Onset of ferromagnetism in a limited temperature interval in paramagnetic materials with a $\chi(T)$ maximum

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The possibility of a phase transition to the ferromagnetic state in a paramagnetic materials, which has a maximum in the temperature dependence of the paramagnetic susceptibility $\chi(T)$, is predicted. The onset of ferromagnetism is observed in the temperature interval ΔT_c near the $\chi(T)$ maximum. The intermediate valence is examined in detail.

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It is clear from the general point of view[1)] that the existence of a peak in $\chi(T)$ at $T=0$ creates highly favorable conditions for ferromagnetic ordering in the region of the highest values of $\chi(T)$, i.e., near the peak. Thus, for example, for paramagnetic materials with an exchange enhancement α

$$\chi_{\alpha}(T) = \frac{\chi(T)}{1-\alpha\chi(T)} \tag{1}$$

the ferromagnetism criterion $\alpha\chi(T)=1$ for a given value of α may be realized for two values $T=T_c^{\pm}$ (see Fig. 1); therefore, ferromagnetism occurs in the interval $\Delta T_c = T_c^+ - T_c^-$. Outside of this interval (i.e., for $T<T_c^-$ and $T>T_c^+$) $\alpha\chi(T)$ is still <1; because of this, there exists a region of low-temperature paramagnetism

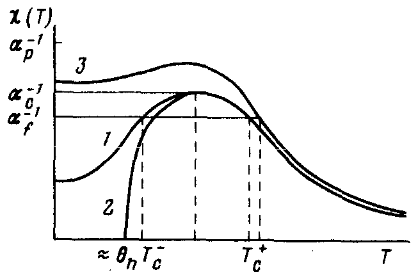

FIG. 1. Graphic determination of the region of possible ferromagnetism $\Delta T_c = T_c^+ - T_c^-$. Curve 1, $\chi(T) = \chi_\alpha/(1+\alpha\chi_\alpha)$ (χ_α is a value measured experimentally); curve 2 is a theoretical curve plotted according to Eq. (2); curve 3 corresponds to a strong decrease of hybridization in the alloy in which T_c^- vanishes. The values of α^{-1}, which correspond to the paramagnetic and ferromagnetic phases, are plotted along the Y axis.

$0 < T < T_c^-$, in contrast to the usual cases.

By changing the parameter α, we can realize a phase transition of the system from a purely paramagnetic phase ($\alpha\chi < 1$ at all T) to a ferromagnetic phase ($\alpha\chi > 1$ at $T_c^- < T < T_c^+$). Under real conditions $\chi(T)$ generally varies as a result of variation of α. If the relative $\chi(T)$ maximum decreases (curve 3 in Fig. 1), then this may lead to a disappearance of the low-temperature paramagnetic phase.

The $\chi(T)$ peak in specific materials occurs quite frequently in the case of intermediate valence (see, for example, Ref. 1). Irkhin[2] studied the hybridization of the conduction electrons with the localized magnetic electrons and calculated the paramagnetic susceptibility $\chi(T)$ of this system, which simulates a crystal with an intermediate valence. A peak, in fact, appears in $\chi(T)$ as a result of suppression of the Curie paramagnetism at $T \lesssim \Theta_h$ (Θ_h is the hybridization temperature). The analytic expression[2)] for large values of T ($T \gg \Theta_h$) is comprised of the Curie, Pauli, and hybridization-type contributions

$$\chi(T) = \chi_c(T) + \chi_p^s(T) + \chi_h(T), \quad \left(T \gg \Theta_h = \frac{aV^2}{k\epsilon_l}\right), \tag{2}$$

where

$$\chi_c(T) = \frac{N\mu_{\text{eff}}^2}{kT}, \quad \chi_p^s = \frac{6N_1\mu_{\text{eff}}^2}{\epsilon_l}, \quad \chi_h = -\chi_c\frac{\Theta_h}{T}. \tag{3}$$

The symbols in Eqs. (2) and (3) are as follows: V is the hybridization parameter, μ_{eff} is the effective magnetic moment per atom, $N_1 = N(\epsilon_l/\Delta)^{3/2}$, ϵ_l is the energy of the localized magnetic level, which is measured from the bottom of the conduction band of width Δ, $a \approx 1$, and $2N$ is the total number of electrons.

Writing the ferromagnetism criterion $\alpha\chi(T) = 1$ according to Eq. (1), we obtain an equation for the critical temperature T_c from Eqs. (2) and (3)

$$\alpha\chi_c(T_c)\left(1 - \frac{\Theta_h}{T_c}\right) = 1 - \alpha\chi_p^s. \tag{4}$$

In spite of the fact that Eq. (2) (curve 2 in Fig. 1 corresponds to this equation) was obtained for $T \gg \Theta_h$, we can use it for a qualitative analysis in a broader temperature range. Although the specific form of the temperature dependence $\chi(T)$ in the region

$T \approx \Theta_h$ in this case is different [low-temperature decomposition at $T - \Theta_h \ll \Theta_h$, according to Irkhin,[2] gives $\chi(T) \approx \chi_c(T) \left(\frac{T - \Theta_h}{\Theta_h} \right)^{3/2}$], its qualitative nature (the presence of a peak that vanishes when $T < \Theta_h$) does not change.

Introducing the paramagnetic Curie temperature $\Theta_p = \frac{\alpha}{k} N\mu_{\text{eff}}^2$, we obtain from Eq. (4)

$$\frac{\Theta_p}{T_c} - \frac{\Theta_p \Theta_h}{T_c^2} = 1 - \alpha \chi_p^s \tag{5}$$

where

$$T_c^{\pm} = \frac{1}{2} \Theta_p' \left[1 \pm \left(1 - 4 \frac{\Theta_h}{\Theta_p'} \right)^{1/2} \right], \Theta_p' = \frac{\Theta_p}{1 - \alpha \chi_p^s} . \tag{6}$$

Equation (6) gives the correct limit $T_c = \Theta_p'$ at $\Theta_h = 0$. At $\Theta_h > \frac{1}{4} \Theta_p' T_c$ is imaginary, which means that there is no ferromagnetism. Finally, we obtain two values $T_c = T_c^{+}$ at $\Theta_h < \frac{1}{4} \Theta_p'$, which satisfy the ferromagnetism criterion. These values correspond to the upper and lower boundaries of the temperature interval within which ferromagnetism can occur.

Thus, the ratio Θ_h / Θ_p' can be used as a parameter for the classification of magnetic materials: 1) $\Theta_h = 0$ represents normal ferromagnetic materials, 2) $0 < \Theta_h < \frac{1}{4} \Theta_p'$ applies to ferromagnetism that can occur in the interval $\Delta T_c = T_c^+ - T_c^- = \Theta_p' \left(1 - 4 \frac{\Theta_h}{\Theta_p'} \right)^{1/2}$, and 3) $\Theta_h > \frac{1}{4} \Theta_p'$ corresponds to paramagnetic materials in which the ferromagnetism has been suppressed by hybridization in the entire temperature region. The crystal can presumably be changed from one phase to another by changing the ratio Θ_h / Θ_p' in some way (i.e., by applying a pressure or adding impurities).

Suppose that the crystal is placed in a paramagnetic state with $\Theta_h > \frac{1}{4} \Theta_p'$. After adding a suitable "ferromagnetic" substitutional impurity, we can increase Θ_p' by increasing the average molecular field (i.e., by increasing α). As a result, Θ_h will also change. If the level of the localized magnetic moment of an impurity electron lies some distance from the Fermi energy, then it will virtually not participate in the hybridization.

In the linear approximation of the impurity concentration $x \ll 1$, we can write

$$\Theta_p'(x) = \Theta_p' + x \Delta \Theta_p' , \quad \Theta_h(x) = \Theta_h(1 - x). \tag{7}$$

Substituting Eq. (7) in Eq. (6), we obtain

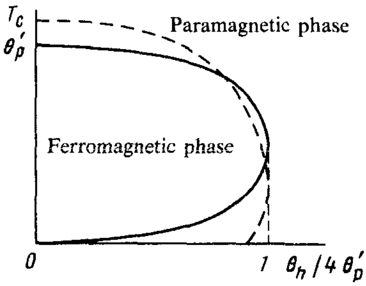

FIG. 2. Phase diagram of the effect. The solid curve corresponds to Eq. (6) and to curve 2 in Fig. 1. The dashed curve corresponds to type-1 curves in Fig. 1.

$$T_c^{\pm}(x) = \frac{1}{2}\Theta_p'(x)\left\{1 \pm \left[1 - 4\frac{\Theta_h}{\Theta_p'}\left(1 - x - x\frac{\Delta\Theta_p'}{\Theta_p'}\right)\right]^{1/2}\right\}, \quad (8)$$

where the critical concentration of the transition from the paramagnetic state to the ferromagnetic state is

$$x_c = \frac{1 - \Theta_p'/4\Theta_h}{1 + \Delta\Theta_p'/\Theta_p'}. \quad (9)$$

Since $\Theta_h > \frac{1}{4}\Theta_p', T_c$ in Eq. (8) is real only when $x > x_c$, when ferromagnetism is possible.

The lower limit of T_c can differ markedly from the value in (8) (see the dashed curve in Fig. 2) when the $\chi(T)$ dependence is real (curve 1 in Fig. 1); however, the qualitative features of the effect remain the same.

Among the specific materials that can have this effect, we can include the compounds and rare-earth alloys that contain elements with intermediate valence Ce, Sm, Eu, Tm, and Yb (see Refs. 1 and 4). Most of these materials apparently are predisposed to antiferromagnetic ordering. It should not be ruled out, however, that a ferromagnetic state is also possible here, especially after the addition of ferromagnetic impurities. The so-called nearly ferromagnetic materials are also of interest. Specifically, Pd, which has a $\chi(T)$ peak at $T = 80K$, becomes ferromagnetic when only 2.3% Ni is added to it.[5] Although the $Pd_{1-x}Ni_x$ system has been thoroughly investigated, an unambiguous picture of its magnetic properties for small x is still missing. Because the $\chi(T)$ peak in Pd is small, a thorough investigation of it in the region $x < 0.02$ is of great interest for the effect under consideration. Finally, the actinides may also be suitable for this purpose [see, for example, the data for NpSb (Ref. 6)].

[1)]As far as we know, this has not been mentioned previously.

[2)]The numerical calculations in a similar model were also performed by other authors (see, for example, Ref. 3).

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