PHYSICAL REVIEW B VOLUME 52, NUMBER 23 15 DECEMBER 1995-I

Multiple-scattering approach to the *s*-*f* model in ferromagnetic semiconductors above the Curie temperature

Masao Takahashi and Kazuhiro Mitsui
Kanagawa Institute of Technology, 1030 Simo-Ogino, Atsugi, Kanagawa 243-02, Japan

Masakatsu Umehara
National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

(Received 8 December 1994; revised manuscript received 31 July 1995)

For the *s*-*f* model in ferromagnetic semiconductors, it is necessary to treat simultaneously multiple scattering on the same site and scattering due to *f* spin correlation between different sites. In this paper, one-site multiple scattering is taken into account using a *t*-matrix formalism, and the exchange scattering via *f* spin correlation between different sites is treated using a two-spin correlation function and an appropriate decoupling scheme. The results show good agreement with those of the coherent potential approximation in the high-temperature limit. The calculated energy of the bottom of the band is reasonable, even at the Curie temperature (T_C), for a wide range of IS/W, where W is the bandwidth of the conduction band and IS is the exchange interaction energy.

The *s*-*f* exchange model is currently accepted as a basis for studying the conduction electron in ordinary magnetic semiconductors.[1-3] In this model, there are magnetic moments on the regular sites and a well-defined conduction band. A single conduction electron (hereafter referred to as the *s* electron) moves in the crystal, while interacting with localized magnetic moments (hereafter referred to as *f* spins) through the *s*-*f* exchange interaction.

Studies on the *s*-*f* exchange model in ferromagnetic semiconductors may be classified into two groups. One is the coherent-potential approximation (CPA) (Refs. 4 and 5) and the other is the perturbation theory.[3,6-8] The CPA is a good approximation for a wide range of IS/W when the directions of *f* spins are completely random. The following point was deduced by the CPA:[4,5] for the case of weak *s*-*f* exchange interaction, the conduction band in the high-temperature limit retained a single band, whereas for the case of strong interaction, it split into two subbands characterized by electron spin parallel or antiparallel to the directions of *f* spins. This result is reasonable. However, as the temperature decreases, the CPA is no longer effective, since the short-range order of *f* spins is developed.

On the other hand, the perturbation theory can take into account the effect of the *f* spin correlation, which is particularly important around T_C.[3,6-8] However, the perturbation theory is not suited for strong *s*-*f* exchange interaction. In the previous paper,[3] we investigated the application range of the perturbation theory; we studied the conduction-electron state, using a Green's-function technique, in which the second-order self-energy in the *s*-*f* exchange interaction with a dressed electron propagator was used together with a static two-spin correlation function. As a result, it was revealed that the perturbation theory was not suited for the case of strong *s*-*f* exchange interaction, $IS/W \gtrsim 0.1$, although it yielded reasonable results even at T_C for the case of weak *s*-*f* exchange interaction. Furthermore, band splitting for strong *s*-*f* exchange interaction was not obtained; this may be ascribed to the fact that multiple scattering was not suitably taken into account in the previous study.

So far, reasonable results at paramagnetic temperatures have not been obtained for strong *s*-*f* exchange interaction. In order to formulate an improved theory for the *s*-*f* model applicable to wide ranges of IS/W and temperature, it is necessary to treat simultaneously multiple scattering on the same site and scattering due to *f* spin correlation between different sites. The aim of this paper is to investigate the effect of multiple scattering on the conduction electron, by applying the multiple-scattering theory[9] to the *s*-*f* exchange model.

For this purpose, we use the same Hamiltonian (and the same notation) as in the previous study;[3] the total Hamiltonian H_t is expressed as

$$H_t = H_s + H_f + H_{sf} , \tag{1}$$

where

$$H_s = \sum_{k\mu} \varepsilon_k a^\dagger_{k\mu} a_{k\mu} , \tag{2}$$

$$H_f = -\sum_{mn} J_{mn} \mathbf{S}_m \cdot \mathbf{S}_n , \tag{3}$$

$$H_{sf} = -I \sum_{m\mu\nu} a^\dagger_{m\mu} \boldsymbol{\sigma} \cdot \mathbf{S}_m a_{m\nu} . \tag{4}$$

Here, H_s represents the transfer energy of an *s* electron, H_f is the Heisenberg exchange interaction between *f* spins, and H_{sf} is the *s*-*f* exchange interaction.

We define the single-electron Green's function by

$$G(\omega) = \frac{1}{\omega - H} , \tag{5}$$

where

$$H = H_s + H_{sf} , \tag{6}$$

and write its thermal average for *f* spins as $G_{\mathrm{av}} = \langle G \rangle_{\mathrm{av}}$.

In order to apply the multiple-scattering theory[9] to the *s*-*f* exchange model, we add an auxiliary quantity Σ to the original Hamiltonian H, and then subtract it. The reference Hamiltonian K is written as

$$K=\sum_{k\mu}(\varepsilon_k+\Sigma)a_{k\mu}^{\dagger}a_{k\mu}\ . \tag{7}$$

The perturbation term V, which can be expressed as a sum over each lattice site, is written as

$$V=\sum_m v_m\ , \tag{8a}$$

$$=\sum_{\substack{m\\ \mu\nu}} a_{m\mu}^{\dagger}(-I\sigma\cdot\mathbf{S}_m-\Sigma\delta_{\mu\nu})a_{m\nu}\ . \tag{8b}$$

Note that K involves no f spin operator. Σ is generally complex and is ω dependent; it will be determined later.

The single-electron Green's function, defined by Eq. (5), is now written as

$$G=P+PTP\ . \tag{9}$$

Here, T is the total scattering operator, and P is the reference Green's function defined by

$$P(\omega)=\frac{1}{\omega-K}\ . \tag{10}$$

Using the t matrix defined by

$$t_m=v_m[1-Pv_m]^{-1}\ , \tag{11}$$

T is expressed as

$$T=\sum_m t_m+\sum_m t_mP\sum_{n(\neq m)}v_n+\sum_m t_mP\sum_{n(\neq m)}v_nP\times T\ . \tag{12}$$

Equation (12) is the rigorous expression. By introducing the decoupling approximation

$$T_{\text{av}}=\sum_m\langle t_m\rangle_{\text{av}}+\sum_m\sum_{n(\neq m)}\langle t_mPv_n\rangle_{\text{av}}$$

$$+\sum_m\sum_{n(\neq m)}\langle t_mPv_n\rangle_{\text{av}}P\times T_{\text{av}}\ , \tag{13}$$

we obtain $T_{\text{av}}(\equiv\langle T\rangle_{\text{av}})$ as

$$T_{\text{av}}=(1-Q_{\text{av}}P)^{-1}\times\left[\sum_m\langle t_m\rangle_{\text{av}}+Q_{\text{av}}\right]\ , \tag{14}$$

with

$$Q_{\text{av}}=\sum_m\sum_{n(\neq m)}\langle t_mPv_n\rangle_{\text{av}}\ . \tag{15}$$

In Eq. (14), $\langle t_m\rangle_{\text{av}}$ gives the effect of the one-site multiple scattering, and Q_{av} gives the effect of the scattering between different sites through the f spin correlation.

Now we define the total self-energy operator Σ_t by the following equation:

$$G_{\text{av}}=\frac{1}{\omega-H_s-\Sigma_t}\ . \tag{16}$$

In this study, for Σ, we simply take the self-energy Σ_{CPA} determined by the CPA. This means setting

$$\langle t_m\rangle_{\text{av}}=0 \tag{17}$$

in Eq. (14). Since $\langle\mathbf{S}_m\rangle_{\text{av}}=0$ for paramagnetic temperatures, the self-energy in this study is finally expressed in the following simple form:

$$\Sigma_t(k)\equiv\langle k|\,\Sigma_t\,|k\rangle_{\text{av}} \tag{18a}$$

$$=\Sigma_{\text{CPA}}+\langle k|Q_{\text{av}}|k\rangle \tag{18b}$$

$$=\sum_m\sum_n\langle k|t_mPv_n|k\rangle_{\text{av}}\ . \tag{18c}$$

In order to visualize the physical meaning of the present approximation, we draw the self-energy diagram shown in Fig. 1.

Now we show the explicit expression for paramagnetic temperatures. The matrix element of P in the Bloch representation is diagonal, and is expressed as

$$P(k)=\langle k|P|k\rangle=\frac{1}{\omega-\varepsilon_k-\Sigma}\ . \tag{19}$$

Then, the Wannier representation of P, $F(\omega)=\langle m|P|m\rangle$ (independent of m), is given by

$$F(\omega)=\frac{1}{N}\sum_k\frac{1}{\omega-\varepsilon_k-\Sigma} \tag{20a}$$

$$=\frac{3}{W}\int_0^1dx\,\frac{x^2}{\left[\dfrac{\omega-\Sigma}{W}\right]-x^2}\ . \tag{20b}$$

In the derivation of Eq. (20), as in the previous study,[3] we simply assume a free-electron-like band ε_k with bandwidth W, and replace the summation of k in the first Brillouin zone by the integration within the Debye sphere of radius q_D.

The t matrix of the s-f exchange interaction defined by Eq. (11) is a matrix of 2×2 components:

$$t_m=\begin{bmatrix}\langle m\uparrow|t_m|m\uparrow\rangle & \langle m\uparrow|t_m|m\downarrow\rangle\\ \langle m\downarrow|t_m|m\uparrow\rangle & \langle m\downarrow|t_m|m\downarrow\rangle\end{bmatrix}$$

$$=\frac{1}{B}\begin{bmatrix}-\Sigma+F(IS+\Sigma)[I(S+l)-\Sigma]-IS_{mz} & -IS_{m^-}\\ -IS_{m^+} & -\Sigma+F(IS+\Sigma)[I(S+1)-\Sigma]+IS_{mz}\end{bmatrix}\ , \tag{21}$$

where

$$B=\{1+F(IS+\Sigma)\}\{1-F[I(S+1)-\Sigma]\}\ . \tag{22}$$

Because $\langle\mathbf{S}_m\rangle_{\text{av}}=0$ for paramagnetic temperatures, the CPA condition, Eq. (17), leads to the following equation for the self-energy:[4,5]

$$-\Sigma_{\text{CPA}}+F(IS+\Sigma_{\text{CPA}})\{I(S+1)-\Sigma_{\text{CPA}}\}=0\ . \tag{23}$$

In the CPA, both F and $\Sigma(=\Sigma_{\text{CPA}})$ are self-consistently determined by Eqs. (20) and (23) as a function of ω/W.

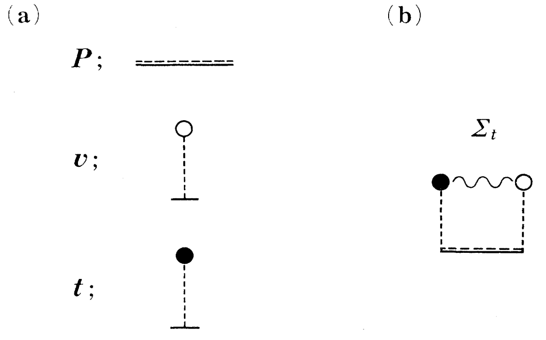

FIG. 1. (a) Diagrammatic representation of P, v_m, and t_m. (b) Diagram for the self-energy defined by Eq. (26). The wavy line represents the correlation between different sites.

In this study, as previously mentioned, we take Σ_{CPA} in place of Σ in Eq. (7). The t-matrix elements then become simply

$$t_m = \frac{1}{B}\begin{bmatrix} -IS_{mz} & -IS_{m^-} \\ -IS_{m^+} & +IS_{mz} \end{bmatrix}, \tag{24}$$

with

$$B = 1 + F(\Sigma_{\text{CPA}} - I) \ . \tag{25}$$

Using Eqs. (24) and (25), the total self-energy of Eq. (18) for both up- and down-spin electrons is now given as

$$\Sigma_t(k) = \frac{1}{N}\sum_m \sum_n \langle m\uparrow | t_m P v_n | n\uparrow \rangle_{\text{av}} \tag{26a}$$

$$= \frac{I^2}{BN^2}\sum_q P(q) \sum_m \sum_n \langle \mathbf{S}_m \cdot \mathbf{S}_n \rangle_{\text{av}} e^{i(k-q)(m-n)} \ . \tag{26b}$$

By using the Ornstein-Zernike two-spin correlation function, as in the previous paper,[3] the total self-energy in this study is finally obtained as

$$\Sigma_t(x)/W = \frac{1}{B}\left[\frac{IS}{W}\right]^2 \left[1+\frac{1}{S}\right] C(\epsilon)(\epsilon+1) \times \frac{3}{4Ax}\int_0^1 dy \frac{y}{\left[\dfrac{\omega-\Sigma}{W}\right] - y^2} \times \ln\frac{\epsilon + A(x+y)^2}{\epsilon + A(x-y)^2} \ . \tag{27}$$

Here, $\epsilon \equiv (T-T_C)/T_C$ is a reduced temperature, A is a constant which depends on the crystal structure, and $C(\epsilon)$ is a coefficient determined by the sum rule for the f spin system.

The density of states $D(\omega)$ is calculated by

$$D(\omega)W = -\frac{W}{\pi N}\sum_k \text{Im}\frac{1}{\omega - \varepsilon_k - \Sigma_t(k)} \tag{28a}$$

$$= -\frac{1}{\pi}\text{Im}\int_0^1 dx \frac{3x^2}{\left[\dfrac{\omega - \Sigma_t(x)}{W}\right] - x^2} \ . \tag{28b}$$

Since the main purpose of this work is to improve the previous study, detailed numerical calculations have been performed for the paramagnetic temperature region with the same parameters as in the previous paper: $A = \pi(\pi/3)^{1/3}$ for fcc ferromagnetic semiconductors and $S = \frac{7}{2}$ for Eu chalcogenides. The results are shown as a function of IS/W and T/T_C.

In the high-temperature limit, there is no correlation between the f spins on the different sites: $\langle \mathbf{S}_m \cdot \mathbf{S}_n \rangle_{\text{av}} = 0$ for $m \neq n$. This leads to $Q_{\text{av}} = 0$, and thus the total self-energy Σ_t agrees with the self-energy of the CPA [see Eq. (18)]. The results of the present approximation, therefore, show good agreement with those of the CPA in the high-temperature limit.

As the temperature decreases, the effect of the f spin correlation on the s electron becomes so important that the CPA becomes ineffective. We have taken account of this effect on the self-energy, as previously mentioned. In Fig. 2, the results of the density of states calculated in the present study are presented for $T = \infty$, $2T_C$, and T_C.

When the value of IS/W is small (see the case of $IS/W = 0.1$), the density of states shifts downward as the temperature approaches T_C from $T = \infty$. This feature is similar to that obtained by the self-consistent treatment in the previous study. With the increase in IS/W, however, the results are considerably different from the previ-

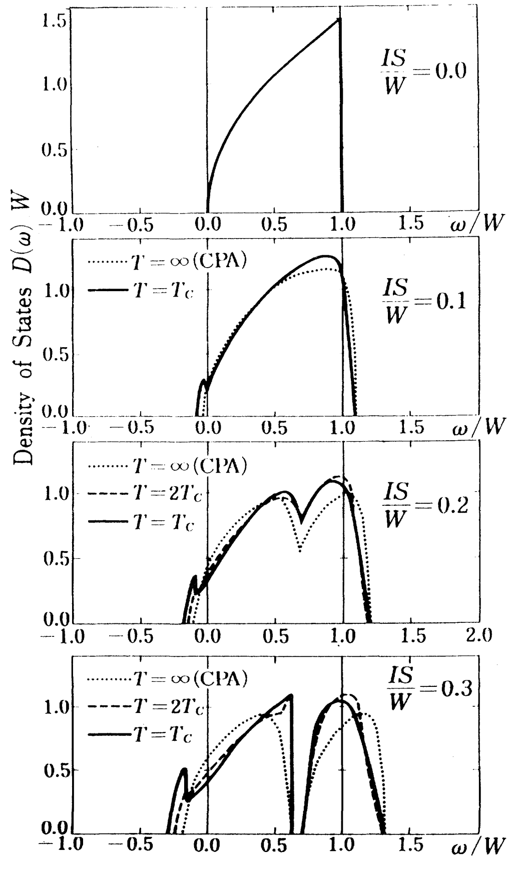

FIG. 2. Density of states at $T = \infty$ (CPA), $2T_C$, and T_C for IS/W=0.0, 0.1, 0.2, and 0.3.

ous ones. For $IS/W=0.2$, the density of states has two peaks that correspond to the states of electron spin parallel or antiparallel to the direction of f spins. When the value of IS/W increases further (for example, $IS/W=0.3$), the conduction band becomes two completely separated subbands at all paramagnetic temperatures. Furthermore, the bottom of the band extends rapidly to the lower-energy side as the temperature approaches T_C.

Thus, the results obtained in this study seem to be reasonable for a wide range of IS/W at paramagnetic temperatures. On the other hand, the previous result retains a single-band structure even for large values of IS/W, which is evidently unphysical. Therefore, the application of the multiple-scattering theory to the *s-f* model noticeably improves upon the previous study. Furthermore, although an approximate treatment is used in this study, the total density of states is confirmed as

$$\int_{-\infty}^{\infty} D(\omega)d\omega = 1.0 \tag{29}$$

throughout the present numerical calculation.

In Fig. 3, the energy position of the bottom of the band is shown as a function of IS/W both for $T=\infty$ and $T=T_C$. The calculated result at $T=\infty$ simply reproduces the result of the CPA. The result at $T=T_C$ gives a finite energy, which is not lower than $-IS$. On the other hand, in the previous method, the unphysical result that the energy lowering exceeds IS for $IS/W \gtrsim 0.1$ was obtained (see also the Erratum of the previous paper[3]). These results suggest an improvement in the energy of the bottom of the band for a wide range of IS/W at paramagnetic temperatures.

The physical origin of this energy lowering is the strong scattering of the s electron via the f spin correlation between different sites. Around $T \simeq T_C$, the short-range order of f spins is developed, and in particular at $T=T_C$, the correlation length between f spins becomes infinite. The s electron tends to localize with a finite probability in the region where the f spins are nearly aligned. This quasilocalized state should have lower energy than the broad-spreading state. A peak near the bottom of the band shown in Fig. 2 may be related to such a quasilocalized state.

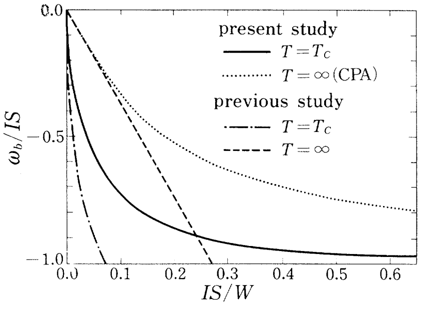

FIG. 3. Energy of the bottom of the conduction band normalized by the exchange interaction energy IS, ω_b/IS, is shown as a function of IS/W. The result of the present study is shown by the solid line for $T=T_C$, and by the dotted line for $T=\infty$ (CPA). The result of the previous study is shown by the broken line for $T=T_C$ and by the dashed line for $T=\infty$.

This small peak at the bottom of the band, however, rises to almost the same level of energy as that obtained by the CPA. Note that the total self-energy Σ_t does not have a suitable imaginary part in the energy region where the imaginary part of $\Sigma_{\rm CPA}$ is zero, and that the contribution to the density of states comes from the k point at which $\omega-\varepsilon_k-\Sigma_t(k)=0$ in Eq. (28a). The physical significance of the obtained small peak, therefore, may be questionable. For a more precise study of this point, the self-consistent treatment is necessary.

The advantages of the present study are considered to be as follows.

(i) The one-site multiple scattering, due to the *s-f* exchange interaction, is taken into consideration. Consequently, the present approximation agrees with the CPA in the high-temperature limit and recovers the band splitting for large values of IS/W even at paramagnetic temperatures.

(ii) When IS/W is as small as $IS/W \lesssim 0.1$, the present method reproduces the previous results obtained by the self-consistent treatment.

(iii) The energy of the bottom of the band, obtained by the present method, is improved for an extended range of IS/W at paramagnetic temperatures.

On the other hand, we cannot give a definitive physical meaning for the small peak in the band tail near T_C, because the present study does not use the self-consistent treatment. When a few electrons are injected into the conduction band, they move near the bottom of the band. The self-consistent treatment for the band tail is particularly important.

One of the authors (M.T.) would like to express his thanks to Professor Y. Kamezawa and Y. Baba (General Manager of Kanagama Institute of Technology) for their continuous encouragement.

---

[1] A. Mauger and C. Godart, Phys. Rep. **141**, 51 (1986).

[2] P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), p. 507.

[3] M. Takahashi, K. Mitsui, and M. Umehara, Phys. Rev. B **48**, 17 053 (1993); **50**, 17 759(E) (1994).

[4] A. Rangette, A. Yanase, and J. Kübler, Solid State Commun. **12**, 171 (1973).

[5] K. Kubo, J. Phys. Soc. Jpn. **36**, 32 (1974).

[6] C. Haas, Phys. Rev. **168**, 531 (1968).

[7] F. Rys, J. S. Helman, and W. Baltensberger, Phys. Konden. Mater. **6**, 105 (1967).

[8] J. Sinkkonen, Phys. Rev. B **19**, 6407 (1979).

[9] H. Ehrenreich and L. M. Schwartz, in *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1976), Vol. 31, p. 149.