

Weak ferromagnetism in $\text{CeMn}_{2-x}\text{Si}_{2+x}$ crystals with a mixed cerium valence

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The appearance of a weak ferromagnetism in the antiferromagnetic manganese sublattice and a simultaneous change in the properties of the electronic structure of the crystal near the Fermi level due to $4f$ states of valence-unstable cerium have been observed in $\text{CeMn}_{2-x}\text{Si}_{2+x}$ alloys of variable composition upon the substitutions $\text{Mn} \rightleftharpoons \text{Si}$.

Ternary cerium compounds of the type CeMn_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) and solid solutions based on them are among the most interesting complex rare-earth compounds today. In these compounds, the magnetic order of the manganese may be accompanied by a mixed-valence state or a state of a concentrated Kondo system of cerium.^{1,2}

The Néel temperature for the manganese sublattice in the compound CeMn_2Si_2 is³ $T_N = 380$ K. It has been established by L_{III} x-ray spectroscopy that the cerium ions have a mixed-valence state with an effective valence⁴ $v_{\text{eff}} = 3.13$. Some $\text{CeMn}_{2-x}\text{Si}_{2+x}$ alloys were synthesized in an effort to determine how the mutual substitutions $\text{Mn} \rightleftharpoons \text{Si}$ affect the properties of the electronic state of Ce and those of the magnetic state of the Mn sublattice. The Ce concentration was 20 at. %. The Mn and Si concentrations were varied under the constraint that their sum was 80 at. %. The electronic transport and magnetic properties were measured by a computer-based data acquisition complex using a DVK-3M/2 computer, a CAMAC crate, and a vibration magnetometer.

It was found that the constants a and c of the tetragonal lattice of these $\text{CeMn}_{2-x}\text{Si}_{2+x}$ alloys were essentially independent of the composition. The approximate equality of the Mn and Si atomic radii may be the reason for this result. Upon the substitutions $\text{Si} \rightarrow \text{Mn}$, the positive peak $T_{\alpha_{\text{max}}}$ caused in the differential thermopower by the mixed-valence state of the cerium² shifts more than 40 K up the temperature scale. In other words (Fig. 1), despite the stability of the lattice constants of the alloys, substantial changes occur in the electronic structure near the Fermi level, ϵ_F . A slightly unexpected result was the appearance of a low-temperature peak ($T_{\alpha_{\text{min}}} = 45$ K) in the thermopower in the samples containing less than 40 at. % Si. This peak is similar to one found in the concentrated Kondo system of CeCu_2Si_2 . Further experiments will be necessary to determine the nature of this peak.

The rise of $T_{\alpha_{\text{max}}}$ and the observed increase in the effective valence v_{eff} of the cerium (v_{eff} was determined by L_{III} x-ray absorption spectroscopy), from 3.08 (45 at. % Si) to 3.16 (38 at. % Si), suggest that the substitution $\text{Si} \rightarrow \text{Mn}$ leads to an increase in the width (Γ_f) of the f resonance (Fig. 1). A calculation of the energy gap between the Fermi level and the f resonance, i.e., $|\epsilon_F - \epsilon_f|$, based on the model of a local

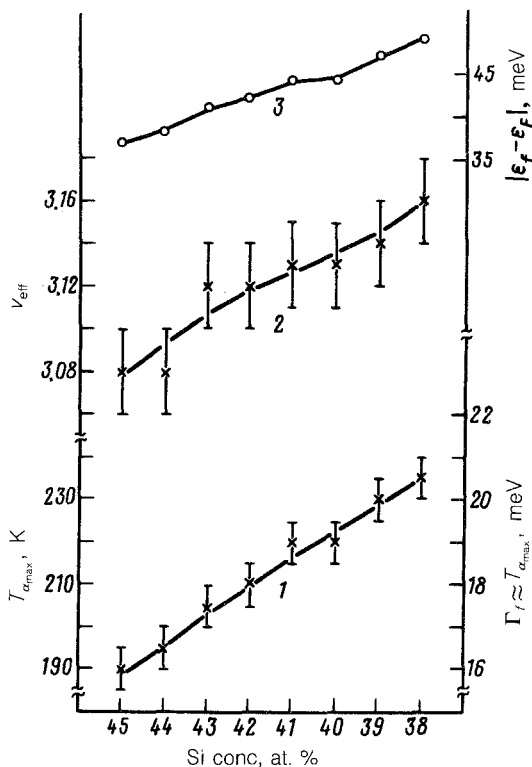


FIG. 1. Plot of several properties of $\text{CeMn}_{2-x}\text{Si}_{2+x}$ alloys versus the silicon concentration. 1—Width of the f resonance, $\Gamma_f \approx T_{\sigma_{\max}}$; 2—effective valence ν_{eff} ; 3—energy gap $|\epsilon_F - \epsilon_f|$.

Fermi liquid⁶ shows that this gap increases in size upon the substitution $\text{Si} \rightarrow \text{Mn}$, from 37 to 49 meV (the f resonance is above ϵ_F). The density of electron states at the Fermi level also decreases, from 38 to 28 states/[eV · (unit cell)].

The temperature dependence of the specific saturation magnetization σ_{sat} suggests that the $\text{Mn} \rightarrow \text{Si}$ substitution is accompanied by a change from a behavior characteristic of an antiferromagnet (curves 1 and 2 in Fig. 2) to a behavior typical of a ferromagnet (curves 3–5). Above the Curie and Néel magnetic-transition temperatures, which have the same value (380 K), the magnetic susceptibility is described by an ordinary Curie–Weiss law, with an effective magnetic moment of $(2.5\text{--}3.1)\mu_B$ per Mn atom.

In the crystals with ferromagnetic properties, the specific saturation magnetization is directly proportional to the degree of the $\text{Mn} \rightarrow \text{Si}$ substitution. The magnetic moment per substituted Si atom is $\approx 0.35\mu_B$. The field dependence reveals an ordinary hysteresis loop with a remanent magnetization of 0.3–1.5 emu/g at $T = 77$ K and a coercive force $H_c = 500\text{--}1400$ Oe. By way of comparison, the coercive force of the compound LaMn_2Si_2 , which exhibits an ordinary ferromagnetism, is $H_c < 12$ Oe.

The observed nature of the antiferromagnetism \rightleftharpoons ferromagnetism transition for intermetallic compounds is quite unusual. It would be natural to try to explain it in terms of a change in the resultant magnetization in the Mn sublattice.

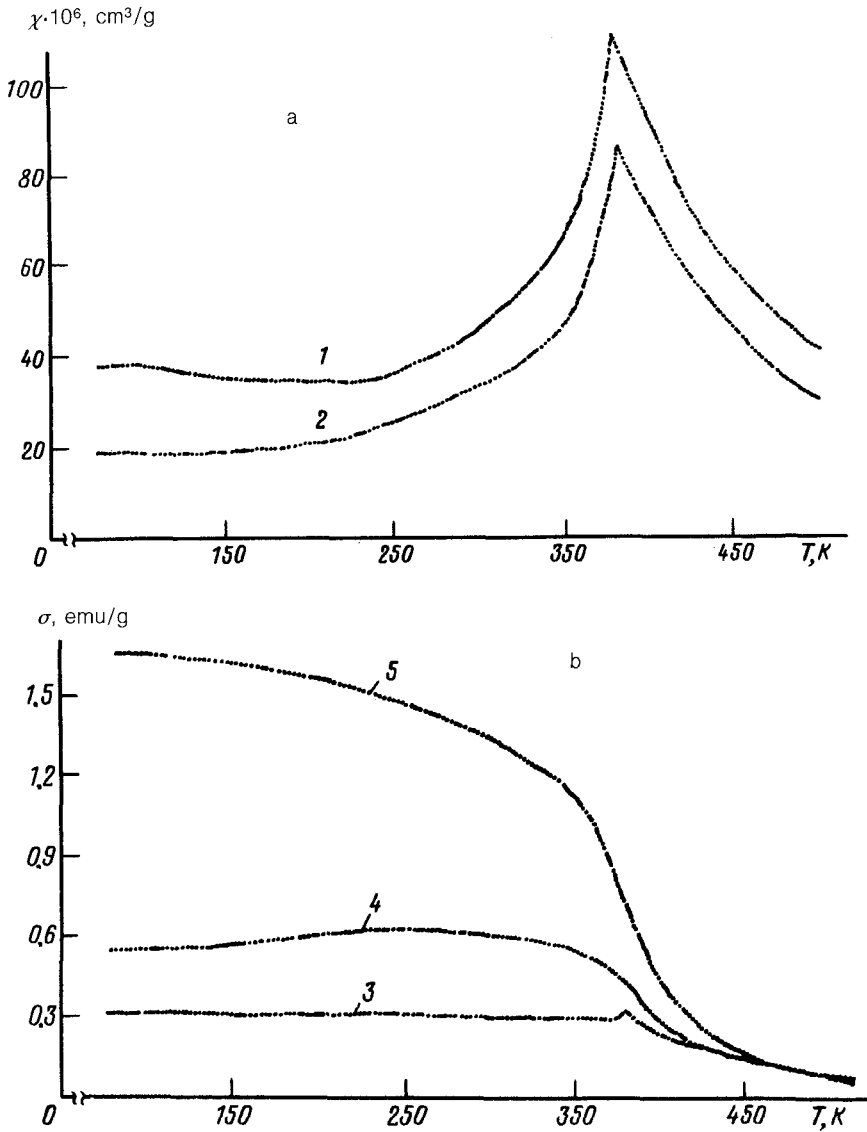


FIG. 2. Temperature dependence of (a) the magnetic susceptibility and (b) the magnetization of CeMn_{2-x}Si_{2+x} alloys. 1—38 at. % Si; 2—39; 3—41; 4—43; 5—45 at. % Si.

The magnetic structure of crystals of this sort is formed by Mn-atom layers separated by ≈ 0.5 nm and running perpendicular to the z axis. The order of the localized magnetic moments of the Mn atoms in one layer is always ferromagnetic, while that of the atoms in different layers may be either ferromagnetic or antiferromagnetic, depending on the composition.¹

In addition to the isotropic exchange interaction of the electrostatic type, magne-

tic crystals may exhibit an anisotropic interaction,⁷ so the relative orientation of the magnetic sublattices may change in uniaxial antiferromagnets with tetragonal symmetry, and a weak ferromagnetism may appear.

The only way to explain the appearance of a ferromagnetic component in the antiferromagnetic sublattice of manganese in $\text{CeMn}_{2-x}\text{Si}_{2+x}$ alloys is to assume that a deviation from a collinear arrangement of the localized magnetic moments of some of the Mn atoms arises because of the appearance of anisotropic forces in the plane perpendicular to the z axis. The reason for the appearance of these forces may be a change in the nature of the Mn–Si chemical bonds near a Si atom occupying a Mn site.

A detailed study of the possible magnetic structures of the Mn sublattice indicates that the vector magnetic moments of the Mn atoms with noncollinear localized magnetic moments in different layers may add up along the x and y axes, while cancelling out along the z axis. An estimate of the angular deviation of the magnetic moment of the Mn atoms near a substituent Si atom from the z axis yields $3\text{--}4^\circ$ [the effective magnetic moment per substituted atom in the ferromagnetic alloys ($\approx 0.35\mu_B$) and the magnetic moment of the Mn atom according to neutron diffraction¹ ($2.3\mu_B$) have been taken into account here].

In summary, the substitutions $\text{Si} \rightleftharpoons \text{Mn}$ in crystals of the variable-composition compound $\text{CeMn}_{2-x}\text{Si}_{2+x}$ are accompanied by changes in the properties of the mixed-valence state of the cerium and in the behavior of the resultant magnetization of the layered Mn sublattice. In other words, the chemical composition affects the state of the two electronic subsystems (f and d) simultaneously. Crystals of this sort are of much interest for research on the interrelationships among the crystal magnetic fields and transport effects in metallic systems with resonant electron states near the Fermi level and also on local correlation effects.

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