sd-Hybridization and paramagnetic susceptibility of transition metals

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Analytical expressions for the chemical potential $\eta(T)$ and the susceptibility $\chi(T)$ are obtained within the context of a simple sd model. Hybridization severely suppresses the Curie paramagnetism for $T \lesssim T_g \approx V_{sd}^2/\Delta$ (Δ is the width of the s band). The theory, which gives a fractional magnetic moment, can explain the maximum of $\chi(T)$ in Pd at $T \approx 80$ K.

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The paramagnetic susceptibility χ of many transition metals has no generally accepted, satisfactory explanation. As is known, a rather strong temperature dependence $\chi(T)$ has been observed experimentally in wide interval of T, and a Curie–Weiss-type paramagnetism, which is difficult to explain from the view-point of the collectivized-electron theory, has been observed at the end of the 3, 4, and 5 d-periods.

These peculiarities of $\chi(T)$ are undoubtedly associated with the peculiarities in the electron spectrum of d metals: however, the specific reasons for their occurrence remain a subject of discussion.[1–4] It is currently fashionable to assume that hybridization of conduction electrons with d-electrons plays an important role in transition metals.[5–7] A general consideration of a system of s and d electrons with allowance for sd-hybridization leads to rather complicated mathematical expressions that permit only a numerical solution. In this paper we examine a simple, special case which makes it possible to obtain analytical results and, consequently, a clearer physical picture of the entire effect.

We write the Hamiltonian of the s- and d-electron system in the form

$$\hat{\mathscr{H}} = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} a_{\mathbf{k}\sigma}^{+} a_{\mathbf{k}\sigma} + \sum_{\nu,\sigma} \epsilon_{d\sigma} a_{\nu\sigma}^{+} a_{\nu\sigma}$$

$$+ \sum_{\mathbf{k},\nu,\sigma} (V e^{i\mathbf{k}\nu} a_{\mathbf{k}\sigma}^{+} a_{\nu\sigma} + \text{Hermitian conjugate}), \tag{1}$$

where $\mathbf{k}$ is the quasi momentum, ν is the node number, and V is the hybridization matrix element. The intrinsic width of the d band is ignored in Eq. (1) and V is assumed to be independent of $\mathbf{k}$.

Diagonalization of Eq. (1) gives the known spectrum with the hybridization gap[5–7]:

$$E_{1,2}(\mathbf{k}) = \frac{1}{2} \{ \epsilon_d + \epsilon_{\mathbf{k}} \pm [(\epsilon_d - \epsilon_{\mathbf{k}})^2 + 4V^2]^{1/2}. \tag{2}$$

The density of states $g(E) = (k^2/\pi^2)(dE/dk)^{-1}$ can be written in analytical form for a

quadratic dispersion law $\epsilon_k = h^2 k^2/2m$ (a is the lattice parameter)

$$g(E) = \beta \left(E + \frac{V^2}{\epsilon_d - E} \right)^{1/2} \left[1 + \frac{V^2}{(\epsilon_d - E)^2} \right], \quad \beta = \frac{1}{2\pi^2} \left(\frac{2ma^2}{\hbar^2} \right)^{3/2}. \tag{3}$$

The simple formula,

$$\chi(T) = 2\mu_B^2 \int (-\partial f/\partial E) \, g(E) \, dE, \tag{4}$$

can be used to calculate $\chi(T)$, where an expansion in $(E - \eta)/kT$ can be used [instead of the usual approximation $\partial f/\partial E = -\delta(E - \eta)$, η is the chemical potential] for the $f(E)$ distribution function, in view of the strong $g(E)$ dependence near ϵ_d. The value χ depends on T both directly and through $\eta(T)$, which must be determined from the neutrality equation

$$\int f(E) \, g(E) \, dE = N \tag{5}$$

Equation (5) corresponds to half-filling of the s and d bands.

We write a linear approximation in $(E - \eta)/kT$ ($2\delta = 5.5kT$)

$$f(E - \eta) = \begin{cases} 1 & E < \eta - \delta \\ 0 & E > \eta + \delta \end{cases}; \quad f(E - \eta) = \frac{1}{2} \left(1 - \frac{E - \eta}{\delta} \right), \eta - \delta \leqslant E \leqslant \eta + \delta. \tag{6}$$

Substitution of Eqs. (3) and (6) in Eq. (5) after integration leads to a transcendental equation with elliptic integrals E and F for $\alpha(\theta) = \eta(\theta) - \eta(0)$ ($\theta = \delta - \delta_0$, $b = \epsilon_d$) of the form:

$$\left(D - \frac{5}{2}\theta^- \Delta \right) \Delta^{1/2} - [D + \theta^- (\theta^- - 2b - 2d^-)][b + d^- - \theta^- + b^+ b^-/(d^-$$

$$- \theta^-)]^{1/2} + [A^+ + \theta^+ (\theta^+ + 2b^+)][b^+ + \theta^+ - b^+ b^-/(b^- - \theta^+)]^{1/2}$$

$$+ (b^+ - b^-)^{1/2}\{(A^+ + A^-)[E(\gamma_0, q) - E(\gamma, q) - E(\mu, q)] - A^- [F(\gamma_0, q)$$

$$- F(\gamma, q) - F(\mu, q)]\} = 0, \tag{7}$$

where

$$D = d^-(2b + d - 6d^+), \quad A^\pm = b^\pm(b^\pm + 7b^\mp), \quad \theta^\pm = \theta \pm a(\theta),$$

$$\Delta = b + d, \quad \delta_0 = -\frac{1}{2}(b^- + d^-), \quad \eta(0) = b + \frac{1}{2}(d^- - b^-)$$

$$x^\pm = \frac{1}{2}(x \pm \sqrt{x^2 + 4V^2}), \quad (x = b, d), \quad q = [(b - b^-)/(b^+ - b^-)]^{1/2}, \tag{8}$$

$$\gamma = \arcsin\left(1 + \frac{d^- - \theta^-}{b^+}\right)^{1/2} , \quad \mu = \arcsin\left(\frac{\theta^+}{\theta^+ - b^-}\right)^{1/2}, \quad \gamma_0 = \gamma\,(\theta^- = 0).$$

As $q \to 1$ (i.e., $V^2/b \ll 1$) the elliptic integrals can be represented in the form $(q'^2 = 1 - q^2)$

$$E\,(\gamma, q) = \sin\gamma + \frac{1}{2}\,q'^2\left[\ln \text{tg}\left(\frac{\pi}{4} + \frac{\gamma}{2}\right) - \sin\gamma\right],$$

$$F\,(\gamma, q) = \ln \text{tg}\left(\frac{\pi}{4} + \frac{\gamma}{2}\right) - \frac{1}{4}q'^2\left[\text{tg}\,\gamma\,/\cos\gamma - \ln \text{tg}\left(\frac{\pi}{4} + \frac{\gamma}{2}\right)\right]. \quad (9)$$

The solution of Eq. (7) determines the temperature dependence θ of the chemical potential η as a function of the parameters ϵ_d and V (the width Δ of the s band can be assumed equal to unity without any loss of generality). Equation (7) with the use of the approximation (9) allows an analytical treatment. We obtain from Eqs. (7) and (9) at low and high temperatures

$$\eta\,(\theta) = \eta\,(0) + \theta, \quad (\theta \ll V^2/b), \quad (10)$$

$$\eta\,(\theta) = \eta\,(0) + (1 - 2\,n_1)\,\theta, \quad (\theta \gg V^2/b), \quad (11)$$

where $n_1 = N_1/N = (b/\Delta)^{3/2}$ is the number of electrons in the s band before the hybridization V is taken into account, and $n_2 = 1 - n_1$. We can see from (10) and (11) that $\eta(\theta)$ increases $\sim\theta$ for low θ, whereas for high it increases $\sim(1 - 2n_1)\theta$, where $1 - 2n_1 < 0$ for the s band that is at least one-half filled, and > 0 for one that is filled less than one-half. The $\eta(\theta)$ value decreases monotonically in the intermediate interval.

We can now use the expressions found for $\eta(T)$ to calculate $\chi(T)$ from Eq. (4). Here, analogously to Eq. (6), we can assume that $\partial f/\partial E = 0$ everywhere except in the interval $\eta - \delta \leqslant E \leqslant \eta + \delta$, in which $\partial f/\partial E \equiv -(1/4kT) - \cosh^{-2}((E - n)/kT)$ can be assumed equal to its value for $E = \eta(0)$; after substitution of $\eta(T)$ in (10) and (11) we have, respectively, $\partial f/\partial E \approx -(1/2\delta)$ $(\theta \ll V^2/b)$ and $\partial f/\partial E \approx -n_1 n_2/kT$ $(\theta \gg V^2/b)$. Here, the values $n_1, n_2 = 0,1$ (the d level is located at the edge of the s band) are excluded; we can therefore expand in $\frac{1}{2}(n_2 - n_1)^2 \ll 1$. Finally, we obtain

$$\chi(T) = \frac{N\mu_B^2}{\delta}\,(\theta/2\delta_0)^{3/2}, \quad \delta_0 = \frac{V^2\Delta}{2bd}, \quad (\theta \ll \delta_0), \quad (12)$$

$$\chi(T) = \chi_c\,[1 + 3n_1\delta/\epsilon_d - 3V^2/(2n_2\epsilon_d\delta)], \quad (\theta \gg \delta_0), \quad (13)$$

where

$$\chi_c = N\mu_{\text{eff}}^2/kT, \quad \mu_{\text{eff}} = (2n_1 n_2)^{1/2}\mu_B. \quad (14)$$

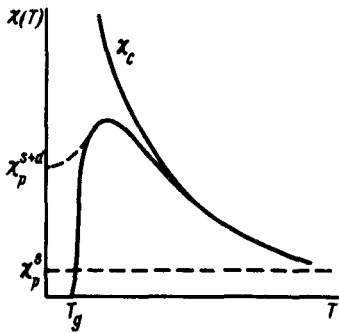FIG. 1. General form of the susceptibility $\chi(T)$ and its components. The solid curved with a maximum was obtained from the solution of Eqs. (7), (12), and (13). χ_c is the Curie susceptibility in absence of hybridization. The dashed line corresponds to the finite width $\Delta_d (\neq 0)$ of the d band.

Thus, starting from $T = T_g [= (2/5.5)\delta_0]$ ($2\delta_0$ is the width of the hybridization gap), the susceptibility first increases rapidly $\sim [(T - T_g)/T_g]^{3/2}$, then it reaches a maximum and starts to decrease, approaching the Curie law in accordance with (13) (see Fig. 1). As Eq. (13) shows, at high T values $\chi(T)$ consists of three contributions: Curie, Pauli (χ_p^s) for s electrons, and hybridization. Equation (14) corresponds to the divisibility of the magnetic moment, which is automatically present in the model being considered.

For $T < T_g$ the hybridization completely cancels out χ, since kT is less than the hybridization gap. However, when the intrinsic width of the d band or the $V(k)$ dependence is taken into account, the gap will disappear (for $\Delta_d > V^2/\Delta$), so that at $T = 0$ the Pauli contribution from the d band $\chi_p^d \approx N_2 \mu_B^2/\Delta_d$ can exist. In this case χ_p^s, which is frozen in (12) by the hybridization gap (see dashed line in Fig. 1), is partially thawed out. A curve of the type shown in Fig. 1 is observed in Pd, and its explanation has been a subject of discussion. Thus, it is pointed out[1] that the maximum of $\chi(T)$ in Pd may be due to a saddle-point-type singularity in the carrier spectrum. Our result seems to correspond to that of Ref. 1, but it contains a clearer physical picture that explicitly reflects the effect of sd-hybridization on $\chi(T)$.

For comparison with the experiment we can take into account the exchange enhancement α: $\chi_{\text{enhan}}(T) = \chi(T)/[1 - \alpha\chi(T)]$. This effect is uaually used to obtain the strong T-dependence of the susceptibility observed in transition metals. Our calculation shows that the hybridization effect can also give a strong T-dependence of χ even when the enhancement is disregarded.

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