Free-Energy Shift of Conduction Electrons Due to the *s-d* Exchange Interaction

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(Received 1 November 1965)

A free-energy shift of the conduction electrons due to magnetic impurity immersed into an otherwise pure metal is calculated up to the fourth order in the *s-d* exchange interaction. The results obtained show that there appears no anomalous term of the form $T^n \ln T$ up to this order in the magnetic-field–independent part of the free energy and that anomalous $\ln T$ terms are included only in the magnetic-field–dependent part.

INTRODUCTION

IT has been pointed out by Kondo[1] that the electrical resistivity of dilute alloys due to the *s-d* exchange interaction with magnetic impurities immersed in otherwise pure metals shows a singular behavior described by a logarithmic function of temperature which arises from the second Born approximation. Similar logarithmic singularities also appear in the expressions for the spin polarization of the conduction electrons due to the magnetic impurities and for the magnitude of the localized spin, as has recently been shown by Okiji and one of the present authors.[2] According to their results, this singular behavior of dilute alloys including magnetic impurities can be attributed to a reduction of the magnitude of the localized spin as far as the magnetic properties are concerned.

In this paper, we shall calculate the magnetic-field–independent part of the free-energy shift of a free-electron gas due to a magnetic impurity immersed into it, up to the fourth order in the exchange interaction, and we shall show that there appears no logarithmic term up to this order. In conflict with the result recently obtained by Engelsberg,[3] this result means that the logarithmic singularities appear only in the magnetic-field–dependent part of the free energy.

EXPRESSION FOR THE FREE-ENERGY SHIFT

We consider the Hamiltonian of the system consisting of the conduction electrons and one localized spin situated at the origin, which can be written as

$$H=H_0+V$$
$$=\sum_{\mathbf{k}s} \epsilon_{\mathbf{k}} a_{\mathbf{k}s}{}^* a_{\mathbf{k}s}-(J/2N)\sum_{\mathbf{k}\mathbf{k}'}\{(a_{\mathbf{k}'\uparrow}{}^* a_{\mathbf{k}\uparrow}-a_{\mathbf{k}'\downarrow}{}^* a_{\mathbf{k}\downarrow})S_z + a_{\mathbf{k}'\uparrow}{}^* a_{\mathbf{k}\downarrow}S_- + a_{\mathbf{k}'\downarrow}{}^* a_{\mathbf{k}\uparrow}S_+\}, \quad (1)$$

where *s-d* exchange interaction is assumed to be δ-function-like. $\mathbf{S}$ means the spin operator of the impurity atom, and $S_\pm$ the usual spin raising and lowering operators

$$S_\pm = S_x \pm iS_y.$$

$a_{\mathbf{k}}{}^*{}_\uparrow$ and $a_{\mathbf{k}\uparrow}$ are, respectively, the creation and annihilation operators for the conduction electron with the wave vector $\mathbf{k}$ and the up spin, and $\epsilon_{\mathbf{k}}$ is the band energy of the conduction electron with the wave vector $\mathbf{k}$.

The usual method of perturbation gives rise to the following energy shift for the ground-state energy of the conduction electrons up to the fourth order in J:

$$\Delta F = 2S(S+1)\left(-\frac{J}{2N}\right)^2 \sum_{\mathbf{k}\mathbf{k}'} \frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}} - 2S(S+1)\left(-\frac{J}{2N}\right)^3 \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \left\{\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})} + \frac{(1-f_{\mathbf{k}})f_{\mathbf{k}'}f_{\mathbf{k}''}}{(\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}})}\right\}$$
$$+\{2S^2(S+1)^2+2S(S+1)\}\left(-\frac{J}{2N}\right)^4 \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \left\{\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}''})(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})} + \frac{(1-f_{\mathbf{k}})f_{\mathbf{k}'}f_{\mathbf{k}''}f_{\mathbf{k}'''}}{(\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}'''}-\epsilon_{\mathbf{k}})}\right\}$$
$$-3\{2S^2(S+1)^2-2S(S+1)\}\left(-\frac{J}{2N}\right)^4 \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})f_{\mathbf{k}''}(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})}$$
$$-4S(S+1)\left(-\frac{J}{2N}\right)^4 \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})f_{\mathbf{k}''}(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''})[(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''})+(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})](\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})} + \cdots. \quad (2)$$

Here, the unperturbed ground state is assumed to be the state in which all the one-electron states below the Fermi energy are occupied by the electrons with up and down spins and the state of the localized spin is in one of $(2S+1)$ states in each of which the z component of $\mathbf{S}$ takes one of the integers ranging from S to $-S$. The function $f_{\mathbf{k}}$ is zero for $\epsilon_{\mathbf{k}} > \epsilon_F$ and unity for $\epsilon_{\mathbf{k}} < \epsilon_F$ where ϵ_F denotes the Fermi energy.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[2] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 505 (1965).
[3] S. Engelsberg, Phys. Rev. **139**, A1194 (1965).

Equation (2) is originally an expression for the energy shift at the absolute zero of temperature. However, if one takes the Fermi distribution function as $f_{\mathbf{k}}$ it turns out to be the expression for the free-energy shift with the fixed Fermi energy at finite temperatures. This fact can actually be shown for the present Hamiltonian up to the fourth order in J. The contributions to the free energy from the change in the Fermi energy are not expected to give any anomalous term. Therefore, these will be disregarded in the following calculation. The free-energy shift of the third order in J has already been given in the paper by Engelsberg.[3]

THIRD-ORDER ENERGY SHIFT

It is easy to show that the second-order term has no logarithmic component. In order to see whether the third-order term has logarithmic components or not, we have to carry out the summation over $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$. In order to do this, we assume the following simple state density for the conduction electrons:

$$\begin{aligned}\rho(\epsilon)&=\rho \quad \text{for} \quad D\geq\epsilon\geq -D\\ &=0 \quad \text{for} \quad D<|\epsilon|\end{aligned} \tag{3}$$

and take the Fermi energy as an origin of energy. Then, the first term can be integrated as follows:

$$\begin{aligned}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''}\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})}&=\rho^3\int_{-D}^{D}f_{\mathbf{k}}\,d\epsilon_{\mathbf{k}}\left\{\ln|D-\epsilon_{\mathbf{k}}|+\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}\right\}^2\\ &=\rho^3\left\{\int_{-D}^{D}f_{\mathbf{k}}(\ln|D-\epsilon_{\mathbf{k}}|)^2\,d\epsilon_{\mathbf{k}}+2\int_{-D}^{D}f_{\mathbf{k}}\ln|D-\epsilon_{\mathbf{k}}|\,d\epsilon_{\mathbf{k}}\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}\right.\\ &\qquad\left.+\int_{-D}^{D}f_{\mathbf{k}}\,d\epsilon_{\mathbf{k}}\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}\right\},\end{aligned} \tag{4}$$

where small quantities proportional to $\exp(-D/kT)$ have been omitted. As is easily seen, the first term gives no singular term. The last term can be expressed by partial integration as

$$f_{\mathbf{k}}G(\epsilon_{\mathbf{k}})\Big|_{-D}^{D}-\int_{-D}^{D}\frac{df_{\mathbf{k}}}{d\epsilon_{\mathbf{k}}}G(\epsilon_{\mathbf{k}})d\epsilon_{\mathbf{k}},$$

where $G(\epsilon_{\mathbf{k}})$ is the indefinite integral of the function g of $\epsilon_{\mathbf{k}}$ given by the last factor, including a double integration with respect to ϵ' and ϵ'',

$$g(\epsilon_{\mathbf{k}})=\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}.$$

The contributions from the band edges do not give any singular term with respect to T. On the other hand, since $df_{\mathbf{k}}/d\epsilon_{\mathbf{k}}$ is an even function of $\epsilon_{\mathbf{k}}$, and $G(\epsilon_{\mathbf{k}})$ is an odd function of $\epsilon_{\mathbf{k}}$, the contribution from the central part vanishes.

The second term of Eq. (4) converges near both ends of the band. Therefore, we can expand the first logarithmic function with respect to ϵ/D. Then, we obtain the following type of integral:

$$\int_{-D}^{D}f_{\mathbf{k}}\epsilon_{\mathbf{k}}^{n}\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}, \tag{5}$$

where $\epsilon_{\mathbf{k}}^{n}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|$ can be integrated with respect to $\epsilon_{\mathbf{k}}$ as $[(\epsilon_{\mathbf{k}}^{n+1}-\epsilon_{\mathbf{k}'}^{n+1})/(n+1)]\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|+$nonlogarithmic terms. Obviously, the contributions from the band edges give no singular terms, and further the contribution from the central part is given by

$$-\iint_{-D}^{D}\frac{df_{\mathbf{k}}}{d\epsilon_{\mathbf{k}}}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{\epsilon_{\mathbf{k}}^{n+1}-\epsilon_{\mathbf{k}'}^{n+1}}{n+1}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon\,d\epsilon_{\mathbf{k}'}.$$

This integral vanishes because the interchange of $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}'}$ changes the sign. The considerations made so far also apply to the second term of the third-order energy shift. Thus, the third-order energy shift is found to have no singular term.

Engelsberg[3] adopted a parabolic form for the state density and approximated the Fermi distribution function by a simple integrable form. Such a method of calculation gives no logarithmic term in the third-order energy shift either.

FOURTH-ORDER ENERGY SHIFT

There are three kinds of integrals which we must now calculate for the fourth-order energy shift.

The first one is calculated as

$$\sum_{\mathbf{k}} f_{\mathbf{k}}\left(\sum_{\mathbf{k}'}\frac{1-f_{\mathbf{k}'}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}}\right)^3=-\rho^4\int_{-D}^{D} f_{\mathbf{k}}\,d\epsilon_{\mathbf{k}}\left\{\ln|\epsilon_{\mathbf{k}}-D|+\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}\right\}^3$$

$$=-\rho^4\int_{-D}^{D} f_{\mathbf{k}}\,d\epsilon_{\mathbf{k}}\Bigg[(\ln|D-\epsilon_{\mathbf{k}}|)^3+3(\ln|D-\epsilon_{\mathbf{k}}|)^2\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}$$

$$+3\ln|D-\epsilon_{\mathbf{k}}|\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}$$

$$+\iiint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\frac{df_{\mathbf{k}'''}}{d\epsilon_{\mathbf{k}'''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}d\epsilon_{\mathbf{k}'''}\Bigg]. \quad (6)$$

The first term of this equation has no $\ln T$ term. The second term has no $\ln T$ term either because the integral given by expression (5) has no $\ln T$ term. Since the fourth term is an integral of the product of $f_{\mathbf{k}}$ and an even function with respect to $\epsilon_{\mathbf{k}}$, no logarithmic function of temperature appears from this term. Thus, what we have to study is the following integral:

$$\int_{-D}^{D} f_{\mathbf{k}}\ln|D-\epsilon_{\mathbf{k}}|\,d\epsilon_{\mathbf{k}}\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}. \quad (7)$$

The second type of integral which appears in the fourth-order energy shift can be rearranged as follows:

$$\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})f_{\mathbf{k}''}(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})}=\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\left\{\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}''})(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})}-\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})}\right\}. \quad (8)$$

The first term is just of the first type of integral which we have considered above. The second term can be calculated as follows:

$$-\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''})(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'''})}=\rho^3\sum_{\mathbf{k}} f_{\mathbf{k}}\ln\left|\frac{D-\epsilon_{\mathbf{k}}}{D+\epsilon_{\mathbf{k}}}\right|\Bigg\{(\ln|D-\epsilon_{\mathbf{k}}|)^2+2\ln|D-\epsilon_{\mathbf{k}}|\int_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\,d\epsilon_{\mathbf{k}'}$$

$$+\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''}\Bigg\}. \quad (9)$$

It can easily be seen that neither the first nor the second term has any $\ln T$ term. The third term has a similar form to the integral (7). These two integrals have no singularity at the ends of the band. Therefore, in order to show that they have no $\ln T$ term at all we have only to show that the following integral

$$I_1=\int_{-D}^{D} f_{\mathbf{k}}\epsilon_{\mathbf{k}}^n\,d\epsilon_{\mathbf{k}}\iint_{-D}^{D}\frac{df_{\mathbf{k}'}}{d\epsilon_{\mathbf{k}'}}\frac{df_{\mathbf{k}''}}{d\epsilon_{\mathbf{k}''}}\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|\ln|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}''}|\,d\epsilon_{\mathbf{k}'}d\epsilon_{\mathbf{k}''} \quad (10)$$

has no $\ln T$ term. The evaluation of this integral will be given in the Appendix A.

The third type of integral can be rearranged as follows:

$$-\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})f_{\mathbf{k}''}(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''})[(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''})+(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})](\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})}$$

$$=\sum_{\mathbf{k}''\mathbf{k}'''}\frac{f_{\mathbf{k}''}(1-f_{\mathbf{k}'''})}{(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''})^2}\sum_{\mathbf{k}\mathbf{k}'}\left\{\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})}{(\epsilon_{\mathbf{k}''}-\epsilon_{\mathbf{k}'''}+\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})}-\frac{f_{\mathbf{k}}(1-f_{\mathbf{k}'})}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})}\right\}. \quad (11)$$

The second factor enclosed in curly brackets can be calculated as follows:

$$\{-(2D-\epsilon)\ln|2D-\epsilon|+2D\ln|2D|\}$$
$$-\int\frac{df_k}{d\epsilon_k}\{(D+\epsilon_k-\epsilon)\ln|D+\epsilon_k-\epsilon|+(D-\epsilon_k-\epsilon)\ln|D-\epsilon_k-\epsilon|-(D+\epsilon_k)\ln|D+\epsilon_k|-(D-\epsilon_k)\ln|D-\epsilon_k|\}\,d\epsilon_k$$
$$-\int\int\frac{df_k}{d\epsilon_k}\frac{df_{k'}}{d\epsilon_{k'}}(\epsilon_{k'}-\epsilon_k-\epsilon)\ln|\epsilon_{k'}-\epsilon_k-\epsilon|\,d\epsilon_k d\epsilon_{k'},\quad \epsilon=\epsilon_{k''}-\epsilon_{k'''}. \tag{12}$$

Since the first and the second terms of Eq. (12) do not show a singular behavior for small ϵ, these terms are not of interest. With the use of (12) in Eq. (11), the essential part of Eq. (11) can be expressed as

$$\begin{aligned}&\int\int d\epsilon_{k''}d\epsilon_{k'''}\frac{f_{k''}}{(\epsilon_{k''}-\epsilon_{k'''})^2}\int\int\frac{df_k}{d\epsilon_k}\frac{df_{k'}}{d\epsilon_{k'}}(\epsilon_k-\epsilon_{k'})\ln|\epsilon_{k'''}-\epsilon_{k''}-(\epsilon_k-\epsilon_{k'})|\,d\epsilon_k d\epsilon_{k'}\\&+\int\int d\epsilon_{k''}d\epsilon_{k'''}\frac{f_{k''}}{(\epsilon_{k''}-\epsilon_{k'''})}\int\int\frac{df_k}{d\epsilon_k}\frac{df_{k'}}{d\epsilon_{k'}}\ln|\epsilon_{k'''}-\epsilon_{k''}-(\epsilon_k-\epsilon_{k'})|\,d\epsilon_k d\epsilon_{k'}.\end{aligned} \tag{13}$$

Integrating with respect to $\epsilon_{k'''}$ and omitting normal terms, we find that the first term gives

$$-\int f_{k''}d\epsilon_{k''}\left[\int\int\frac{df_k}{d\epsilon_k}\frac{df_{k'}}{d\epsilon_{k'}}d\epsilon_k d\epsilon_{k'}\left\{\frac{\epsilon_k-\epsilon_{k'}}{D-\epsilon_{k''}}\ln|D-\epsilon_{k''}-(\epsilon_k-\epsilon_{k'})|+\frac{\epsilon_k-\epsilon_{k'}}{D+\epsilon_{k''}}\ln|D+\epsilon_{k''}+(\epsilon_k-\epsilon_{k'})|\right\}\right]. \tag{14}$$

There is no problem at all for small $\epsilon_{k''}$ in this expression. However, some care may be needed for the band edges where $D\pm\epsilon_{k''}=x$ becomes small. The two functions of $\epsilon_{k''}$ enclosed by the square brackets in (14) are even functions of x. Therefore, the indefinite integrals of these two functions with respect to x become odd and vanish as x tends to zero apart from an integration constant. Thus, it is found that no $\ln T$ term arises from the first term of the expression (13).

The second integral

$$I_2=\int d\epsilon_{k''}d\epsilon_{k'''}\frac{f_{k''}}{(\epsilon_{k''}-\epsilon_{k'''})}\int\int\frac{df_k}{d\epsilon_k}\frac{df_{k'}}{d\epsilon_{k'}}\times\ln|\epsilon_{k'''}-\epsilon_{k''}-(\epsilon_k-\epsilon_{k'})|\,d\epsilon\,d\epsilon_{k'}, \tag{15}$$

is somewhat difficult to evaluate. For evaluations of this integral and also the integral given by Eq. (10), a simplified distribution function is assumed. The evaluation of I_2 will be described in Appendix B. From the results of these calculations, we cannot expect any $\ln T$ term in the free-energy shift due to the s-d exchange interaction at least up to the fourth order in J.

DISCUSSION

As may easily be seen, there exists no divergence in the perturbational expansion of the energy shift of the conduction electrons due to the s-d exchange interaction at the absolute zero of temperature. At finite temperatures, however, it might be expected that such logarithmic functions of T as $T^n\ln T$ would appear in the free-energy shift. The present calculations show that there appears no such logarithmic function of T at least up to the fourth order in J in the absence of an external magnetic field. It seems likely that this holds in any order in J.

This conclusion is not surprising, but rather reasonable. As has recently been shown by Yosida and Okiji,[2] the essential effect of the higher order perturbation of the s-d exchange interaction is to decrease the magnitude of the localized spin, and the logarithmic functions of T are included in the expression for it. The contraction of the localized spin has no influence on its entropy. Thus, no singular term would be expected in the magnetic-field–independent part of the free energy.

The free energy is expanded in the presence of the external magnetic field as follows:

$$F=F_0+\Delta F-\tfrac{1}{2}\chi H^2+\cdots.$$

Here, ΔF includes no singular term, but χ, which is proportional to the square of the magnitude of the localized spin, as Miwa[4] has shown, includes logarithmic functions. Thus, the present results also suggest that the origin of the logarithmic singularity due to the s-d exchange interaction is in the magnitude of the localized spin.

ACKNOWLEDGMENT

The authors would like to express their sincere thanks to A. Okiji for his valuable discussions.

APPENDIX A: EVALUATION OF I_1

In order to make the calculations for I_1 and I_2 easier, we approximate the Fermi distribution function f_k by

[4] H. Miwa, Progr. Theoret. Phys. (Kyoto) 34, 1040 (1965).

the following functional form:

$$f(\epsilon)=1, \quad \epsilon<-a,$$
$$=\tfrac{1}{2}(1-\epsilon/a), \quad -a\leq\epsilon\leq a, \tag{A1}$$
$$=0, \quad a<\epsilon.$$

Here, if we take $2kT$ for a, the slope of this approximate distribution function at the origin coincides with that of the true Fermi function.

With the use of (A1), the double integration with respect to ϵ' and ϵ'' can easily be carried out and I_1 becomes

$$I_1=\int_{-D}^{-a}\epsilon^nF(\epsilon)\,d\epsilon+\frac{1}{2}\int_{-a}^{a}\epsilon^nF(\epsilon)\,d\epsilon-\frac{1}{2a}\int_{-a}^{a}\epsilon^{n+1}F(\epsilon)\,d\epsilon, \tag{A2}$$

$$F(\epsilon)=1-\frac{1}{a}\{(\epsilon+a)\ln|\epsilon+a|-(\epsilon-a)\ln|\epsilon-a|\}$$
$$+\frac{1}{4a^2}\{(\epsilon+a)^2(\ln|\epsilon+a|)^2+(\epsilon-a)^2(\ln|\epsilon-a|)^2-2(\epsilon+a)(\epsilon-a)\ln|\epsilon+a|\ln|\epsilon-a|\}. \tag{A3}$$

Here, $F(\epsilon)$ is an even function of ϵ. Therefore, if n is even, the third integral of (A2) vanishes and the second integral is completely cancelled by the contribution of the first integral from the upper bound. Thus, there appears no $\ln T$ term for this case. If n is odd, the second integral vanishes. Then we have only to calculate the first and the third integrals.

First, we consider the second term of $F(\epsilon)$. The indefinite integral of the product of ϵ^n and this term is calculated as

$$\int^{\epsilon}\epsilon^n\{(\epsilon+a)\ln|\epsilon+a|-(\epsilon-a)\ln|\epsilon-a|\}\,d\epsilon\to\frac{\epsilon^{n+2}-(-a)^{n+2}}{n+2}\ln|\epsilon+a|+a\frac{\epsilon^{n+1}-(-a)^{n+1}}{n+1}\ln|\epsilon+a|$$
$$-\frac{\epsilon^{n+2}-a^{n+2}}{n+2}\ln|\epsilon-a|+a\frac{\epsilon^{n+1}-a^{n+1}}{n+1}\ln|\epsilon-a|, \tag{A4}$$

where only the terms which include logarithmic functions are retained. Inserting the upper bound $\epsilon=-a$ into Eq. (A4), we obtain the contribution from the first integral of (A2),

$$(2/(n+2))a^{n+2}\ln|2a|.$$

The contribution from the third integral of (A2) can also be obtained by replacing n by $n+1$ in (A4) and inserting $\epsilon=a$, as

$$-(2/(n+2))a^{n+2}\ln|2a|.$$

Thus, two contributions cancel out each other and no $\ln T$ term comes out of the second term of (A3).

Next, we consider the third term of $F(\epsilon)$. The indefinite integral of $\epsilon^n\{(\epsilon+a)^2\ln^2|\epsilon+a|+(\epsilon-a)^2\ln^2|\epsilon-a|\}$ can be calculated as

$$\int^{\epsilon}\epsilon^n\{(\epsilon+a)^2\ln^2|\epsilon+a|+(\epsilon-a)^2\ln^2|\epsilon-a|\}\,d\epsilon$$
$$\to\left\{\frac{1}{n+3}(\epsilon^{n+3}-(-a)^{n+3})+2a\frac{1}{n+2}(\epsilon^{n+2}-(-a)^{n+2})+a^2\frac{1}{n+1}(\epsilon^{n+1}-(-a)^{n+1})\right\}\ln^2|\epsilon+a|$$
$$-2\frac{1}{n+3}\left\{\sum_{r=0}^{n+2}\frac{1}{(n+3-r)}\frac{(n+3)!}{r!(n+3-r)!}(-a)^r(\epsilon+a)^{n+3-r}\right\}\ln|\epsilon+a|$$
$$-4a\frac{1}{n+2}\left\{\sum_{r=0}^{n+1}\frac{1}{(n+2-r)}\frac{(n+2)!}{r!(n+2-r)!}(-a)^r(\epsilon+a)^{n+2-r}\right\}\ln|\epsilon+a|$$
$$-2a^2\frac{1}{n+1}\left\{\sum_{r=0}^{n}\frac{1}{(n+1-r)}\frac{(n+1)!}{r!(n+1-r)!}(-a)^r(\epsilon+a)^{n+1-r}\right\}\ln|\epsilon+a|$$
$$+(\text{corresponding terms derived by replacing } a \text{ by } -a), \tag{A5}$$

where only the terms with logarithmic functions are retained. Inserting $\epsilon=-a$ in this expression, we obtain the contribution from the upper bound of the first integral of (A2) as

$$(4/(n+2))a^{n+3}(\ln|2a|)^2-2\{L(n+3)+L(n+2)+\tfrac{1}{4}L(n+1)\}(2a)^{n+3}\ln|2a|\,, \tag{A6}$$

where $L(n)$ is defined by

$$L(n)=\frac{1}{n}\int_0^1\frac{1}{x}\{(x-\tfrac{1}{2})^n-(-\tfrac{1}{2})^n\}\,dx\,. \tag{A7}$$

Putting $\epsilon=a$ in (A5) with the replacement of n by $n+1$, we obtain the third integral of Eq. (A2) as

$$-(2/(n+4)+2/(n+2))a^{n+3}(\ln|2a|)^2+4\{L(n+4)+L(n+3)+\tfrac{1}{4}L(n+2)\}(2a)^{n+3}\ln|2a|\,. \tag{A8}$$

The sum of (A6) and (A8) becomes

$$2((n+2)^{-1}-(n+4)^{-1})a^{n+3}(\ln|2a|)^2+\{4L(n+4)+2L(n+3)-L(n+2)-\tfrac{1}{2}L(n+1)\}(2a)^{n+3}\ln|2a|\,. \tag{A9}$$

The indefinite integral of $\epsilon^n(\epsilon+a)(\epsilon-a)\ln|\epsilon+a|\ln|\epsilon-a|$ can be calculated as

$$\int^\epsilon \epsilon^n(\epsilon+a)(\epsilon-a)\ln|\epsilon+a|\ln|\epsilon-a|\,d\epsilon$$

$$\begin{aligned}\rightarrow&\left\{\frac{1}{n+3}\epsilon^{n+1}(\epsilon^2-a^2)+a^2\left(\frac{1}{n+3}-\frac{1}{n+1}\right)(\epsilon^{n+1}-a^{n+1})\right\}\ln|\epsilon+a|\ln|\epsilon-a|\\
&-\frac{1}{n+3}\Bigg[\sum_{r=0}^{n+2}\frac{1}{(n+3-r)}\frac{(n+3)!}{r!(n+3-r)!}a^r\{(\epsilon-a)^{n+3-r}-(-2a)^{n+3-r}\}\ln|\epsilon+a|\\
&\qquad+\sum_{r=0}^{n+2}\frac{1}{(n+3-r)}\frac{(n+3)!}{r!(n+3-r)!}(-a)^r\{(\epsilon+a)^{n+3-r}-(2a)^{n+3-r}\}\ln|\epsilon-a|\Bigg]\\
&+\frac{a^2}{n+1}\Bigg[\sum_{r=0}^{n}\frac{1}{(n+1-r)}\frac{(n+1)!}{r!(n+1-r)!}a^r\{(\epsilon-a)^{n+1-r}-(-2a)^{n+1-r}\}\ln|\epsilon+a|\\
&\qquad+\sum_{r=0}^{n}\frac{1}{(n+1-r)}\frac{(n+1)!}{r!(n+1-r)!}(-a)^r\{(\epsilon+a)^{n+1-r}-(2a)^{n+1-r}\}\ln|\epsilon-a|\Bigg],\quad\text{for odd } n.\end{aligned} \tag{A10}$$

For even n, the first term is replaced by

$$\begin{aligned}&\left\{\frac{1}{n+3}\epsilon^{n+1}(\epsilon^2-a^2)+a^2\epsilon^{n+1}\left(\frac{1}{n+3}-\frac{1}{n+1}\right)\right\}\ln|\epsilon+a|\ln|\epsilon-a|\\
&-\left(\frac{1}{n+3}-\frac{1}{n+1}\right)a^{n+3}\left[\ln|2a|(\ln|\epsilon-a|-\ln|\epsilon+a|)-\sum_{l=1}^{\infty}\frac{1}{l^2}\left\{(-1)^l\left(\frac{\epsilon-a}{2a}\right)^l-\left(\frac{\epsilon+a}{2a}\right)^l\right\}\right].\end{aligned} \tag{A11}$$

Inserting $\epsilon=-a$ into (A10), we obtain the contribution of the upper bound of the first integral of (A2) as

$$\{L(n+3)-\tfrac{1}{4}L(n+1)\}(2a)^{n+3}\ln|2a|\,. \tag{A12}$$

The contribution from the third integral of (A2) can be calculated with the use of (A11) and (A10) as

$$-((n+4)^{-1}-(n+2)^{-1})a^{n+3}(\ln|2a|)^2+2\{L(n+4)-\tfrac{1}{4}L(n+2)\}(2a)^{n+3}\ln|2a|\,. \tag{A13}$$

The summation of (A12) and (A13) gives

$$\{2L(n+4)+L(n+3)-\tfrac{1}{2}L(n+2)-\tfrac{1}{4}L(n+1)\}(2a)^{n+3}\ln|2a|+((n+2)^{-1}-(n+4)^{-1})a^{n+3}(\ln|2a|)^2. \tag{A14}$$

Equation (A9) and -2 times (A14) are completely cancelled. Thus, there appears no $\ln T$ term at all from the integral I_1.

APPENDIX B: EVALUATION OF I_2

The simplified distribution function given by Eq. (A1) enables us to carry out the integration with respect to ϵ and ϵ' in the integral I_2. The result is

$$I_2=\int_{-D}^{D} f(\epsilon'')\,d\epsilon''\int_{-D}^{D} d\epsilon'''[h_a(\epsilon''-\epsilon''')+h_b(\epsilon''-\epsilon''')],\tag{B1}$$

$$h_a(x)=\frac{1}{8a^2}[(x-2a)\ln|x-2a|+(x+2a)\ln|x+2a|-2a\{\ln|x-2a|-\ln|x+2a|\}-2x\ln|x|],\tag{B2}$$

$$h_b(x)=\frac{1}{2x}\{\ln|x-2a|+\ln|x+2a|-3\}.\tag{B3}$$

It is easy to show that $h_a(x)$ does not give any logarithmic term. Therefore, we now consider the integral of one of the two terms included in $h_b(x)$, namely,

$$\int_{-D}^{D} f(\epsilon'')\,d\epsilon''\int_{-D}^{D} d\epsilon'''\frac{\ln|\epsilon'''-\epsilon''+2a|}{\epsilon'''-\epsilon''}.\tag{B4}$$

If one changes the integration variables ϵ'' and ϵ''' to ϵ'' and $x=\epsilon'''-\epsilon''$, the region of integration is divided into

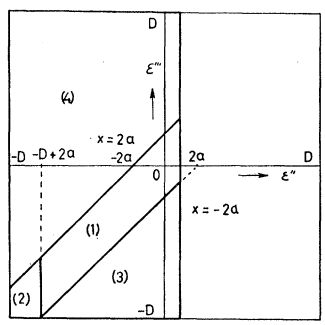

FIG. 1. Four regions of integration for the integral (B4).

four subregions shown in Fig. 1. The integral over region (1) is calculated as

$$\left\{\int_{-D+2a}^{-a} d\epsilon''+\frac{1}{2}\int_{-a}^{a}\left(1-\frac{\epsilon''}{a}\right)d\epsilon''\right\}\int_{-2a}^{2a}\left\{\ln|2a|\frac{1}{x}+\frac{1}{x}\ln\left|1+\frac{x}{2a}\right|\right\}dx\rightarrow 0,\tag{B5}$$

retaining only $\ln T$ terms. The contribution from region (2) becomes

$$\int_{-D}^{-D+2a} d\epsilon''\int_{-(\epsilon''+D)}^{2a}\ln|2a|\frac{1}{x}\,dx=2a\ln|2a|.\tag{B6}$$

Region (3) gives

$$\left\{\int_{-D+2a}^{-a} d\epsilon''+\frac{1}{2}\int_{-a}^{a}\left(1-\frac{\epsilon''}{a}\right)d\epsilon''\right\}\int_{-(\epsilon''+D)}^{-2a}\frac{\ln|x|}{x}\,dx\rightarrow \tfrac{1}{2}D(\ln|2a|)^2-2a\ln|2a|.\tag{B7}$$

Region (4) contributes

$$\left\{\int_{-D}^{-a} d\epsilon''+\frac{1}{2}\int_{-a}^{a}\left(1-\frac{\epsilon''}{a}\right)d\epsilon''\right\}\int_{2a}^{-(\epsilon''-D)}\frac{\ln|x|}{x}\,dx\rightarrow -\tfrac{1}{2}D(\ln|2a|)^2.\tag{B8}$$

The sum of (B6), (B7), and (B8) vanishes. Thus, the integral I_2 includes no logarithmic function at all.