behavior has been observed in ytterbium-based systems.[9,10] [It should be pointed out that crystal fields will have negligible effects on $\Theta(x)$ and $T_{max}(x)$ for the same reasons as in γ-$Ce_{1-x}Th_x$,[5,7] although they may affect the properties somewhat for $T < T_{SF}$.]

The striking and unexpected feature of Fig. 2 is that T_{SF} does not vary in a monotone fashion with increasing x.[11] One would expect that since tin has a larger e/a ratio than indium, tin dilution would stabilize the intermediate-valence state of cerium ions to higher temperatures (such an effect occurs, for example, in $Ce_{1-x}M_x$ alloys,[12] where M is a rare-earth element); hence the characteristic energy $T_{SF}(x)$ should simply increase with increasing x. We argue here that the oscillation[13] observed in $T_{SF}(x)$ in our data arises because the characteristic energy depends on the conduction-electron density of states $N(\epsilon_F)$ {e.g., either via $kT_{SF} \sim N(\epsilon_F)V_{kf}^2$ or via $T_{SF} \sim \exp[-1/N(\epsilon_F)J]$ as in the Kondo problem} and because the density of states in this material itself oscillates with x. This latter can be inferred from the work by Toxen, Gambino, and Welsh[6] on the closely related nonmagnetic system La-$In_{3-x}Sn_x$. Utilizing measurements of superconducting T_c's, linear coefficients of specific heat,[14] and Debye temperatures, they apply the McMillan formula to show that $N(\epsilon_F)$ exhibits an oscillation with x strikingly similar to that exhibited by $T_{SF}(x)$. This is demonstrated in Fig. 3. They indicate that the oscillation is a fairly general electronic property in a class of related systems possessing the $AuCu_3$ crystal structure. We assume that in $CeIn_{3-x}Sn_x$ the bare density of states for conduction electrons (treated prior to hybrid-
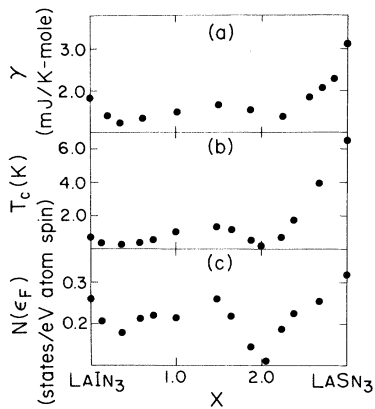
FIG. 3. Electronic behavior of the nonmagnetic, iso-structural system $LaIn_{3-x}Sn_x$. (a) Linear coefficient of specific heat (Ref. 13). (b) Transition temperatures for superconductivity (Ref. 6). (c) Density of states at the Fermi level, obtained in Ref. 6 as discussed in the text. The density of states for $CeIn_{3-x}Sn_x$, prior to hybridization with the $4f$ states, should be essentially identical to that exhibited here.

ization with $4f$ states) exhibits the same behavior as in $LaIn_{3-x}Sn_x$, i.e., that the electronic properties of the latter are identical to the former except for the absence of the $4f$ electron. We then conclude that our data provide strong evidence for the role played by the conduction electrons in controlling $T_{SF}(x)$.

We next consider the microscopic origin of the characteristic energy behavior. Two mechanisms can, in principle, lead to the demagnetization phenomenon: Kondo-like spin fluctuations, where the cerium $4f$ state is always populated, and valence fluctuations ($4f$- to band-state charge fluctuations) where on the time average the $4f$ spin is only fractionally occupied. To determine the mechanisms involved in $CeIn_{3-x}Sn_x$ we consider the room-temperature lattice-constant measurement, Fig. 2(b). The data clearly exhibit an oscillatory deviation from Vegard's law.[13] For $x > 0.8$, the valence (obtained by interpolation) increases and decreases with increasing and decreasing characteristic energy. This suggests that valence fluctuations (accompanied by local cell-volume changes) are dominant. For $x < 0.8$, the lattice constant suggests trivalence; in addition, the low-temperature susceptibility differs from that for $x > 0.8$ in that it does not flatten or attain a maximum in the vicinity of T_{SF} even though the magnitude of $\Theta(x)$ does not differ appreciably in the two regimes. Since $CeIn_3$ possesses a resistance minimum[3] it is natural to

infer that Kondo fluctuations are significant in determining T_{SF} for $x < 0.8$; such processes would not be as strongly coupled to the local cell volume as direct hopping from a $4f$ state into the band. It should also be pointed out that magnetic exchange may contribute to $\Theta(x)$ for $x < 0.4$; hence whereas T_{SF} clearly tracks $N(\epsilon_F)$ in the intermediate-valence regime this may not be the case for the trivalent material. This would be consistent with the flattening observed in $C/\chi(x;0)$ for small x. In any case it is clear that the magnetic behavior in the trivalent regime is qualitatively different from the behavior in the noninte-gral-valence regime. It seems reasonable to infer that in $CeIn_{3-x}Sn_x$ a real distinction must be made between "Kondo-metal" and intermediate-valence behavior.

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[11]W. Dykman and F. R. deBoer, have also recently observed nonmonotonic behavior of $T_{max}(x)$ in $CeIn_{3-x}Sn_x$ (private communication).

[12]M. A. Manheimer and R. D. Parks, in Valence Instabilities and Related Narrow Band Phenomena, edited by R. D. Parks (Plenum, New York, 1977), p. 447.

[13]The magnitude of the oscillation in Fig. 2 is well outside the bounds of error, which are less than ± 10% for $\Theta(x)$, and are ± 2% for $T_{max}(x)$ and $C/\chi(x;\ 10\ K)$; for $a_0(x)$ the relative error ± 0.002 Å.

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[15]For both $CeIn_3$ and $CeSn_3$ our a_0 values are larger than those of Ref. 2 by 0.018 Å. We believe this difference represents a calibration error which does not affect the relative variation of a_0 with x, since our results were reproducible. Taking this difference into account, the Vegard's-law prediction was obtained from Ref. 2.

Ion Desorption by Core-Hole Auger Decay

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We present evidence for a fundamentally new mechanism for impact-induced desorption, viz., core-hole Auger decay. We thereby explain why observed thresholds for electron-stimulated desorption (ESD) of positive ions (O^+, OH^+, and F^+) from certain d-band metal oxides (TiO_2, V_2O_5, and WO_3) correlate in energy with the ionization potential of the highest-lying atomic core levels. We conclude that electron-stimulated desorption is in many interesting cases an atom-specific, valence-sensitive probe of surfaces.

In this Letter we present evidence for a fundamentally new mechanism of impact-stimulated ion desorption. We show that this mechanism, namely Auger decay of a core hole,[1] explains both the observed thresholds and the large charge transfers involved in the electron-stimulated desorption (ESD) of positive ions (O^+, OH^+, and F^+) from maximal-valence transition-metal oxides (TiO_2, V_2O_5, and WO_3), whereas the commonly accepted picture of ESD[2,3] does not. We also show that the identification of this new mechanism means that ESD is an atom-specific, defect-sensitive probe of bonding at an important class of surfaces.

The usual picture of ESD, due to Menzel and Gomer,[2] and Redhead,[3] is that the incident beam excites a bonding electron to an antibonding or nonbonding state; as a result, the effective potential between surface atom and solid becomes repulsive, and the atom desorbs. In this model the theoretical threshold for desorption is typically predicted to be low, on the order of 15–20 eV. Additionally this model leaves open the question of how a highly electronegative atom such as O, which is typically bonded with a charge between − 1 and − 2, manages to desorb as O^+—a feat which requires the transfer of 2 to 3 electrons.

The data which underlie our model come from ESD, Auger and low-energy electron-loss spectroscopy (LEELS)[4] measurements that we have made on a series of transition-metal–oxide samples (TiO_2, V_2O_x, WO_3, Cr_2O_3, and NiO). All of the samples were single crystals, except the V_2O_x which was glassy or polycrystalline, and were sputter cleaned and electron-beam annealed.

In Fig. 1 we show the O^+ desorption currents versus incident electron energy (corrected for cathode work function) from annealed, defect- and impurity-free TiO_2, WO_3, and V_2O_5. We also indicate observed LEELS peak energies, by arrows. Note that for each metal-atom core-level loss peak there is a correlated threshold in the O^+ yield (which lies at a slightly lower energy than the loss peak, i.e., in the neighborhood of the loss onset). There is also in each case a very weak O^+ desorption threshold at the oxygen L_1 energy (roughly three decades down from the saturation O^+ current—see, e.g., Fig. 1, inset for TiO_2).

At the outset we note that the valence-electron bonding-antibonding transitions (the arrows in Fig. 1 at energies ≲ 15 eV), which in the classi-