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Simultaneously optimizing the interdependent thermoelectric parameters in $Ce(Ni_{1-x}Cu_x)_2Al_3$

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Substitution of Cu for Ni in the Kondo lattice system $CeNi_2Al_3$ results in a simultaneous optimization of the three interdependent thermoelectric parameters: thermoelectric power, electrical, and thermal conductivities, where the electronic change in conduction band induced by the extra electron of Cu is shown to be crucial. The obtained thermoelectric figure of merit zT amounts to 0.125 at around 100 K, comparable to the best values known for Kondo compounds. The realization of ideal thermoelectric optimization in $Ce(Ni_{1-x}Cu_x)_2Al_3$ indicates that proper electronic tuning of Kondo compounds is a promising approach to efficient thermoelectric materials for cryogenic application.

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Thermoelectric (TE) materials are used to construct all solid-state power generator or Peltier cooler. Current TE materials such as Bi_2Te_3-Sb_2Te_3 alloy have a dimensionless figure of merit $zT \sim 1$ at near or above room temperature.[1] zT, defined as $TS^2/\rho\kappa$, determines the efficiency of TE conversion at a particular temperature T, with S being the thermoelectric power, ρ the electrical resistivity, and κ the thermal conductivity which consists of electronic part κ_e and lattice part κ_L. In normal metals or semiconductors, S, ρ, and κ are not independent. The classical route to high-efficiency TE materials is based on doping or alloying an appropriate semiconductor into a degenerate regime of carrier concentration $n \sim 10^{19}$ cm^{-3}, where a good compromise between S and ρ is reached with a high thermoelectric power factor S^2/ρ.[1] Modern electronic technology has created a strong demand for TE materials operating at cryogenic temperatures, to provide applications such as spot cooling microelectronic superconducting devices. The aforementioned concept, unfortunately, does not seem to hold true for development of TE materials below 200 K.[2]

One promising candidate for cryogenic TE application is heavy-fermion (HF) or intermediate-valence (IV) metals, which are characterized by the so-called Kondo resonance of conduction electrons screening the magnetic moment of f or d electrons. Kondo resonance produces a sharp feature in the electronic density of states (DOS), leading to a 2–3 orders of magnitude enhancement of the effective charge-carrier mass m^* and a large S amounting to several tens of μV/K at around Kondo temperature T_K.[3] As metals, they have relatively large κ_e that is tied to metallic ρ by Wiedeman-Franz law ($\rho\kappa_e/T = L_0$, with $L_0 = 2.44 \times 10^{-8}$ V^2/K^2). A simple calculation neglecting κ_L indicates that $S > 156$ μV/K is necessary to achieve a practical zT above unity. The largest S so far known in metallic Kondo systems is ~ 120 μV/K observed in $CePd_3$, with $zT < 0.25$ at around 200 K.[1,4] Further enhancement of zT was not achieved for HF or IV systems, though a value as high as 14 has been predicted.[5]

Like the current TE materials in use, high-zT materials for cryogenic application might emerge by optimizing an appropriate parent system. The key point, therefore, is to identify this system and the mechanisms that might lead to optimization of the TE parameters. In this Brief Report, we report a simultaneous optimization of S, ρ, and κ_L in a Kondo lattice system $Ce(Ni_{1-x}Cu_x)_2Al_3$ realized by substitution. The Ce ion in $CeNi_2Al_3$ experiences a nearly tetravalent[6,7] or IV state,[8] which, by replacing Ni with Cu, an atom with larger volume as well as an extra conduction electron, evolves into HF and eventually magnetically ordered state. The evolution accompanies an enhancement of the maximum thermoelectric power (Fig. 1, lower panel) and its shift to lower temperature. Concomitant reductions in ρ and κ_L due to the electronic change in conduction band and the chemical disorder, respectively, are also realized, resulting in a substantially enhanced zT ~ 0.125 at around 100 K. The largely enhanced electronic specific-heat coefficient γ and $\alpha = S/T$ ($T \to 0$ K) (Fig. 1, upper panel) point to the formation of heavy quasiparticles with substitution. At below 100 K, the observed zT values largely exceed that of $CePd_3$, the so-called "best" TE material in Kondo systems.[4] The decisive impetus for the simultaneous optimization of S, ρ, and κ_L is to be discussed in terms of the electronic change in conduction band. A further development of more efficient TE materials for cryogenic application along the lines should be largely expected.

Polycrystalline $Ce(Ni_{1-x}Cu_x)_2Al_3$ compounds with various x were prepared by arc-melting stoichiometric amounts of constituent elements in a high-purity argon atmosphere. The purities of the starting elements are 99.9%, 99.997%, 99.999%, and 99.999% for Ce, Ni, Cu, and Al, respectively. No annealing treatment was carried out. Power x-ray diffraction spectra confirmed the formation of the hexagonal $PrNi_2Al_3$-type structure of the samples with $x < 0.5$, with tiny impurity peak appearing at around $2\theta \sim 50°$ as reported previously.[6,9] For $x > 0.5$, a trace of second phase, which was determined to be $CeCuAl_3$,[10] appears gradually. The second phase in the sample of $x = 0.6$, i.e., the upper substitution limit in this work, was estimated to be less than 3%. For this composition, a magnetic transition was observed at 2.3 K and it increases rapidly with x. The continuous expansions of the lattice constants a and c (Fig. 1, inset) indicate successful substitution of Cu atoms. A change in the slopes of a and c as a function of x is discerned at around $x = 0.4$, the critical concentration between the nonmagnetic and magnetic regimes.[11] The thermoelectric properties were measured by either a home-build cryostat with a slowly varying-gradient technique (chromel/Au+0.07% Fe thermocouple as ΔT detector) or a commercial physical properties measurement system [physical property measurement system (PPMS), Quantum Design]. The discrepancies between the two tech-

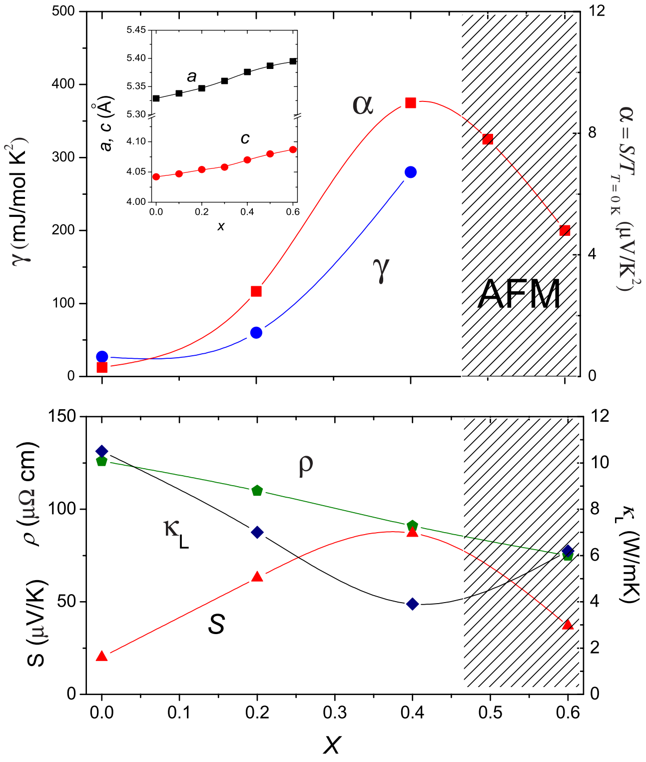

FIG. 1. (Color online) Upper panel: x dependence of γ and α, the zero-temperature linear coefficients of electronic specific heat and thermoelectric power of $\mathrm{Ce(Ni_{1-x}Cu_x)_2Al_3}$, respectively. The enhancement of both quantities with x indicates the formation of heavy-fermion state with enhanced effective charge-carrier mass m^*. Lower panel: x dependence of the three thermoelectric parameters S, ρ, and κ_L at $T=100$ K. Their simultaneous optimization with increasing x results in an enhanced thermoelectric figure of merit at $x=0.4$. For the compounds with $x>0.5$, antiferromagnetic (AFM) order is confirmed. Inset shows smooth increase in the lattice parameters a and c as a function of x.

niques were found in less than 5% with a typical sample dimension of $1\times1\times5\ \mathrm{mm}^3$.

The most impressive feature in the $S(T)$ curves (Fig. 2) is a largely enhanced, positive maximum $S_{\max}$, as observed in many other Ce-contained HF or IV compounds.[1] For $x\le0.4$, while the position of $S_{\max}$ in temperature decreases, its value increases largely with x. The enhanced $S_{\max}$ value for the compound of $x=0.4$, 90 μV/K at 70 K, was confirmed by the two measurement techniques given above. The previous studies on annealed samples presented a $S_{\max}$ of only 60 μV/K for $x=0.4$.[9] The difference with the present results most likely reflects the sensitivity of electron-electron correlations with respect to composition in the vicinity of the critical concentration: for example, γ and α show dramatic change at around $x=0.4$ (Fig. 1, upper panel). Looking carefully into the previous results,[9] one also notice that the real $S_{\max}$ for $x=0.4$ could be higher: while γ doubles by varying x from 0.3 to 0.4, α does not follow γ but remains flat. As estimated from the value of $1/\gamma$ and the position of $S_{\max}$, Kondo temperature T_K decreases gradually with x. The enhancement of $S_{\max}$ with x tracks the enhancement of the effective mass m^* ($\sim\gamma$) as a consequence of the reduction in T_K. The correspondence of the enhanced γ and α (Fig. 1, upper panel) follows the general behavior expected for correlated systems,[12,13] unambiguously evidencing the realization of HF state. Further substitution exceeding $x=0.4$ reduces $S_{\max}$, due to the onset of magnetic ordering and the consequent diminish of m^*.

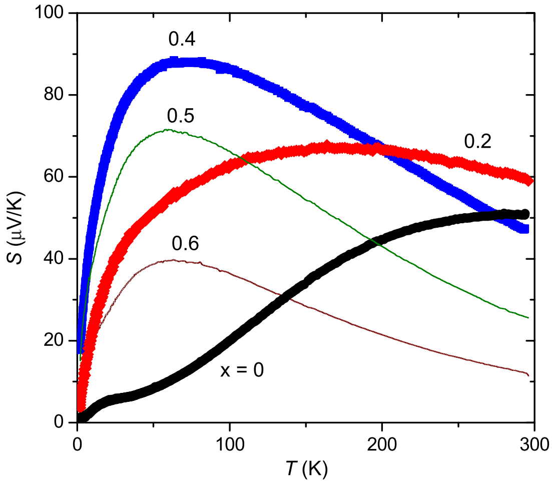

FIG. 2. (Color online) The thermoelectric power S as a function of temperature for various $\mathrm{Ce(Ni_{1-x}Cu_x)_2Al_3}$ compounds. While the position of $S_{\max}$ in temperature decreases with substitution up to $x=0.4$, its value increases largely. Above this critical concentration, the compounds order magnetically and their $S_{\max}$ decreases dramatically with x.

Upon increasing x from 0.0 to 0.6, the electrical resistivity ρ (Fig. 3, upper panel) evolves from a monotonically increasing to a monotonically decreasing function of temperature, again pointing to the decrease in T_K. The broad maximum in $\rho(T)$, another estimate of T_K, shifts from $\sim$200 K for $x=0.2$ to $\sim$100 K for $x=0.4$. Remarkably, ρ above 70 K exhibits a systematic reduction with increasing x, in spite of the increasing residual resistivity ρ_0. In combination with the enhancement of $S_{\max}$, this indicates a simultaneous optimization of ρ and $S_{\max}$ that is impossible in classical metals.

The overall resistivity of a nonmagnetic isoelectronic reference system $\mathrm{La(Pd_{1-x}Ag_x)_2Al_3}$ (Ref. 14) exhibits behaviors characteristic of a normal metal and decreases steadily with increasing x (inset of Fig. 3). For instance, ρ at room temperature changes from 150 $\mu\Omega$ cm for $x=0.0$ to 35 $\mu\Omega$ cm for $x=0.6$, reflecting the electronic-structure change in the conduction band. The evolution of ρ in the reference system hints that the decrease in ρ with x in $\mathrm{Ce(Ni_{1-x}Cu_x)_2Al_3}$ shares the same origin: it is due to a decrease in the usual electron-phonon-scattering term ρ_p, assuming that $\rho=\rho_0+\rho_p+\rho_m$, where ρ_0 is the residual resistivity and ρ_m is the magnetic part occurring only in the Ce compounds. On the other hand, γ diminishes with x in $\mathrm{La(Pd_{1-x}Ag_x)_2Al_3}$,[15] indicative that the full-filled d band of Cu triggers a shift of the Fermi level away from the enhanced DOS of d character. Similar effect is confirmed both experimentally and theoretically in $\mathrm{Ce(Pd_{1-x}Cu_x)_2Si_2}$.[16] The shift of conduction band from d- to s- or p-like bands can naturally account for the decrease in ρ, as well as the decease in $T_K\sim\exp[-1/\mathrm{DOS}(\epsilon_F)J]$, as a function of x in $\mathrm{Ce(Ni_{1-x}Cu_x)_2Al_3}$. $\rho(T)$ for $x=0.4$ shows an up-

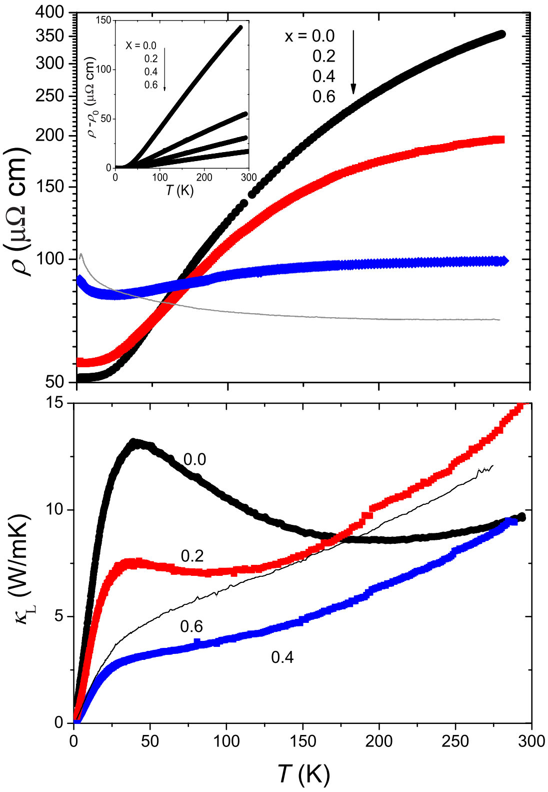

FIG. 3. (Color online) The electrical resistivity, ρ (upper panel), and the lattice contribution to thermal conductivity, κ_L (lower panel), as a function of temperature for various $Ce(Ni_{1-x}Cu_x)_2Al_3$ compounds. For the estimation of κ_L, the Wiedemann-Fran law and the Sommerfeld value of L were employed. Inset shows $\rho - \rho_0(T)$ of a reference system, $La(Pd_{1-x}Ag_x)_2Al_3$, which follows the Bloch-Grüneisen function typical of normal metals with a remarkable reduction in the overall values with increasing x. The residual resistivity ρ_0 of the reference compounds is 3.9, 28.9, 18.8, and 17.2 μΩ cm for $x=0.0$, 0.2, 0.4, and 0.6, respectively.

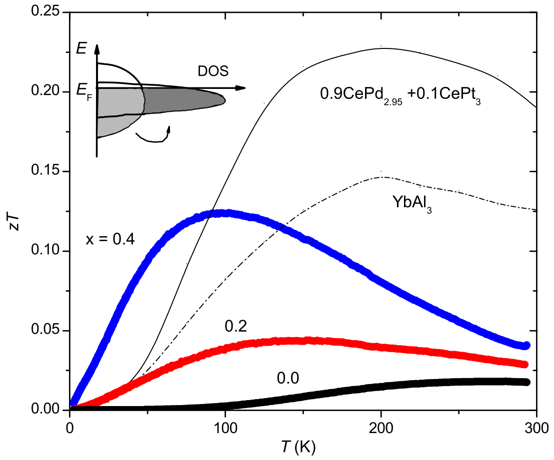

FIG. 4. (Color online) The dimensionless thermoelectric figure of merit zT of $Ce(Ni_{1-x}Cu_x)_2Al_3$, in comparison to that of optimized $CePd_3$ and $YbAl_3$.[4] Inset illustrates the evolution of the DOS of heavy quasiparticles at near the Fermi level from IV to HF state, which in principle accounts for the enhancement of S in the present $Ce(Ni_{1-x}Cu_x)_2Al_3$ system.

turn below 20 K as well as a broad hump at 100 K. This is a sign of the crystal electric field splitting effect on the sixfold-degenerate Ce^{3+} state, indicating that not only the ground Kramers doublet, but also one excited multiplet are perhaps involved in the transport properties. The ground-state degeneracy was only recently recognized to be important for TE properties in Kondo systems.[17]

The lattice thermal conductivity κ_L in $CeNi_2Al_3$ (Fig. 3, lower panel) is characterized by a maximum at $T \approx 40$ K, a fingerprint of crystalline solid. The κ_L maximum smears out with substituting Cu, leading to a largely reduced κ_L for $x=0.4$ over the whole temperature range. The reduction in κ_L is attributed to the substitutional chemical disorder that is frequently employed in modern TE development. To better understand the evolution of κ_L with x in the present system, however, it is necessary to consider another phonon-scattering process by, i.e., valence fluctuation, which was recently shown to be an effective way to reduce κ_L in HF or IV systems.[18] The decrease in Kondo temperature T_K with x in the present system evidences the decrease in phonon-scattering rate by valence fluctuation, which gives the reason why κ_L of $x=0.6$ is higher than that of $x=0.4$. Furthermore, it should be noticed that the increase in κ_L with temperature for the substituted compounds is not typical of a crystalline solid, and instead is reminiscent of the typical κ_L observed in amorphous systems.

The simultaneous optimization of S, ρ, and κ_L realized in the present substitutional $Ce(Ni_{1-x}Cu_x)_2Al_3$ leads to a systematic substantial enhancement of zT values, as well as a shift of the zT maximum to lower temperature (Fig. 4). In particular at $T=100$ K, S is enhanced by a factor of 4.3 by varying x from 0.0 to 0.4, together with a reduction in ρ and κ_L by a factor of 1.5 and 2.7, respectively (Fig. 1, lower panel). At this temperature zT for $x=0.4$ assumes its peak with $zT_{max}=0.125$, amounting to half of the maximum zT value observed in optimized $CePd_3$.[4] Much higher zT than that of $CePd_3$ is observed at below 100 K in the present system. Comparing the zT values of $x=0.4$ to that of $x=0.0$ ($zT_{max} < 0.02$ at 280 K) reveals that the enhancement of zT is considerably significant. Noticeably, the most important among our observations is that the enhancement of S_{max} concomitant to the reduction in T_K is not specific to the present system. This is a general expectation for HF or IV systems without magnetic ordering,[19] and has been confirmed in different systems such as $Ce(Ni_xPd_{1-x})_2Si_2$,[20] though not as apparent as in $Ce(Ni_{1-x}Cu_x)_2Al_3$.

An independent control of S, ρ, and κ_L has been theoretically shown to be feasible by confining electrons into a low-dimensional system, and properly fabricated thin-film superlattice or nanowire indeed show enhanced thermoelectric properties.[21] By contrast, the simultaneous optimization of the three interdependent thermoelectric parameters in $Ce(Ni_{1-x}Cu_x)_2Al_3$, in particular of S and ρ, is owing to the local interaction between the f and conduction bands. The substitution of Cu for Ni in $CeNi_2Al_3$ modifies the d-like conduction band with enhanced DOS to s- or p-like bands with charge carriers that are much more mobile. This modification on conduction band leads to not only an increase in electrical conductivity but also an enhancement of the Kondo resonance peak in the DOS of the heavy quasiparticles (inset of Fig. 4) due to reduction in T_K, the latter being crucial for the enhancement of S that measures the energy derivative of DOS at the Fermi level. Further enhancement of the thermoelectric figure of merit in $Ce(Ni_{1-x}Cu_x)_2Al_3$ seems achievable through (i) substitution with heavier atoms instead of Cu, such as Ag, to further reduce κ_L, or (ii) approaching the best substitution amount in the vicinity of the critical concentration, $x=0.4$. Along the same lines, we also stress the significance to study other Kondo compounds which already exhibit moderately enhanced zT, for example, $CePd_3$ or systems with large ground-state degeneracy. It should be reminded that for cryogenic application a comparable efficiency as for high-temperature application is not necessarily crucial; a moderately enhanced zT might make a significant impact in this field. Furthermore, in identification of an appropriate starting Kondo system and the best elements for substitution, theoretical prediction may play an important role. For instance, band-structure calculation with respect to a specific Kondo system could predict the suitable elements that might give rise to an ideal TE optimization as observed in the present system.

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