High-field magnetization of RCo9Si2 compounds
van der Gijp, K.; Bruck, E.H.; Buschow, K.H.J.; de Boer, F.R.

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We have studied magnetic, electrical and specific heat behaviour of \((U_{1-x}Y_x)NiAl\), \((U(Ni_{1-x}Co_x)Al\) and \((U(Ni_{1-x}Fe_x)Al\) pseudoternary compounds derived from the itinerant antiferromagnet UNiAl. Y, Co or Fe substitutions in UNiAl lead to a rapid disappearance of long range magnetic order, however, the strong magnetic uniaxial anisotropy (characteristic for UNiAl) persists. Anomalies in the specific heat and the enhancement of \(\gamma\) values indicate pronounced spin-fluctuation effects.

1. Introduction

UNiAl is a member of a large family of uranium ternary intermetallic compounds \(UTX\) possessing the same hexagonal structure of the \(Fe,P\) (ZrNiAl) type. The systems of ground-state properties within this group shows that UNiAl is situated near the cross-over from the spin-fluctuation behaviour to the ordering of stable 5f magnetic moments [1]. This fact is documented, e.g., by the UNiAl series where \(T\) is spanning a particular transition-metal row. Here the gradual filling of \(d\) states leads to the reduction of the 5f–d hybridization and the consequent localization of 5f electrons. In the U3dAl series, UFeAl behaves as an exchange-enhanced Pauli paramagnet [2], UCoAl is a band metamagnet [1, 3, 4] and finally UNiAl has been described as an itinerant antiferromagnet with high \(\gamma \approx 165 \text{ mJ/mol K}^2\) [1]. We report on the influence of Y, Co and Fe substitution in UNiAl on magnetic and other electronic properties.

2. Experimental

Polycrystalline samples were prepared by arc-furnace melting in an argon atmosphere. An adiabatic technique was used for specific heat measurements in the temperature range 1.2–40 K in magnetic fields up to 5 T. The temperature dependence of the magnetic susceptibility was measured in a pendulum magnetometer. The Amsterdam High-Field Installation was used for magnetization studies in fields up to 35 T at 4.2 K. Temperature dependence of the electrical resistance was measured by means of a standard ac four-probe method.

The effect of the substitution of Y for U in UNiAl was studied for Y concentrations up to \(x = 0.4\). Further substitutions resulted into multiphase samples. YNiAl itself crystallizes in the ZrNiAl structure type with lattice parameters \(a = 703.60 \text{ pm}\) and \(c = 383.80 \text{ pm}\) (for UNiAl \(a = 673.3 \text{ pm}\) and \(c = 403.5 \text{ pm}\)). X-ray analysis revealed a statistical occupation of \(3d\) sites by U and Y atoms. The lattice parameter \(c\) linearly decreases with increasing content of Y while the parameter \(a\) follows the opposite trend, which leads to an increase of the nearest U–U spacing.

The relatively sharp maximum, found in \(\chi(T)\) for pure UNiAl, is gradually smeared out and shifted towards lower \(T\) and it finally disappears for 20% Y [5]. \(\Theta_m\) proceeds to higher negative values whereas the effective moment per U atom is almost unchanged upon the Y substitutions. The specific heat (fig. 1) displays a low-temperature upturn of \(C/T\) developing gradually with increasing Y content, which is not sensitive to applied field of \(H > 1\). It can be fitted by the formula including an additional term \(8T^2 \ln T\) which could point to the increasing significance of low-energy magnetic fluctuations (spin fluctuations). The \(\gamma\)-value increases and reaches a maximum of 240 mJ/mol U K\(^2\) for \(U_{0.8}Y_{0.2}\)NiAl. In spite of a low magnetic entropy (estimated as \(\approx 10\% R \ln 2\) [6]) for pure UNiAl a clear-cut anomaly was found [1] at 18 K, but this feature is suppressed already for 5% Y. Somewhat contrasting is the magnetic behaviour where both the maximum in \(\chi(T)\) and the visible S-shape of \(M(T)\) curves at 4.2 K (fig. 2) persist up to 10% Y, although...
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R.T. [mJ/mol K²]

Fig. 1. Temperature dependence of the specific heat of \( U_{1-x}Y_xNiAl \) for \( x = 0.0 (\triangle), 0.05 (\square), 0.1 (\smile), 0.2 (\bigcirc) \) and 0.4 (\lozenge).

being gradually smeared out. The low-field susceptibility (the slope of \( M(B) \) below the field-induced transition) varies only slightly with the concentration up to 10% Y while it decreases considerably for higher Y content. The magnetization of all samples tends to saturate in high magnetic fields and \( M(35 \text{T}) \) decreases with increasing \( x \).

Substitutions of Co or Fe for Ni lead also to the gradual suppression of the field-induced transition in \( M(B) \) measured at 4.2 K (fig. 3). The effect is to a certain extent reminiscent to the impact of increasing temperature in pure UNiAl. The initial slope of \( M(B) \) dependence increases and the positive curvature is converted to a negative one with increasing concentration of Co (Fe). The S-shape disappears between 10 and 20% Co or 5 and 10% Fe. In fields above 20 T, the saturation tendency of the magnetization of UNiAl turns, however, into an almost linear increase with a significant slope already for 5% of substituents. The absolute values of the high-field magnetization are reduced upon the substitution (but much less than for Y substitutions). The strong magnetic uniaxial anisotropy persists in all Y, Co or Fe-substituted compounds. It should be stressed that YNiAl, where no 5f electrons are in the game, exhibits isotropic behaviour.

The low-temperature specific heat reflects the shift of the magnetic transition with increasing Co concentration (fig. 4). However, the entropy connected with the transition is gradually reduced, and finally the transition is embedded into the gradually developing low-temperature upturn of \( C/T \).

A narrow-band character of magnetism in UNiAl is documented by the high value of \( \gamma \approx 165 \text{ mJ/mol K}^2 \) unaffected by applied magnetic fields up to 5 T, low magnetic entropy, low magnetic moment (simple extrapolation from high fields to 0 T yields \( \approx 0.6 \mu_\text{B}/U \)) in comparison with the effective moment of 2.9 \( \mu_\text{B}/U \)

\[ M \] [\( \mu_\text{B}/\text{U atom} \)]

Fig. 2. Magnetization curves measured at 4.2 K on field-oriented powders of \( U_{1-x}Y_xNiAl \) for \( x = 0.0 (\times), 0.05 (\Box), 0.1 (\triangle), 0.2 (+) \) and 0.4 (\lozenge).

\[ M \] [\( \mu_\text{B}/\text{U atom} \)]

Fig. 3. Magnetization curves measured at 4.2 K on field-oriented powders of UNi\(_{1-x}\)Co\(_x\)Al for \( x = 0.0 (\times), 0.05 (\Box), 0.1 (\triangle), 0.2 (+) \) and 0.4 (\lozenge).
Fig. 4. Temperature dependence of the specific heat of UNi$_{1-x}$Co$_x$Al for $x = 0.0$ (△), 0.05 (○), 0.1 (▽), 0.2 (□) and 0.4 (△).

and by the anomalous sensitivity to substitutions both on U and 3d metal sites. We can suppose that the narrowing of the 5f band in UNiAl with respect to UFeAl and UCoAl is the consequence of the reduction of 5f–3d hybridization connected with the increased separation of 5f and 3d states in energy scale. The hybridized 5f–3d band can be expected especially with respect to the situation within the basal plane with close packing of U and Ni atoms. The interuranium distance within this plane is ≈350 pm, i.e., that the delocalizing effect of the direct overlap of 5f wave functions should also be taken into account. In the anisotropy of hybridization we can find a natural source of the magnetic anisotropy with magnetic moments which are locked in the direction perpendicular to the basal plane. The estimated anisotropy energies in UTX compounds, which are at least of the order of 10 meV, are moreover comparable with hybridization energies. Note that the anisotropic behaviour is not by far limited to the magnetically-ordered state.

Besides the delocalization of U-moments due to strengthening of 5f 3d hybridization the substitution of Fe or Co favours apparently the correlations of the ferromagnetic type, as deduced from the shape of magnetization curves. This situation is in contrast with the Y-substituted compounds where the antiferromagnetic correlations persist in the form of spin fluctuations even in the paramagnetic regime.

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References