Appearance of a europium Kondo lattice in $EuCu_2(Si_xGe_{1-x})_2$

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The first case in which europium exhibits the properties of a Kondo system has been observed during the initiation of a transition of europium from the Eu^{2+} ($x = 0$) state into a regime of interconfiguration fluctuations ($x = 1$) in $EuCu_2(Si_xGe_{1-x})_2$ crystals. The amplitude of the resonant scattering of the band electrons reaches a maximum near the presumed inversion of the europium ground state, from the magnetic Eu^{2+} state to the nonmagnetic Eu^{3+} state.

Several metal crystals, in which europium ions may be in a stable state, Eu^{2+} ($^8S_{7/2}$ ground state) or Eu^{3+} ($^7F_0$), or in a regime of interconfiguration fluctuations with $\tau_{fl} \approx 10^{-12}$ s (depending on the composition) have now been identified.[1] On the other hand, previous observations have not revealed a Kondo effect for europium. A Kondo effect has been observed repeatedly in metals containing a cerium impurity or cerium in regular positions in a lattice (a so-called Kondo lattice occurs in the intermetallic compounds $CeAl_3$, $CeCu_2Si_2$, etc.).[2]

Lustfeld[3] has shown that evidence of a Kondo effect with $T_K = 1$ K can be seen in a metallic matrix containing europium when the excitation energy $\epsilon_{ex}(Eu^{2+} \rightarrow Eu^{3+}) \approx 86$ meV is reached. In stable divalent europium we have $\epsilon_{ex} \approx 2$ eV (Ref. 3); in the state of interconfiguration fluctuations, e.g., in the intermetallic compound $EuCu_2Si$, we have $^4\epsilon_{ex} \approx 70$ meV. The presence of divalent europium[5] in $EuCu_2Ge_2$ crystals makes it possible to study the manifestations of the Kondo effect in the $EuCu_2(Si_xGe_{1-x})_2$ system, where the "chemical" compression which results from the substitution Ge→Si should initiate a decrease in the energy ϵ_{ex} and a transition of europium ions to the regime of interconfiguration fluctuations.

Analysis of diffraction patterns of $EuCu_x(Si_xGe_{1-x})_2$ alloys synthesized with $x = 0, 0.1, 0.1, \ldots, 1.0$ by a procedure similar to that of Ref. 6 shows that a substitutional solid solution forms at all values of x in this system. As the Si concentration is increased, decreases occur in the lattice parameters a and c (found within $\pm 10^{-4}$ nm in numerical calculations) of the tetragonal structure of the crystals. The reason for this decrease is the difference between the atomic radii of Si ($r_a = 0.1319$ nm) and Ge($r_a = 0.1369$ nm). For the concentration dependence $a^2c \sim f(x)$ we find two linear regions; at $x > 0.7$, the change in a^2c is more rapid.

The temperature dependence of the resistivity $\rho(T)$ for the compound $EuCu_2Ge_2$ ($x = 0$) in the temperature interval 4.2–350 K shows (Fig. 1) that the ordinary "metallic" behavior with $\rho_{300K} = 20\,\mu\Omega\cdot$cm. The substitution Ge→Si to $x = 0.6$ gives rise to a maximum ρ'_{max} at $T_{\rho'_{max}} = 15$ K on the $\rho(T)$ curve. In a sample with $x = 0.7$, the height of this maximum reaches $1.26\rho_{300K}$ at a constant value of $T_{\rho'_{max}}$. At $0.8 \leqslant x < 1.0$

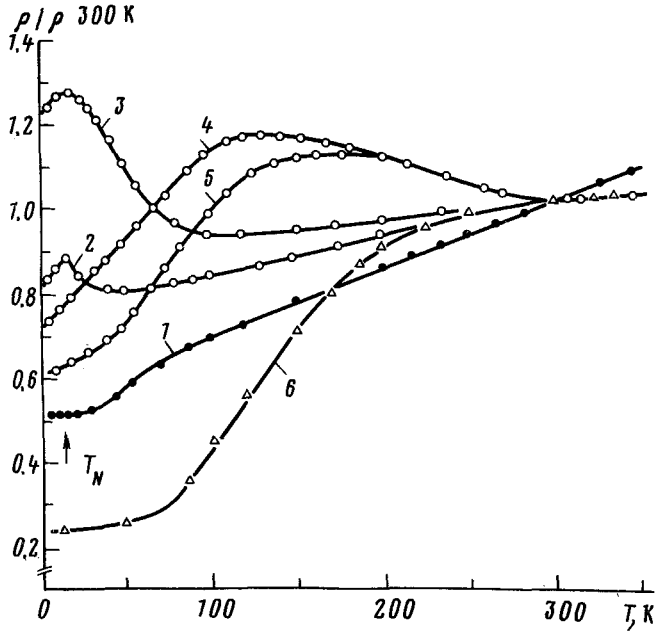

FIG. 1. Temperature dependence of the resistivity, $\rho(T)$ (normalized to ρ_{300K}), for the $EuCu_2(Si_xGe_{1-x})_2$ system. 1—$x = 0$; 2—0.6; 3—0.7; 4—0.8; 5—0.9; 6—1.0.

the $\rho(T)$ dependence becomes a curve with a high-temperature minimum ρ''_{max}, whose temperature, $T_{\rho''_{max}}$, increases at a rate of 15 K/(at.% Si), and its height decreases with increasing x. The resistivity of the samples of this group is $\rho_{300K} \approx 250\ \mu\Omega\cdot$cm. The maximum ρ''_{max} is not found in $EuCu_2Si_2$ ($x = 1$), and we have $\rho_{300K} = 80\ \mu\Omega\cdot$cm.

The differential thermal emf of $EuCu_2Ge_2$ is negative and depends only slightly on the temperature (Fig. 2). The substitution Ge→Si gives rise to a positive maximum

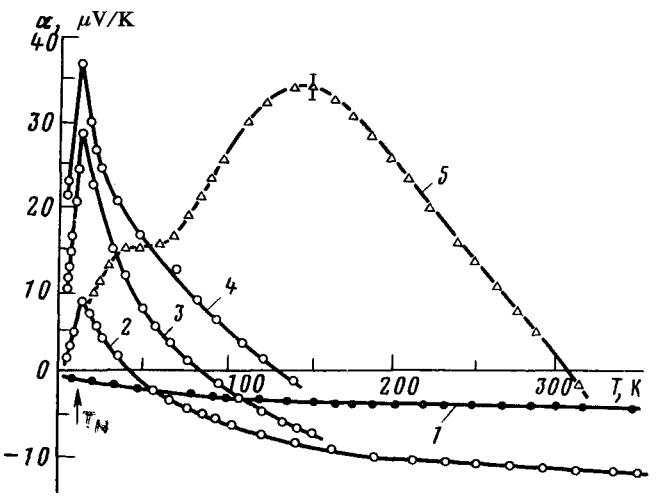

FIG. 2. Temperature dependence of the differential thermal emf, $\alpha(T)$, for the $EuCu_2(Si_xGe_{1-x})_2$ system. 1—$x = 0$; 2—0.5; 3—0.6; 4—0.7; 5—1.0.

$\alpha'_{\max}$ ($x = 0.5$) on the $\alpha(T)$ curve. The height of this maximum increases with increasing x. Its temperature is $T_{\alpha'_{\max}} = 15$ K, and it remains at the same place over the composition interval $0.5 \leqslant x \leqslant 0.7$. The maximum value, $\alpha'_{\max} = 38\ \mu$V/K, is observed at $x = 0.7$. The peak of the thermal emf has a width that is very small in comparison with that in metals exhibiting interconfiguration fluctuations of europium: $\cong 30$ K at a height of $0.5\alpha_{\max}$, which is comparable to a width $\cong 40$ K at an amplitude $\alpha_{\min} = -32\ \mu$V/K and a temperature $T_{\alpha_{\min}} = 20$ K in the compound $CeCu_2Si$ with a cerium Kondo lattice.[2,7] As x is increased further, the $\alpha(T)$ curve changes to a curve with a broad ($\cong 160$ K) high-temperature peak $\alpha''_{\max}$. In $EuCu_2Si_2$ we have $T_{\alpha''_{\max}} = 150$ K; the low-temperature buildup on the $\alpha(T)$ curve may be due to an $\alpha'_{\max}$ maximum.

An estimate of the effective valence of europium, v_{eff}, in samples with $0.5 \leqslant x \leqslant 0.8$ based on x-ray L_{III} absorption spectroscopy at $T = 300$ K yields the same value, within ± 0.03: $v_{\text{eff}} = 2.16$. For $EuCu_2Si_2$ ($x = 1$) we find $v_{\text{eff}} = 2.41 \pm 0.03$. In the limit $T \to 0$, the effective valence of europium in $EuCu_2Si_2$ increases to $\cong 2.8$, according to data from Mössbauer spectroscopy[4]; i.e., the europium ground state is Eu^{3+}.

According to the ionic model for interconfiguration fluctuations, v_{eff} is determined by the probability ($p_{3+} = 1 - p_{2+}$) for europium ions to be in the Eu^{3+} state. This probability can be described as a function of the temperature and of the energy for excitation from the conduction band to the $4f$ level,[1] ϵ_{ex} ($Eu^{3+} \to Eu^{2+}$), by[1,4]

$$\frac{1-p_{3+}}{p_{3+}} = [8\exp(-\epsilon_{ex}/kT)]/[1+3\exp(-\epsilon_1/kT)+5\exp(-\epsilon_2/kT)],$$

where 8 is the multiplicity of the Eu^{2+} ground state, 3 and 5 are the multiplicities of the first and second Eu^{3+} excited states, and $\epsilon_1 = 0.041$ and $\epsilon_2 = 0.114$ eV are the energy gaps between the ground state and the two excited states. The value of ϵ_{ex} calculated from this expression for $EuCu_2Si_2$ is 33 meV ($v_{\text{eff}} = 2.43$) or 50 meV ($v_{\text{eff}} = 2.60$; Ref. 4). For an effective europium valence $v_{\text{eff}} = 2.16 \pm 0.03$ (for the samples with $0.5 \leqslant x \leqslant 0.8$) the excitation energy ϵ_{ex} is approximately zero. A variation of this energy over the interval $-1.3 \leqslant \epsilon_{\text{ex}} \leqslant 1.3$ meV corresponds to a change in the effective valence of the europium in the interval $2.16 \leqslant v_{\text{eff}} \leqslant 2.18$ at $T = 300$ K or $2.04 \leqslant v_{\text{eff}} \leqslant 2.25$ at liquid-helium temperatures. In other words, the europium ground state in samples with $x < 0.5$ is Eu^{2+}.

The resonant nature of the curves of $\rho(T)$ and $\alpha(T)$ for samples of the $EuCu_2(Si_xGe_{1-x})_2$ system with $0.5 \leqslant x \leqslant 0.8$ at $T = 15$ K (at a temperature close to that, $T_N = 13$ K, of the antiferromagnetic ordering of the europium sublattice in $EuCu_2Ge_2$; Ref. 7) suggests that in this case we are observing a Kondo-lattice state for europium for the first time.[2] The experimental value of the Kondo temperature, T_K^{expt}, is an order of magnitude higher than the theoretical prediction[3] T_K^{theor}, and the experimental thermal emf ($\alpha_{\max}^{\text{expt}} = 38\ \mu$V/K) is much lower than the theoretical prediction ($\alpha_{\max}^{\text{theor}} = -100\ \mu$V/K) and opposite in sign.

In summary, the transition of europium from the Eu^{2+} state to a regime of interconfiguration fluctuations upon chemical compression of a crystal can occur, as in the case of cerium, through a Kondo-lattice state. A conversion of europium from

the magnetic Eu^{2+} state to the nonmagnetic Eu^{3+} state apparently occurs near the ground-state inversion in the $EuCu_2(Si_xGe_{1-x})_2$ system.

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[1]I. Nowik, Hyperfine Interact. **13**, 89 (1983).
[2]F. G. Aliev, N. B. Brandt, V. V. Moshchalkov, O. V. Petrenko, S. M. Chudinov, and R. I. Yasnitskiĭ, Zh. Eksp. Teor. Fiz. **86**, 255 (1984) [Sov. Phys. JETP **59**, 145 (1984)].
[3]H. Lustfeld, Physcia **106B**, 213 (1981).
[4]E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. **30**, 1053 (1973).
[5]I. Felner and I. Nowik, J. Phys. Chem. Solids **39**, 763 (1978).
[6]E. M. Levin, I. N. Stets', O. I. Bodak, and B. D. Oniskovets, Fiz. Tverd. Tela (Leningrad) **26**, 2347 (1984) [Sov. Phys. Solid State **26**, 1424 (1984)].
[7]W. Franz, A. Grissell, F. Steglich, and D. Wohlleben, Z. Phys. **B**, No. 1, 7 (1978).

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