Giant increase in the Curie temperature of RCo_2 intermetallic rare-earth compounds at low degrees of replacement of magnetic cobalt by nonmagnetic aluminum

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The magnetic-ordering temperature T_c of $R\,Co_2$ compounds (R is a heavy rare-earth metal) has been found to increase at low degrees (on the order of 10%) of replacement of the magnetic Co by nonmagnetic Al. The temperature T_c of $TmCo_2$ increases by a factor of 15, that of $ErCo_2$ by a factor of 4.3, etc. It is concluded that at these degrees of substitution there is an increase in the state density at the Fermi level of a hybridized d band.

The intermetallic rare-earth compounds of the general formula $R\,Co_2$ (a C15 Laves-phase cubic structure) are collinear ferrimagnets and have two magnetic subsystems. One is formed by the localized moments of the rare earth, while the other is formed by the moments of the collectivized $3d$ electrons of cobalt hybridized with $5d$ electrons of the rare earth. The exchange between the d electrons is insufficient for a spontaneous splitting of the d band, so that compounds with nonmagnetic rare earths (YCo_2, $LuCo_2$) are exchange-intensified Pauli paramagnets,[1] and the magnetization of the d-electron subsystem in compounds with magnetic rare earths is due to an R-d exchange interaction, which is strongest in $GdCo_2$.

In accordance with these arguments, in $R\,(Co_{1-x}M_x)_2$ systems, in which magnetic cobalt is replaced by a nonmagnetic element ($M =$ Al, Ni), the magnetic-ordering temperature T_c falls off sharply[2–4] as the cobalt concentration is reduced to the point at which the d subsystem becomes disordered (ordinarily, $x \sim 0.5$). Thereafter, the change in T_c with x becomes smoother. In Refs. 2-4 the effect of the substitutions for cobalt on the properties of $R\,Co_2$ compounds was studied with a large step in the concentration ($\Delta x \approx 0.2$).

In this letter we report a study of the magnetic and magnetoelastic properties of $R\,(Co_{1-x}Al_x)_2$ compounds with a much finer step along the concentration scale ($\Delta x \simeq 0.01$). We have discovered an unusual effect: small degrees of replacement of cobalt by aluminum do not reduce T_c but instead cause a sharp increase in this temperature. As x is increased further, this temperature goes through a maximum (at $x = 0.1$–0.125), and beyond this maximum the $T_c(x)$ behavior corresponds to the picture drawn above[1)] (Fig. 1).

The increase in T_c is comparatively slight in the system with gadolinium, and it increases greatly as we go to the heavy rare earths, reaching huge values in the systems $Ho(Co_{1-x}Al_x)_2$, $Er(Co_{1-x}Al_x)_2$, and, especially, $Tm(Co_{1-x}Al_x)_2$. In the substituted compounds with holmium, for example, the maximum value of T_c is 2.1 times that in

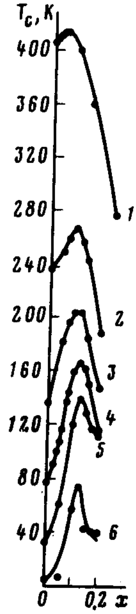

FIG. 1. The magnetic-ordering temperature T_c versus the aluminum concentration x in $R(Co_{1-x}Al_x)_2$ systems. 1—R = Gd; 2—R = Tb; 3—R = Dy; 4—R = Ho; 5—R = Er; 6—R = Tm.

the undiluted $R\,Co_2$ compound, and the corresponding factors for compounds with erbium and thulium are 4.3 and 15.

A discussion of the reasons for the increase in T_c in the mixed compounds $R(Co_{1-x}Al_x)_2$ should take into account, the fact that the substitution of aluminum leads to an increase in the volume of the unit cell.[6] It follows from Refs. 7 and 8 that T_c in $R\,Co_2$ decreases upon hydrostatic compression. Consequently, the increase in the volume of the unit cell when cobalt is replaced by aluminum should result in an increase in T_c. Our calculations show, however, that this "volume effect" is comparable to the experimentally observed increase in T_c only in the systems $Gd(Co_{1-x}Al_x)_2$ and $Tb(Co_{1-x}Al_x)_2$. In other systems this "trivial" contribution to the $T_c(x)$ dependence is considerably smaller than the experimentally observed increase in T_c.

A second possible reason for an increase in the magnetic-ordering temperature in $R(Co_{1-x}Al_x)_2$ mixed compounds is an increase in the density of conduction electrons. The replacement of a cobalt atom by an aluminum atom adds one extra electron to the s band. Since the (rare-earth)-(rare-earth) and (rare-earth)-cobalt exchange occurs through conduction electrons in these compounds, there may be an increase in T_c. This mechanism fails to explain the huge increase in T_c, however, since this increase occurs at low aluminum concentrations. In the RCCI model the exchange interaction is proportional to the square of the density of conduction electrons,[9] and at $x \simeq 0.1$ the total density of conduction electrons increases only slightly (by about 5%). Consequently, the situation in our case is qualitatively different from that observed in the mixed chalcogenides of europium $Eu_{1-x}Gd_xT$ (T = O, S, Se), where the chalcogenides EuO, EuS, and EuSe are insulators (the density of conduction electrons is zero), so that the RCCI mechanism "does not work." Admixtures of trivalent gadolinium "turn on" the exchange through conduction electrons, leading to a dramatic increase[10] in T_c.

We believe that the most probable mechanism for the huge increase in T_c of $R\,Co_2$ compounds upon the replacement of cobalt by aluminum is as follows. According to the present understanding, the Fermi level of the d band in $R\,Co_2$ compounds lies on a descending part of the energy dependence of the state density. This circumstance has some interesting consequences for the magnetic behavior of $R\,Co_2$ as a band metamagnetism of the cobalt subsystem[11]: Magnetic order arises abruptly in the system of d electrons when a certain critical effective field is reached. The introduction of aluminum reduces the density of d electrons, leading to a shift of the Fermi level toward lower energies in the rigid-band model and thus leading to an increase in the state density at the Fermi level, $N(\epsilon_F)$. The system of d electrons approaches satisfaction of Stoner's criterion for band ferromagnetism, $IN(\epsilon_F)>1$ (I is the exchange-interaction integral in the system of d electrons), and the critical field for the transition of the system from the paramagnetic state to the ferromagnetic state decreases. The cobalt is thus magnetized in weaker effective fields exerted by the rare-earth subsystem, and the T_c of the mixed compounds correspondingly increases.

This interpretation is supported by our measurements of the magnetic-volume anomaly in $Ho(Co_{1-x}Al_x)_2$ (Fig. 2). This anomaly is known to be proportional to the square of the magnetic moment of cobalt, μ_{Co}, and to its density:

$$\Delta V/V = n_{\mathrm{Co\,Co}}(1-x)\mu_{\mathrm{Co}}^2$$

It can be seen from Fig. 2 that the quantity $\Delta V/V$ at the very least does not decrease at low aluminum concentrations. This result implies some increase in the magnetic moment of cobalt at these concentrations, in agreement with the suggestion above that the state density at the Fermi level increases at small degrees of replacement of cobalt by aluminum.

The magnetic-volume anomaly, we might note, is more sensitive to small changes in the magnetic moment of cobalt than the magnetization is, since in the latter case these changes must be distinguished against the background of the total magnetic moment of the entire compound. Furthermore, in polycrystalline samples the results of magnetic measurements are strongly affected by the magnetic anisotropy.

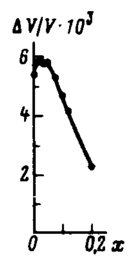

FIG. 2. Concentration dependence of the magnetic-volume anomaly of the $Ho(Co_{1-x}Al_x)_2$ system at 5.5 K.

The suggestion above regarding the mechanism for the increase in T_c upon the replacement of cobalt by aluminum in $R\,(Co_{1-x}Al_x)_2$ compounds also explains why this effect is weakest in the systems with gadolinium and terbium, which have the highest values of T_c among the $R\,Co_2$ compounds. At relatively high temperatures (>200 K) thermal effects change the state-density curve in such a manner that the metamagnetic dependence of the moment of the d electrons on the magnetic field disappears.[11] At the same time, the increase in T_c disappears with decreasing density of d electrons.

[1)]The $R\,(Co_{1-x}Al_x)_2$ compounds are isostructural with the $R\,Co_2$ compounds at small degrees of aluminum substitution ($x \leqslant 0.25$) and at large degrees ($x \geqslant 0.75$), while compositions with intermediate amounts of aluminum ($0.25 < x < 0.74$) form the hexagonal $C\,14$ Laves phase.[5,6] The change in the type of crystal structure is linked with an increase in the density of conduction s electrons upon the replacement of cobalt by aluminum: The structural transitions occur at that density of s electrons at which the Fermi surface intersects the boundary of a Brillouin zone. In the present letter we are discussing only the properties of compounds with small amounts of aluminum (up to $x = 0.2$), which have the $C\,15$ structure.

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