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Valence-fluctuation behavior of Yb ions in YbCuGa

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The compound YbCuGa has been synthesized and is found to crystallize in the orthorhombic $CeCu_2$-type structure. Its magnetic susceptibility has been measured between 4.2 and 300 K and shows a broad maximum at about 190 K. This maximum is a characteristic feature of the mixed-valent Ce- and Yb-based compounds. The temperature-dependent resistivity exhibits an *S*-type behavior. The thermoelectric power is negative between 20 and 300 K and also shows a broad minimum at about 190 K. L_3 x-ray-absorption near-edge-structure (XANES) measurements show the two-peak pattern that corresponds to two different valence states of Yb. Thus, magnetic susceptibility, electrical resistivity, thermoelectric power, and L_3 XANES measurements all point to the mixed-valence nature of Yb ions in YbCuGa.

For the past few years, the rare-earth intermetallic compounds of Ce, Yb, and Eu have attracted considerable attention because of their anomalous properties which are associated with the valence instability of these rare-earth ions. The lattice parameter or the unit-cell volume of a system with rare-earth ions in the valence-fluctuating state is usually intermediate between those of the integral-valence states and deviates from the corresponding lanthanide contraction observed in the case of pure-trivalent ions. The mixed-valent state is also reflected in static dc susceptibility and L_3-edge measurements. In the former a broad maximum is often observed at some temperature, while in the latter, a two-peak pattern that corresponds to two different valence states of the fluctuating rare-earth ion is detected. The resistivity of a valence-fluctuating system deviates from linear T dependence at high temperatures and shows either a T^2 or a T^3 dependence at low temperatures. Although there are several compounds containing Ce which exhibit such phenomena,[1-5] very few compounds containing Yb are known that show similar behavior. Therefore, we have made an intensive search for compounds in which Yb ions exhibit the above-mentioned anomalous physical properties.[6-8] In this Rapid Communication we present the results of magnetic susceptibility, electrical resistivity, thermoelectric power, and L_3 x-ray-absorption near-edge-structure (XANES) measurements on YbCuGa, which we identify to be a new mixed-valent compound of Yb.

Polycrystalline samples of YbCuGa (and LaCuGa) were prepared by arc melting and/or induction melting of stoichiometric amounts of the constituent elements with purity that is better than 99.9% under a continuous flow of argon gas. The weight loss due to the volatile nature of the Yb metal was adequately compensated for, so as to keep the weights of the constituent elements Yb, Cu, and Ga in the stoichiometric ratio of 1:1:1 after the final melt. The as-cast samples were used for further studies. Formation of a single-phase compound was confirmed by powder x-ray-diffraction studies. The magnetic susceptibility was measured using a Faraday method in the temperature range of 4.2–300 K in an applied field of 6 kOe. The electrical resistivity was measured with a four-probe dc technique. The electrical contacts to the sample were made with conducting silver paint. Measurements were made by switching the current direction at each temperature to cancel the effects due to thermal emf's. Data points were taken during the heating cycle from 4.2 to 300 K. Temperatures were measured using a calibrated carbon-glass thermometer between 4.2 and 20 K and a platinum resistance thermometer above 20 K. Thermoelectric power was measured using the differential method in the temperature range between 20 and 300 K.

Powder x-ray-diffraction studies revealed that YbCuGa and LaCuGa are single-phase compounds and their x-ray patterns are similar to those of other *R*CuGa compounds (*R*=rare earths), which are known to crystallize in the orthorhombic $CeCu_2$-type structure (space-group *Imma*). In the $CeCu_2$-type structure of YbCuGa, the Cu and Ga atoms will be randomly distributed on the 8*c* sites. However, with an ordered arrangement of Cu and Ga atoms and a small adjustment in atomic positions, the structure would become the TiNiSi type. Work on a single crystal is needed to further elucidate the structure type. Figure 1 shows a plot of the unit-cell volume of *R*CuGa compounds as a function of the rare-earth ion.[9] In this series, the unit-cell volume of YbCuGa is anomalous; this indicates that Yb ions are not in a trivalent state in this compound but may exist in a divalent or mixed-valent state. Support

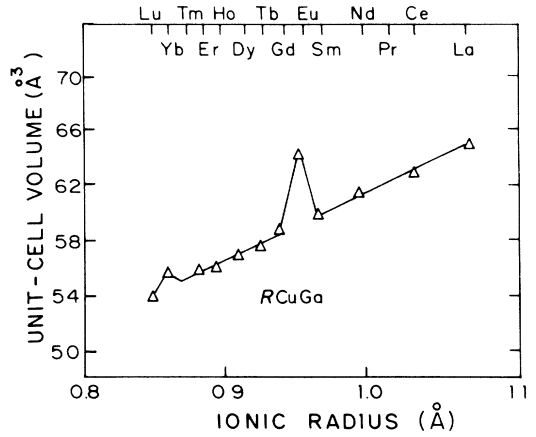

FIG. 1. Unit-cell volume of RCuGa compounds as a function of the rare-earth (R) ionic radius.

regarding the mixed-valent state of Yb comes from the magnetic susceptibility, electrical resistivity, thermoelectric power, and L_3 XANES measurements presented below.

Figure 2 shows the plot of magnetic susceptibility of YbCuGa in the temperature range 4.2–300 K. The interesting feature of this plot is the presence of a broad maximum at about 190 K. The maximum in the susceptibility is a characteristic of mixed-valent Ce- and Yb-based compounds as seen, for instance, in CeRhIn and YbCuAl (Refs. 10 and 11) and can be understood in terms of the ionic-configuration-fluctuation (ICF) model.[12] In this model the rare-earth ion fluctuates between the ground-state configuration and the excited-state configuration which are separated by an energy $E_{\rm exc}$. The observed behavior of the susceptibility of YbCuGa has been analyzed using the above-mentioned model. The ground state of Yb (Yb^{2+},$4f^{14}$) has total angular momentum $J=0$ and effective magnetic moment $\mu_{\rm eff}=0$, while the excited state (Yb^{3+},$4f^{13}$) has $J=\frac{7}{2}$ and $\mu_{\rm eff}=4.54\mu_B$. The susceptibility of the mixed-valent Yb ions in the ICF model is given by the following equation:

$$\chi(T)=(1-n)\frac{N(4.54\mu_B)^2P(T)}{3k(T+T_{\rm sf})}+n\frac{C}{T}+\chi_0, \qquad (1)$$

and

$$P(T)=\frac{8}{8+\exp[E_{\rm exc}/k(T+T_{\rm sf})]}, \qquad (2)$$

where $P(T)$ is the fractional occupation probability of $4f^{13}$ state, $T_{\rm sf}$ is the spin-fluctuation temperature and is a measure of the width of the $4f$ level which is broadened because of hybridization with the conduction electrons, and χ_0 is the temperature-independent susceptibility. The factor n is introduced to account for the upturn in susceptibility at low temperatures caused by paramagnetic impurities which we take to be Yb^{3+} ions. A least-squares-fitting procedure was used to fit Eq. (1) to the experimentally observed susceptibility. A typical fit is shown as a solid line in Fig. 2 with the parameters obtained, $E_{\rm exc}=715$ K, $T_{\rm sf}=141$ K, $n=0.0146$, and $\chi_0=4.4\times10^{-5}$ emu/mol. These values of $E_{\rm exc}$ and $T_{\rm sf}$ are comparable to the values reported for other Yb-based mixed-valent compounds, such as $YbAl_3$.[12] The valence of the Yb ion in YbCuGa that is calculated with this set of parameters and Eq. (2) is 2.61 at room temperature.

The dc resistivity of YbCuGa and LaCuGa as a function of temperature is shown in Fig. 3. The value of the room-temperature resistivity of YbCuGa is 185 $\mu\Omega$ cm, which is of the same order of magnitude as the resistivity that is observed in most other valence-fluctuating Yb-based compounds.[13–15] The resistivity of YbCuGa decreases linearly between 300 and 200 K. Below 200 and down to 90 K, the resistivity continues to decreases linearly with decreasing temperature but with a different slope. The temperature at which the slope change occurs is almost the same temperature at which the magnetic susceptibility exhibits a broad maximum. The resistivity exhibits a T^2 dependence between 4.2 and 92 K, which is similar to the behavior observed in some Yb- and Ce-based mixed-valence and heavy-fermion compounds, e.g., $CeInPt_4$ and $YbAgCu_4$.[16,17] The origin of the T^2 depen-

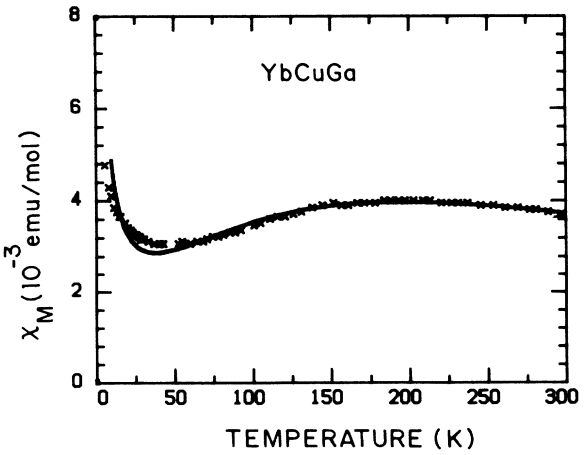

FIG. 2. Magnetic susceptibility of YbCuGa as a function of temperature.

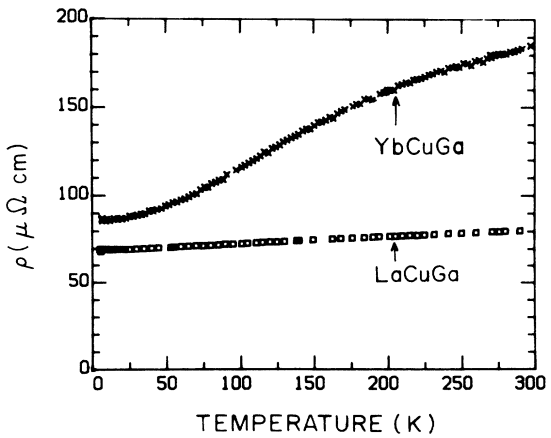

FIG. 3. Electrical resistivity of YbCuGa and LaCuGa as a function of temperature.

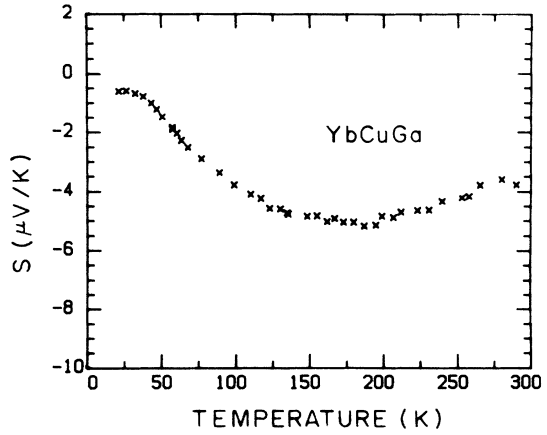

FIG. 4. Thermoelectric power of YbCuGa as a function of temperature.

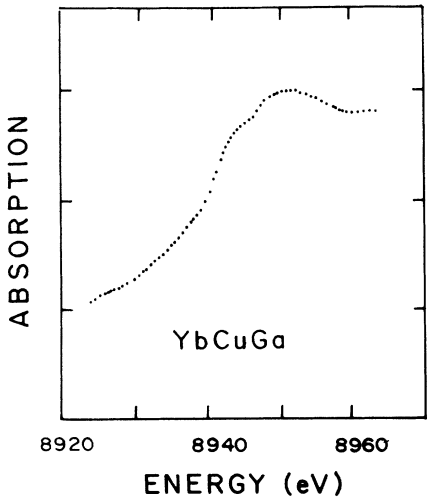

FIG. 5. L_3 XANES of Yb ions in YbCuGa at 300 K.

dence of the resistivity can be understood on the basis of the Fermi-liquid theory.[2,18] The magnetic contribution to the resistivity of YbCuGa was obtained by subtracting the resistivity of LaCuGa. The overall feature of the magnetic-scattering resistivity is similar to that of the total resistivity.

Temperature dependence of the thermoelectric power (TEP) of YbCuGa in the temperature range of 20–300 K is shown in Fig. 4. At room temperature, the TEP is about -3.5 μV/K. The negative sign of the TEP agrees with that observed in most of the Yb-based mixed-valent compounds; this suggests that the majority carriers are electrons. When the temperature decreases from room temperature, the TEP becomes more negative and reaches a maximum absolute value of 5 μV/K at 190 K. Below 190 K, the TEP becomes less negative with decreasing temperature and saturates at low temperature. The TEP is a quantity which depends on the derivative of the density of states at the Fermi level (E_F). The deviation of the TEP from linearity {TEP$=AT$, where $A=K^3/3[d\ln N(E)/dE]$} at $E=E_F$, expected from the electrons-diffusion term, reflects a tendency of Yb ions towards intermediate valence and also reflects the modification with temperature in the electronic density of states at E_F. The maximum in the TEP, which occurs at about the same temperature at which the susceptibility shows a broad maximum, can be qualitatively understood from the large-energy-dependent and strongly temperature-dependent density of states at the Fermi level.[19]

Figure 5 shows the L_3 XANES region of Yb in YbCuGa at 300 K. The XANES spectrum of YbCuGa exhibits two distinct peaks separated by 7 eV. The energy of these peaks is measured and compared with the standard divalent and trivalent Yb compounds.[20] The comparison reveals that the double peak that appears in the absorption spectrum of YbCuGa corresponds to two different valence states of the Yb ion (Yb^{2+} and Yb^{3+}). This implies that Yb ions in YbCuGa are in a mixed-valence state. It should be mentioned that L_3 XANES studies at room temperature alone cannot distinguish between homogeneous and inhomogeneous mixed-valent states. However, taken together with magnetic susceptibility, electric resistivity, and thermoelectric power measurements, this implies a homogeneous mixed-valent behavior of Yb ions in YbCuGa.

In conclusion, magnetic susceptibility, electrical resistivity, thermoelectric power, L_3 XANES, and lattice parameters measurements of YbCuGa compounds all point to the fact that the Yb ions are in the valence-fluctuating or mixed-valence state in YbCuGa.

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