Anomalous Susceptibility Due to Paramagnetic Impurities*

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(Received 12 August 1963; revised manuscript received 1 October 1963)

Thermodynamic properties of a ferromagnet at $T>T_C$ containing a small amount of paramagnetic ions (with spin $\frac{1}{2}$) are studied theoretically. The exact form of the static susceptibility of this system just above the Curie point is given under the following assumptions: (1) The interaction between a paramagnetic impurity and the magnetic carriers of the ferromagnet is described by the usual *s-d* type interaction. (2) Lorentzian decay of the fluctuating component of the magnetization of the host ferromagnet is valid at least for long time behavior of this component. (3) The interaction between impurities is neglected. (4) $kT_C \gg \hbar/\tau_q$, where τ_q is the relaxation time of Lorenzian decay of the magnetization oscillating in space with wave vector q (q being limited to the first Brillouin zone). It is concluded that as $T\rightarrow T_C$ the impurities always decrease the total susceptibility regardless of the sign of the exchange integral between an impurity electron and the magnetic carriers. Thus, the naive picture based on the first-order effect of the *s-d* exchange interaction is subject to a crucial modification at the critical spin fluctuation of the host ferromagnet.

1. INTRODUCTION

WHEN the paramagnetic state of the magnetic carriers of a ferromagnet approaches the transition to the ferromagnetic state, there are large spin fluctuations in the carriers. This fact has been observed in several phenomena. Theoretical predictions of these fluctuations have been given by Landau[1] and Van Hove.[2] So far as the long-range and long-time behavior of the fluctuations is concerned, these theories seem to be general and independent of models for describing the magnetic carriers (i.e., the Heisenberg model and the itinerant electron model, etc.). Accordingly, there are several phenomena whose qualitative nature can be described exactly, at least in the limit of $T\rightarrow T_C$. A typical example of such phenomena is the critical magnetic scattering of neutrons. In this paper it is pointed out that the qualitative nature of the additional susceptibility due to a small number of paramagnetic impurities in a ferromagnet at $T>T_C$ can also be predicted rigorously in the limit of $T\rightarrow T_C$, provided that $kT_C\gg\hbar/\tau_q$, τ_q being the relaxation time of the magnetization oscillating in space with wave vector q in the first Brillouin zone.

For the sake of mathematical simplicity the interaction energy between a paramagnetic impurity (at j) and the magnetic carriers (or d electrons) of the host ferromagnet (or metal)[3] is assumed to be given by

$$\mathcal{H}_j' = -\sum_{\mathbf{q}} J_j(\mathbf{q})\mathbf{M}(\mathbf{q})\cdot\mathbf{S}^j, \qquad (1)$$

where $J_j(\mathbf{q})$ is the Fourier component[4] of the exchange interaction between a paramagnetic spin $\mathbf{S}^j$ and the spins of d electrons, and $\mathbf{M}(\mathbf{q})$ is the Fourier transform of $\mathbf{M}(r)$, the spin density operator of d-electron system. When a magnetic field H is applied to this system, it produces a magnetization of d electrons of

$$\langle M_z(0)\rangle=\chi H,$$

where χ is the spin susceptibility of the d electrons. Then, up to the first-order effect of $\mathcal{H}'$, the energy of the paramagnetic spin is given by

$$-[g\mu_B+J(0)\chi]HS_z{}^j,$$

where μ_B is the Bohr magneton. Accordingly, one can get the conclusion that,

(1) if $J(0)>0$, the paramagnetic spin shows a giant magnetic moment whenever χ becomes very large, and
(2) if $J(0)<0$, it shows a big negative moment,

provided that the second and higher-order effects of $\mathcal{H}'$ are small. An important question arises here about the magnitude of these effects: Do these effects destroy the giant moment or not?

The paramagnetic spin polarizes the d-electron spins around itself. The nature of this polarized spin cloud can be understood at least qualitatively by the second-order effect of $\mathcal{H}'$. The effect of this spin cloud on the additional spin susceptibility due to the paramagnetic impurities must be large in the strongly fluctuating spin state of the d electrons, for the polarization of the d-electron spins due to an impurity is necessarily large in this case. Moreover, the response of this polarized spin cloud to external magnetic field is also enhanced by the fluctuation. Thus it is expected that the second-order effect gives the main feature of the problem in the limit of strong fluctuation. Indeed, as will be shown in this paper, the second-order effect of $\mathcal{H}'$ gives a correct description for the qualitative nature of the dc susceptibility in the limit of $T\rightarrow T_C$, if the interaction between impurities is neglected. Since the second-order effect is

* This work was supported by the U. S. Office of Naval Research and Advanced Research Project Agency.

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[1] L. D. Landau, Z. Soviet Phys. **12**, 123 (1937).

[2] L. Van Hove, Phys. Rev. **95**, 1374 (1954).

[3] From now on a ferromagnet and its magnetic carriers are called a metal and its d electrons, respectively, although the following treatment does not require such a specialization.

[4] $J_j(\mathbf{q})$ depends on j only through its phase factor. $\mathbf{q}$ is limited to the first Brillouin zone.

always connected with the Lenz's law, in general, it is easily expected that the additional susceptibility decreases as $T \to T_C$ in the limit of low concentration of impurities. This property is indeed satisfied by the result of a theoretical calculation presented in the following sections. It is shown that the susceptibility due to the second-order effect is proportional to χ^2 at temperatures slightly above the Curie point, while the first-order one gives the additional susceptibility which is proportional to χ at such temperatures.

The calculation is based on the fluctuation-dissipation theorem, by means of which the contribution to the free energy due to the fluctuation effect of the d electrons is related to their dissipative character. This character is described by Van Hove's phenomenological equation.[2] The validity of this equation is much more general than that of the random-phase approximation or other techniques of the many-body problem and is independent of the model for the d electrons. Since the Lorenzian decay of the deviation of magnetization from its equilibrium value, which is the essential point of the phenomenological equation, is valid for long-time behavior of the deviation and as $T \to T_C$ the small frequency part of the fluctuation gives the main contribution, the result obtained should be exact at least qualitatively.

2. FREE ENERGY

The total Hamiltonian $\mathcal{H}$ of the system under the magnetic field H is divided into two parts:

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2.$$

In the above, $\mathcal{H}_1$ includes the first-order effect of $\mathcal{H}'$

$$\mathcal{H}_1=\mathcal{H}_e-\sum_j \Omega S_z^j, \tag{2}$$

where $\mathcal{H}_e$ is the Hamiltonian of d electrons without impurities under the magnetic field,

$$\Omega\equiv[g\mu_B+\chi J(0)]H, \tag{3}$$

and

$$\chi H\equiv\langle M_z(0)\rangle=\mathrm{Tr}\{\exp(-\beta\mathcal{H}_e)M_z(0)\}/\mathrm{Tr}\exp(-\beta\mathcal{H}_e).$$

From (1) and (2), we get

$$\mathcal{H}_2=\sum_j \mathcal{H}_2{}^j,$$

$$\mathcal{H}_2{}^j\equiv-\sum_q J_j(q)\{\delta M_z(q)S_z{}^j+M_-(q)S_+{}^j+M_+(q)S_-{}^j\}, \tag{4}$$

where

$$\delta M_z(q)\equiv M_z(q)-\delta_{q,0}\chi H, \quad S_\pm{}^j\equiv S_x{}^j\pm iS_y{}^j,$$

and

$$M_\pm(q)\equiv\tfrac{1}{2}\{M_x(q)\pm iM_y(q)\}.$$

The thermodynamic potential

$$A=-kT\ln\mathrm{Tr}\exp(-\beta\mathcal{H})$$

may be expanded as

$$A=A_1+\Delta A,$$

$$A_1=-kT\ln\mathrm{Tr}\exp(-\beta\mathcal{H}_1),$$

$$\Delta A=-\frac{1}{\beta}\sum_{n>0}(-1)^n\int_{\beta>\mu_1>\cdots>\mu_n>0}d\mu_1\cdots d\mu_n \times\langle\mathcal{H}_2(\mu_1)\cdots\mathcal{H}_2(\mu_n)\rangle_C{}^1, \tag{5}$$

where

$$\mathcal{H}_2(\mu)\equiv\exp(\mu\mathcal{H}_1)\mathcal{H}_2\exp(-\mu\mathcal{H}_1),$$

and

$$\langle\cdots\rangle^1\equiv\mathrm{Tr}\{\exp(-\beta\mathcal{H}_1)\cdots\}/\mathrm{Tr}\exp(-\beta\mathcal{H}_1).$$

In (5) the suffix C indicates that only the connected diagrams defined properly should be taken.[5]

For the sake of mathematical simplicity, each impurity is assumed to have single paramagnetic electron. Diamagnetism is neglected throughout this paper. Since the first-order term in (5) vanishes, we get up to the second-order effect

$$\Delta A=-\frac{1}{\beta}\int_0^\beta d\mu_1\int_0^{\mu_1}d\mu_2\sum_{n,\sigma}\frac{e^{-\beta E_{n\sigma}}}{Z_1}\langle n\sigma|\mathcal{H}_2(\mu_1)\mathcal{H}_2(\mu_2)|n\sigma\rangle. \tag{5'}$$

In the above, n denotes a state of d electrons whose energy is E_n, $\sigma\equiv\{\sigma_1,\sigma_2,\cdots,\sigma_{N_i}\}$ stands for a set of the spin states $\sigma_j(=+\frac{1}{2}$ or $-\frac{1}{2}$; $j=1,2,\cdots,N_i)$ of impurities,

$$|n\sigma\rangle=\Pi_j|n\sigma_j\rangle \quad\text{with}\quad S_z{}^j|n\sigma_j\rangle=\sigma_j|n\sigma_j\rangle,$$

$$\mathcal{H}_1|n\sigma\rangle=E_{n\sigma}|n\sigma\rangle,$$

$$E_{n\sigma}=E_n-\sum_j\Omega\sigma_j,$$

and

$$Z_1=Z_e(e^{\beta\Omega/2}+e^{-\beta\Omega/2})^{N_i},$$

where $Z_e=\mathrm{Tr}\exp(-\beta\mathcal{H}_e)$ and N_i is the number of impurities.

The interactions between impurities are neglected throughout this paper. Then in the expression (5′) we may neglect terms of the form $\langle n\sigma|\mathcal{H}_2{}^j(\mu_1)\mathcal{H}_2{}^k(\mu_2)|n\sigma\rangle$ $(j\neq k)$, when (4) is substituted in (5′). Therefore, after the integration over μ_1 and μ_2 we obtain

$$\Delta A=\sum_j(\Delta A_+{}^j+\Delta A_-{}^j),$$

where

$$\Delta A_\pm{}^j\equiv-\sum_{n,n',\sigma_j'}\frac{e^{-\beta E_n\pm\beta\Omega/2}}{Z_e(e^{\beta\Omega/2}+e^{-\beta\Omega/2})}\times\frac{\langle n,\pm\frac{1}{2}|\mathcal{H}_2{}^j|n',\sigma_j'\rangle\langle n',\sigma_j'|\mathcal{H}_2{}^j|n,\pm\frac{1}{2}\rangle}{E_n'-E_n-\Omega\sigma_j'\pm\Omega/2}. \tag{6}$$

[5] C. Bloch, Nucl. Phys. 7, 451 (1958). C. Bloch and C. DeDominicis, Nucl. Phys. 7, 459 (1958).

Since the volume of the system is macroscopic, the energy of the d electrons must be regarded as being continuous. In this case the principal value should be taken in the integral over n and n' on the right-hand side of the expression (6). Keeping this fact in mind and substituting (4) in (6), we obtain

$$\Delta A_{\pm}{}^{i}=-\sum_{n,n'}\frac{e^{-\beta E_n\pm\beta\Omega/2}}{Z_e(e^{\beta\Omega/2}+e^{-\beta\Omega/2})}\sum_q |J(q)|^2 \times\left\{P\frac{\langle n|M_{\pm}(q)|n'\rangle\langle n'|M_{\mp}(-q)|n\rangle}{E_{n'}-E_n\pm\Omega} +P\frac{\langle n|\delta M_z(q)|n'\rangle\langle n'|\delta M_z(-q)|n\rangle}{E_{n'}-E_n}\right\}, \quad (7)$$

where P indicates the principal value. This expression can be simplified as

$$\Delta A_{\pm}{}^{i}=-\frac{e^{\pm\beta\Omega/2}}{e^{\beta\Omega/2}+e^{-\beta\Omega/2}}\sum_q |J(q)|^2 \times\{S_{\pm\mp}(q,\pm\Omega)+S_{zz}(q,0)\}, \quad (8)$$

where

$$S_{+-}(q,\Omega)\equiv\mathrm{Re}\, i\int_0^\infty dte^{-i\Omega t-0^+t}\langle M_+(q,t)M_-(-q)\rangle \quad (9)$$

and

$$S_{zz}(q,0)\equiv\mathrm{Re}\, i\int_0^\infty dte^{-0^+t}\langle\delta M_z(q,t)\delta M_z(-q)\rangle, \quad (10)$$

with

$$M(q,t)\equiv\exp(i\mathcal{H}_e t)M(q)\exp(-i\mathcal{H}_e t),$$

and

$$\langle\cdots\rangle\equiv\mathrm{Tr}\{\exp(-\beta\mathcal{H}_e)\cdots\}/\mathrm{Tr}\exp(-\beta\mathcal{H}_e)\ .$$

$\hbar$ has been put to 1. Thus, the correction to the thermodynamic potential ΔA due to the impurities is given by

$$\Delta A=\Delta A_1+\Delta A_2+\Delta A_3,$$

$$\Delta A_1=-\frac{N_i}{2}\tanh\left(\frac{\beta\Omega}{2}\right)\sum_q |J(q)|^2 \times\{S_{+-}(q,\Omega)-S_{-+}(q,-\Omega)\}, \quad (11)$$

$$\Delta A_2=-\frac{N_i}{2}\sum |J(q)|^2\{S_{+-}(q,\Omega)+S_{-+}(q,-\Omega)\},$$

$$\Delta A_3=-N_i\sum |J(q)|^2 S_{zz}(q,0).$$

This expression, which is exact up to the second-order effect of $\mathcal{H}'$ so far as the first power of the concentration of impurities is concerned, is the starting point of our calculation. In the following sections the expression (11) is calculated by neglecting H^3 and higher powers of H.

3. FLUCTUATION-DISSIPATION THEOREM AND DIFFUSION EQUATION

First, let us consider ΔA_1 in (11). It is easily shown that

$$S_{+-}(q,\Omega)-S_{-+}(-q,-\Omega) =-\frac{1}{i}\int_0^\infty dte^{-i\Omega t}\langle\{M_+(q,t),M_-(-q)\}\rangle +\frac{1}{i}\int_{-\infty}^0 dte^{-i\Omega t}\langle\{M_+(q,t),M_-(-q)\}\rangle,$$

where $\{A,B\}\equiv\frac{1}{2}(AB+BA)$. Then, introducing the following function

$$G(q,\omega)=\int_{-\infty}^\infty dte^{-i\omega t}\langle\{M_+(q,t),M_-(-q)\}\rangle, \quad (12)$$

we get

$$S_{+-}(q,\Omega)-S_{-+}(q,-\Omega)=-\frac{1}{\pi}P\int_{-\infty}^\infty\frac{d\omega}{\omega-\Omega}G(q,\omega). \quad (13)$$

It should be noted that $G(q,\omega)$ defined by (12) is real.

The fluctuation-dissipation theorem tells us[6] that, for any pair of operators A and B,

$$\int_{-\infty}^\infty dte^{-i\omega t}\langle\{A(t),B\}\rangle =-\tfrac{1}{2}\coth\left(\frac{\beta\omega}{2}\right)\int_{-\infty}^\infty dte^{-i\omega t}\langle[A(t),B]\rangle.$$

Using this theorem and the susceptibility defined by

$$\chi_{+-}(q,\omega)=i\int_0^\infty dte^{-i\omega t}\langle[M_+(q,t),M_-(-q)]\rangle,$$

etc., we obtain

$$G(q,\omega)=-\frac{1}{2i}\coth\left(\frac{\beta\omega}{2}\right)[\chi_{+-}(q,\omega)-\chi_{-+}(-q,-\omega)] =-\coth\left(\frac{\beta\omega}{2}\right)\mathrm{Im}\chi_{+-}(q,\omega). \quad (14)$$

From (13) and (14), we get

$$S_{+-}(q,\Omega)-S_{-+}(-q,-\Omega) =\frac{1}{\pi}P\int_{-\infty}^\infty\frac{d\omega}{\omega-\Omega}\coth\left(\frac{\beta\omega}{2}\right)\mathrm{Im}\chi_{+-}(q,\omega). \quad (15)$$

The dynamical susceptibility may be calculated[7] from

[6] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[7] T. Izuyama, D. Kim, and R. Kubo, J. Phys. Soc. Japan **18**, 1025 (1963).

the first principle by solving the equation of motion for

$$i\langle[M_+(q,t),M_-(-q)]\rangle.$$

In order to obtain a definite result from this calculation one has to introduce some approximation[7] which is standard in many body theories, e.g., ladder approximation or random-phase approximation. Instead of using such an approximation, we will use Van Hove's phenomenological equation[2] for the fluctuation of magnetization. It tells us that the long-time behavior of the deviation of the magnetization from its thermal equilibrium value obeys the following equation:

$$\frac{\partial m_\pm(r,t)}{\partial t}=-\sum_{n=0}^{\infty} D_n\nabla^{2n}m_\pm(r,t)\pm i\gamma H m_\pm(r,t)\,, \quad (16)$$

where $\gamma\equiv g\mu_B$ and $D_0^{-1}=\tau$ is the relaxation time of the d-electron spins to, say, the lattice.

In the original theory of Van Hove, only the term $n=1$ on the right-hand side of Eq. (16) appears and all the other terms are neglected. This is the special case where there is no relaxation of d-electron spins to some external systems and the magnetization $\mathbf{m}(\mathbf{r})$ is a slowly varying function of $\mathbf{r}$. We add the terms $n\neq 1$ to the original Van Hove's equation and postulate that the phenomenological equation (16) gives a reasonable description even for a short-range behavior of $\mathbf{m}(\mathbf{r})$ in space, more specifically, even for the behavior of $\mathbf{m}(\mathbf{r})$ with r comparable to the interatomic distances. The inclusion of the field-dependent term is clearly understood.

It has been shown by Mori and Kawasaki[8] that $m_+(q,t)$, the Fourier component of $m_+(r,t)$ in Van Hove's equation, is just proportional to

$$(M_+(q,t),M_-(-q))\,,$$

where

$$(A,B)\equiv\int_0^\beta d\lambda\langle B(-i\lambda)A\rangle. \quad (17)$$

Thus, according to Mori and Kawasaki,[8] we may express (16) as

$$(M_+(q,t),M_-(-q))\equiv e^{-(1/\tau_q)t+i\gamma Ht}(M_+(q),M_-(-q))\,. \quad (18)$$

Combining this with[6]

$$\chi_{+-}(q,\omega)=(M_+(q),M_-(-q)) -i\omega\int_0^\infty dte^{-i\omega t}(M_+(q,t),M_-(-q))\,,$$

we obtain

$$\chi_{+-}(q,\omega)=\frac{(1/\tau_q-i\gamma H)(1/\tau_q-i(\omega-\gamma H))}{(1/\tau_q)^2+(\omega-\gamma H)^2}\chi_{+-}(q)\,, \quad (19)$$

where $\chi_{+-}(q)\equiv(M_+(q),M_-(-q))$ is the isothermal susceptibility of d electrons. For $H=0$, $\chi_{+-}(q)=\chi_{zz}(q)=\chi(q)$.

From (15) and (19), we get

$$S_{+-}(q,\Omega)-S_{-+}(-q,-\Omega)=-\frac{1}{\pi}\frac{\chi(q)}{\tau_q}\times\int_{-\infty}^{\infty}P\frac{d\omega}{\omega-\Omega}\coth\left(\frac{\beta\omega}{2}\right)\frac{\omega}{(1/\tau_q)^2+(\omega-\gamma H)^2}, \quad (20)$$

where we have set $\chi_{+-}(q)=\chi(q)$, because the contribution of (20) to the thermodynamic quantity is of the order H^2 and, hence, the difference between $\chi_{+-}(q)$ and $\chi(q)$ in (20) may be neglected except when the external magnetic field is so strong that the nonlinear effect of the induced magnetization with respect to H is important. Such nonlinear effect is beyond the scope of this paper. H^3 and higher powers of H in the thermodynamic potential are neglected without any mention throughout this paper. Transforming the variable of integration in (20) by

$$\omega-\Omega=(x/\tau_q)$$

and performing a simple and straightforward calculation, we find (cf., Appendix A)

$$S_{+-}(q,\Omega)-S_{-+}(-q,-\Omega)=S_1+S_2+O(H^3)\,,$$

$$S_1=\frac{4H}{\pi\beta}\tau_q^2\chi(q)\chi J(0)\int_{-\infty}^{\infty}\frac{F(x)dx}{(1+x^2)^2}, \quad (21)$$

$$S_2=-\frac{\Omega}{4\pi}\beta\chi(q)\int_{-\infty}^{\infty}\frac{f(x)dx}{1+x^2},$$

where

$$F(x)\equiv\frac{\beta x}{2\tau_q}\coth\left(\frac{\beta x}{2\tau_q}\right)$$

$$f(x)\equiv\frac{\sinh(\beta x/\tau_q)-(\beta x/\tau_q)}{(\beta x/2\tau_q)\sinh^2(\beta x/2\tau_q)}.$$

In the case of $D_0\equiv\tau^{-1}=0$, it was concluded by Van Hove on the basis of his phenomenological argument

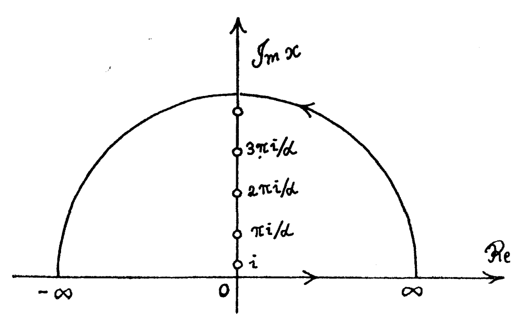

FIG. 1. Poles of $F(x)/(1+x^2)^2$.

[8] H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962).

that D_1 is proportional to χ^{-1}. A more general expression has been derived by Mori and Kawasaki[8] for $1/\tau_q$. It is

$$\frac{1}{\tau_q}=\int_0^\infty (\dot{M}_+(q,t),\dot{M}_-(-q))dt\Big/(M_+(q),M_-(-q)). \quad (22)$$

The torque acting on the spin $\mathbf{M}(q)$ seems to be random. So the numerator in (22) seems to be insensitive on temperatures in the neighborhood of T_C. Thus,[9]

$$\lim_{q\to 0}\lim_{T\to T_C}(1/\tau_q)\to 0.$$

Then S_1 defined by (21) seems to give a much larger contribution than that of S_2. Actually, the leading term proportional to $\tau_q^2\cdot\chi$ in (21) is cancelled by another big term arising from ΔA_2 in (11). Accordingly the calculation of S_1 should include lower order terms with respect to β/τ_q.

The integral appearing in the definition of S_1, (21), can be performed by a contour integral as shown in Fig. 1. Poles of the integrand in the upper half plane are $x=i$ and $x=n\pi i/\alpha$ ($n=1, 2, \cdots$), where $\alpha=\beta/2\tau_q$. Then the integral becomes

$$\frac{\pi}{2}\alpha\cot\alpha-\sum_{n>0}\frac{2\pi^2 n\alpha^3}{(\alpha^2-n^2\pi^2)^2}.$$

For small α it gives

$$\tfrac{1}{2}\pi(1-\tfrac{1}{3}\alpha^2)+0(\alpha^3).$$

Thus

$$S_1=\frac{2H}{\beta}\tau_q^2\chi(q)\chi J(0)-\frac{H}{6}\beta\chi(q)\cdot\chi J(0).$$

Similarly,

$$S_2=-\tfrac{1}{4}\Omega\cdot\beta\cdot\chi(q).$$

Consequently,

$$\Delta A_1=-\frac{N_i}{2}\Omega\chi J(0)H\sum_q\tau_q^2|J(q)|^2\cdot\chi(q)+\frac{N_i}{4}\beta^2\Omega(\tfrac{1}{6}\chi J(0)H+\tfrac{1}{4}\Omega)\sum_q|J(q)|^2\cdot\chi(q), \quad (23)$$

for $kT_C\gg 1/\tau_q$ and $kT_C\gg\Omega$.

As can be seen in the derivation of the above result, overwhelming contribution to ΔA_1 comes from the pole $x=i$ in the integrands of (21) if $kT_c\gg 1/\tau_q$. This is equivalent to the statement that under the condition $kT_c\gg 1/\tau_q$ the overwhelming contribution comes from those $\chi_{+-}(q,\omega)$ for $x\approx 1$ or small ω. Therefore, it is sufficient to consider only the slowly varying part of the fluctuation of magnetization. This is a crucial point, because the basic equation (16) or (18) is valid only for large t and, consequently, (19) is legitimate only for small ω.

Next let us consider ΔA_2 in (11). It is easily verified that

$$S_{+-}(q,\Omega)+S_{-+}(-q,-\Omega)=\mathrm{Re}\chi_{+-}(q,\Omega). \quad (24)$$

From (11), (19), and (24), we get

$$\Delta A_2=-\frac{N_i}{2}\sum_q|J(q)|^2\cdot\chi_{+-}(q)+\frac{N_i}{2}\cdot\Omega\cdot\chi J(0)H\cdot\sum_q\tau_q^2|J(q)|^2\chi(q). \quad (25)$$

Therefore,

$$\Delta A=-\frac{N_i}{2}\sum_q|J(q)|^2\chi_{+-}(q)-N_i\sum_q|J(q)|^2\chi_{zz}(q)+\frac{N_i}{4}\beta^2\cdot\Omega\cdot(\tfrac{1}{6}\chi J(0)H+\tfrac{1}{4}\Omega)\sum_q|J(q)|^2\chi(q). \quad (26)$$

For small q, $\chi(q)$ has the following Ornstein-Zernike's form[1]

$$\chi(q)=(C+Bq^2)^{-1},$$

where $C\propto T-T_C$ at just above the Curie point. Thus, the summation

$$\Lambda\equiv\sum_q|J(q)|^2\chi(q)$$

does not depend sensitively on temperatures in the neighborhood of T_C.

Objections have been raised to the validity of the Ornstein-Zernike-Landau theory since Onsager published his elegant theory[10] of the exact solution of the two-dimensional Ising model which shows some appreciable discrepancies from the Ornstein-Zernike-Landau theory[1] of the second-order phase transition. Although Landau and Lifshitz[11] assert in their textbook that these discrepancies are limited to the case of two-dimensional systems, there are several facts which we have to consider seriously; logarithmic divergence[12] of C_P at the λ point of liquid He^4, the divergence of C_P and other quantities concluded by Tisza in his general theory,[13] and possible form of the susceptibility of an Ising ferromagnet just above T_C shown by Fisher and

[9] This is equivalent to the statement; the long-wavelength component of the magnetization fluctuation decays infinitely slowly in the limit $T\to T_C$. One must not assert that this is an assumption. If the relaxation time of the $q=0$ mode of magnetization were finite at $T=T_C$, the ferromagnetic long-range order could never be established at and slightly below the Curie point.

[10] Lars Onsager, Phys. Rev. **65**, 117 (1944); L. Onsager and B. Kaufman, *Proceedings of the International Conference on Fundamental Particles and Low Temperatures, Cambridge, 1946* (The Physical Society, London, 1947), p. 127.

[11] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Inc., New York, 1958), p. 438.

[12] M. J. Buckingham and W. M. Fairbank, *Progress in Low Temperature Physics*, edited by C. J. Gorter, (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 80.

[13] Laszlo Tisza, *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951), p. 1–35.

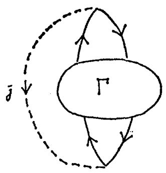

FIG. 2. Diagrams connecting with $\Sigma_q|J(q)|^2S_{+-}(q,\Omega)$. Γ is a connected diagram which does not contain any vertex given by $\mathcal{H}'$. It may contain the interactions that lead to the relaxation of d-electron spins.

other people[14] based on their numerical calculations. This problem is too big to be discussed in this paper and we adopt the Landau theory throughout this paper. It is easily seen, however, that the final conclusion is not sensitive on this form of the susceptibility, though the divergence of $\lim_{T\to T_C}\lim_{q\to 0}\chi(q)$ is crucial in our theory.

4. CONTRIBUTION FROM HIGHER ORDER EFFECTS

So far we have confined ourselves in the second-order effect of $\mathcal{H}'$. In order to analyze the higher-order effects, the d electrons are assumed to be itinerant and the quasi-Fermion operator b_j associated with the localized spin (at j) is introduced as follows

$$b_j^*=S_x^j+iS_y^j,$$
$$b_j=S_x^j-iS_y^j,$$
$$[b_j,b_j^*]_+=1 \quad\text{and}\quad [b_j,b_k^*]_-=[b_j,b_k]_-=0 \quad (j\neq k).$$

Then the expansion (5) for ΔA may be calculated by the diagram method developed by C. Bloch and DeDominicis,[5] provided that $\mathcal{H}_e$ is replaced by $\mathcal{H}_e-\mu N$, N being the number of the itinerant electrons and μ being their chemical potential. The difficulties in applying the Wick's theorem which come from the Bose-like commutation relations between b_j and b_k $(j\neq k)$ do not appear now, for the interaction between impurities are always neglected here.

The term connecting with $S_{+-}(q,\Omega)$ in (11) comes from the diagrams of the type shown in Fig. 2. $S_{-+}(q,\Omega)$ in (11) comes from those shown in Fig. 3. Dashed lines in these diagrams show the contraction between b_j and b_j^*, full lines represent the electron and hole propagators, and Γ_1 and Γ_2 do not contain any dashed line.

The fourth-order term has either the structure shown in Fig. 4 or that shown in Fig. 5. In the case of Fig. 4 the coherence between the electron with up spin and the hole created in the down spin states is completely broken down. Then the diagrams of this type do not give the spin-spin correlation function $S(q,\pm\Omega)$. Thus, its contribution can never be important and is always smaller than the second order effect by the factor $(J/kT)^2$, J being the exchange integral between a localized spin and the itinerant electrons.

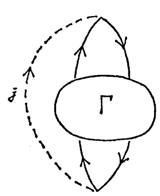

FIG. 3. Diagrams connecting with $\Sigma_q|J(q)|^2S_{-+}(q,-\Omega)$.

In the case of Fig. 5, however, the coherence is maintained. The contribution to the thermodynamic potential by these diagrams is something like

$$\beta\cdot\sum_q\sum_{q'}|J(q)|^2\cdot|J(q')|^2\cdot S(q,\Omega)\cdot S(q',\pm\Omega).$$

The most general diagrams, in which the coherence of the virtually excited spin density waves persists, are shown in Fig. 6. By summing up all of these diagrams we get

$$-\frac{N_i}{e^{\mp\beta\Omega}+1}\sum_q|J(q)|^2S_{\pm\mp}(q,\pm\Omega)\cdot\Gamma^{-1},$$

instead of

$$-\frac{N_i}{e^{\mp\beta\Omega}+1}\sum_q|J(q)|^2S_{\pm\mp}(q,\pm\Omega)$$

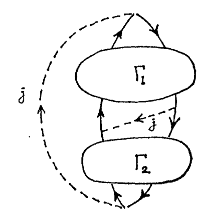

FIG. 4. A 4th order diagram with respect to $\mathcal{H}'$. The coherence of virtual excitation of the spin density wave is destroyed.

in the case of the second-order perturbation, where[15]

$$\begin{aligned}\Gamma\equiv 1&+\frac{\beta}{e^{-\beta\Omega}+1}\sum_q|J(q)|^2S_{+-}(q,\Omega)\\&+\frac{\beta}{e^{\beta\Omega}+1}\sum_q|J(q)|^2S_{-+}(q,-\Omega)\\=1&+\frac{\beta}{2}\tanh\left(\frac{\beta\Omega}{2}\right)\sum_q|J(q)|^2\{S_{+-}(q,\Omega)-S_{-+}(q,-\Omega)\}\\&+\frac{\beta}{2}\sum_q|J(q)|^2\{S_{+-}(q,\Omega)+S_{-+}(q,-\Omega)\}\\=1&+\frac{\beta}{2}\sum_q|J(q)|^2\chi_{+-}(q)-\frac{\beta}{4}\beta^2\Omega\cdot(\tfrac{1}{6}\chi J(0)H+\tfrac{1}{4}\Omega)\\&\times\sum_q|J(q)|^2\chi(q).\end{aligned}$$

Thus, the expression for the correction to the thermodynamic potential (26) should be replaced by

$$\begin{aligned}\Delta A=&-\frac{N_i}{2}\sum_q|J(q)|^2\chi_{+-}(q)\cdot\Gamma^{-1}-N_i\sum_q|J(q)|^2\chi_{zz}(q)\\&+\frac{N_i}{4}\beta^2\Omega(\tfrac{1}{6}\chi J(0)H+\tfrac{1}{4}\Omega)\sum_q|J(q)|^2\cdot\chi(q)\cdot\Gamma^{-1}.\end{aligned}$$

[14] M. E. Fisher, Physica **28**, 172 (1962); M. S. Green, J. Chem. Phys. **33**, 1403 (1960), and many other works. See also, D. R. Fredkin and H. Suhl, J. Phys. Chem. Solids **24**, 217 (1963).

[15] $kT_c\ll\Omega$ is assumed. The nonlinear effect of the induced magnetization with respect to H is again discarded.

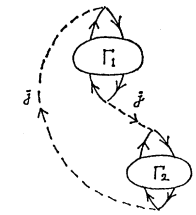

FIG. 5. A 4th order diagram with respect to $\mathcal{H}'$. The coherence of virtual excitation of the spin density wave is maintained.

After a simple manipulation we obtain

$$\Delta A=-\tfrac{1}{2}N_i\cdot\Lambda_+/(1+\tfrac{1}{2}\beta\Lambda_+)-N_i\Lambda_z+\tfrac{1}{4}N_i\cdot\beta^2\Omega\cdot(\tfrac{1}{6}\chi J(0)H+\tfrac{1}{4}\Omega)\cdot\Lambda/(1+\tfrac{1}{2}\beta\Lambda)^2, \quad (27)$$

where $\Lambda_+\equiv\sum|J(q)|^2\cdot\chi_{+-}(q)$, $\Lambda_z\equiv\sum|J(q)|^2\chi_{zz}(q)$, and $\Lambda\equiv\sum|J(q)|^2\chi(q)$. [It should be noted that $\Lambda=(\Lambda_+)_{H=0}=(\Lambda_z)_{H=0}$.] Thus, it has been shown that the higher order corrections do not change the qualitative result of the second-order effect.

5. RESULTS AND DISCUSSIONS

The total susceptibility $\chi_T=-\partial^2F/\partial H^2$ is divided into two parts $\chi_T=\chi_1+\chi_2$, where χ_1 is given by neglecting the second and higher order effects of $\mathcal{H}'$. For canonical ensemble

$$F=A=A_1+\Delta A\,.$$

Therefore,

$$\chi_1=-\partial^2A_1/\partial H^2=\chi+N_ig\mu_B(g\mu_B+\chi J(0))/kT \quad (28)$$

and

$$\chi_2=-\partial^2\Delta A/\partial H^2\,.$$

Using (26) and neglecting the higher-order effect than the second-order one, we get

$$\chi_2=\frac{N_i}{2}\frac{\partial^2\Lambda_+}{\partial H^2}+N_i\frac{\partial^2\Lambda_z}{\partial H^2}-\frac{N_i}{2}\beta^2(\chi J(0)+g\mu_B)\left(\frac{5}{12}\chi J(0)+\frac{1}{4}g\mu_B\right)\Lambda. \quad (29)$$

In order to see the quantitative nature of the first two terms on the right-hand side of (29) we assume at first that the system is isotropic in the absence of the external field. The dependence of Λ_+ on H comes from the fact that the static susceptibility

$$\chi_{+-}(q)=(C+Bq^2+\epsilon q_z^2)^{-1} \quad \text{(for small } q)$$

contains H, because (c.f., Appendix B)

$$C=C_0+\tfrac{1}{2}C_2H^2+\cdots,$$
$$B=B_0+\tfrac{1}{2}B_2H^2+\cdots,$$
$$\epsilon=\tfrac{1}{2}\epsilon_2H^2+\tfrac{1}{4}\epsilon_4H^4+\cdots.$$

In the vicinity of T_C, $C_0\propto T-T_C$, while ϵ, B_0, C_2, and B_2 do not depend appreciably on T. Since the exchange interaction between an impurity spin and a d-electron spin is short ranged, $J(q)$ remains finite for small q. Accordingly (cf., Appendix C),

$$\frac{\partial^2\Lambda_+}{\partial H^2}=-\sum_q|J(q)|^2\frac{C_2}{(C_0+B_0q^2)^2}\propto\frac{1}{C_0^{1/2}}$$

in the limit $T\to T_C$. The same result is obtained for $\partial^2\Lambda_z/\partial H^2$.

It can be shown that this result remains true even if the system is not isotropic. (In order to avoid tedious algebra we will not go into details of this general case.) Thus, the contribution of $\partial^2\Lambda_+/\partial H^2$ and $\partial^2\Lambda_z/\partial H^2$ to the susceptibility is negligible as compared with the zeroth- and first-order contribution given by (28). It should be noted that the latter contribution is proportional to $1/C_0$ instead of $1/C_0^{1/2}$ just above the Curie point.

Consequently, as $T\to T_C$ the total susceptibility should have the following form

$$\chi_T=\chi+n_ia\chi-n_ib\chi^2, \quad (30)$$

where $a=J(0)/kT_c$, n_i is the concentration of impurities (number of impurities per unit volume) and $b>0$, or, more specifically,

$$b=\frac{5}{48}[J(0)/kT_c]^2\Lambda. \quad (31)$$

For a grand canonical ensemble, $A=-PV$ and for a large system $\chi=-\partial^2F/\partial H^2$, where $F=A+\mu N$. It is evident that $A_1+\mu N$ gives the susceptibility χ_1. (The chemical potential of d electrons is not altered by the impurity spins whose state is paramagnetic.) Thus, from (27) we get again the final result (30), where b is now given by

$$b=\frac{5}{48}\left(\frac{J(0)}{kT_c}\right)^2\frac{\Lambda}{[1+(\Lambda/2kT_c)^2]^2}$$

instead of (31). Therefore, the qualitative nature of the DC susceptibility expressed by (30) has been justified rigorously under the following conditions:

(1) The interaction between an impurity and d electrons is described by (1).

(2) Lorenzian decay of the deviation of magnetization from its equilibrium value is valid at least for

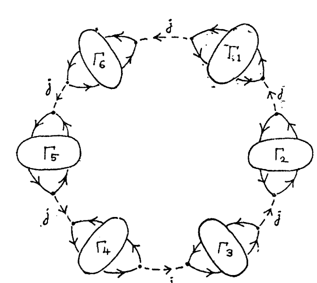

FIG. 6. Structure of the diagrams in which each of the virtually excited spin density wave is coherent.

long-time behavior of the magnetization of d electrons.

(3) The interaction between impurities is neglected, i.e., only the linear term of n_i is considered.

(4) $kT_C \gg \hbar/\tau_q$.

Among these conditions (2) is the most essential one. The Lorenzian decay has been assumed for the components of the fluctuation of magnetization with the wavelengths comparable to interatomic distances as well as for the components with long wavelengths. Discussions on this assumption have been left for future investigations. (1) and (4) have been introduced just for mathematical simplicity. As for (3), one must not be pessimistic about the fact that as $T \to T_C$ Ruderman-Kittel-Yosida's interaction[16] between impurities becomes anomalously long ranged.[17] The result presented here may be regarded as the starting point for further investigation of such a problem. In order to check the formula (30) it would be desirable to investigate the susceptibility of Fe or Ni containing a small amount of rare-earth ions at temperatures slightly above T_C.

It has been emphasized that the large correlation effect in a narrow conduction band, such as the d band of transition metals, may lead to ferromagnetism. If the kinetic energy is slightly larger than the correlation effect and keeps the d electrons in their paramagnetic state, there are large spin fluctuations in the conduction electron spins even at $T=0$. The Pauli susceptibility of the conduction electrons is given by $\chi = g\mu_B\rho(E_F)/A$, where $0<A<1$ and $\rho(E_F)$ is the state density of quasi-particles at E_F, the Fermi level. The enhancement factor $1/A$ goes to infinity as the paramagnetic state of the system approaches to the transition to ferromagnetic state. In this case the second-order effect with respect to $\mathcal{H}'$ becomes dominant. It would be interesting to see the second-order effect on the properties of the localized moment[18] in Pd. (From the observed values of the paramagnetic susceptibility and electronic specific heat of pure Pd metal we get $1/A \cong 5$.) This problem will be considered subsequently.

ACKNOWLEDGMENT

I would like to express my sincere thanks to Professor G. W. Pratt, Jr., who invited the author to his laboratory.

APPENDIX A

Calculation of the integral

$$I \equiv \int_{-\infty}^{\infty} P\frac{d\omega}{\omega-\Omega}\coth\left(\frac{\beta\omega}{2}\right)\frac{\omega}{(1/\tau_q)^2+(\omega-\gamma H)^2}.$$

Introducing $\bar{F}(\omega) \equiv \omega\coth(\frac{1}{2}\beta\omega)$ and an abbreviation $1/\tau_q \equiv \alpha$, we get

$$I = \int_{-\infty}^{\infty} P\frac{d\omega}{\omega}\frac{\bar{F}(\omega+\Omega)}{\alpha^2+(\omega+\chi J(0)H)^2}$$

$$= \int_{-\infty}^{\infty} P\frac{d\omega}{\omega}\frac{\bar{F}(\omega)}{\alpha^2+\omega^2} \quad \text{(A1)}$$

$$-\int_{-\infty}^{\infty} P\frac{d\omega}{\omega}\bar{F}(\omega)\frac{2\omega}{(\alpha^2+\omega^2)^2}\cdot\chi J(0)H \quad \text{(A2)}$$

$$+\int_{-\infty}^{\infty} P\frac{d\omega}{\omega}\bar{F}'(\omega)\frac{1}{(\alpha^2+\omega^2)^2}\cdot\Omega \quad \text{(A3)}$$

$$+0(H^3).$$

(A1) vanishes because $\bar{F}(\omega)=\bar{F}(-\omega)$. It is easy to see that (A2) leads to S_1 in Eq. (21). (A3) is calculated as follows

$$\bar{F}'(\omega) = \coth(\tfrac{1}{2}\beta\omega) - \tfrac{1}{2}\beta\omega\frac{1}{\sinh^2(\frac{1}{2}\beta\omega)}$$

$$= \frac{\sinh(\beta\omega)-\beta\omega}{2\sinh^2(\frac{1}{2}\beta\omega)}.$$

Thus, after a simple algebra we find that (A3) leads to S_2 in Eq. (21).

APPENDIX B

According to Landau,[1] the thermodynamic potential density for an isotropic system in the absence of the external field is given by

$$\Psi_{H=0}(\mathbf{r}) = \Psi_0 + c_0\sum_{\lambda=x,y,z}|m_\lambda(\mathbf{r})|^2 + b_0\sum_\lambda|\nabla m_\lambda(\mathbf{r})|^2,$$

where terms of the order m^4 are neglected. As was shown by Landau, $c_0<0$ for $T<T_c$, $c_0>0$ for $T>T_c$, and consequently, $c_0=0$ at $T=T_c$.

When an external magnetic field is applied along the z axis, the symmetry of the system becomes axial. Then the thermodynamic potential density is

$$\begin{aligned}\Psi(\mathbf{r}) = \Psi_0 - m_z(\mathbf{r})H + c_\perp(|m_x(\mathbf{r})|^2+|m_y(\mathbf{r})|^2) \\ + c_{\parallel}|m_z(\mathbf{r})|^2 + b_\perp(|\nabla m_x(\mathbf{r})|^2+|\nabla m_y(\mathbf{r})|^2) \\ + b_{\parallel}|\nabla m_z(\mathbf{r})|^2 + \bar{\epsilon}(|\partial_z m_x(\mathbf{r})|^2+|\partial_z m_y(\mathbf{r})|^2), \quad \text{(B1)}\end{aligned}$$

where terms of the order m^3 are neglected. $\bar{\epsilon}$, c_μ, and b_μ ($\mu=\parallel$ or $\perp$) in (B1) are

$$\bar{\epsilon} = \tfrac{1}{2}\epsilon_2H^2 + \tfrac{1}{4}\epsilon_4H^4 + \cdots,$$

$$c_\mu = c_0 + \tfrac{1}{2}c_2{}^\mu H^2 + \cdots,$$

and

$$b_\mu = b_0 + \tfrac{1}{2}b_2{}^\mu H^2 + \cdots.$$

For the derivation of $\chi_{+-}(\mathbf{q})$, it is sufficient to consider $|m_+(\mathbf{r})|^2$ and $|\nabla m_+(\mathbf{r})|^2$ in (B1) and only the single Fourier component $m_+(\mathbf{q})$ is our concern.[1] Thus, using

[16] K. Yosida, Phys. Rev. **106**, 893 (1957).

[17] This interaction is described by $\chi(q)$.

[18] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwitt, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

the notation $c_\perp \equiv c$ and $b_\perp \equiv b$, we get

$$\Psi \equiv \int d\mathbf{r}\Psi(\mathbf{r}) \sim (c+bq^2+\bar{\epsilon}q_z^2)|m_+(\mathbf{q})|^2.$$

Then

$$\chi_{+-}(\mathbf{q}) = \text{statistical average of } |m_+(\mathbf{q})|^2$$

$$= \frac{\int d(|m_+(\mathbf{q})|^2)|m_+(\mathbf{q})|^2 e^{-\beta\Psi}}{\int d(|m_+(\mathbf{q})|^2)e^{-\beta\Psi}}.$$

This is nothing but the procedure adopted by Landau.[1] Repeating his calculation, we get

$$\chi_{+-}(\mathbf{q}) = -\frac{\partial}{\partial\beta(c+bq^2+\bar{\epsilon}q_z^2)} \ln \int d(|m_+(\mathbf{q})|^2)e^{-\beta\Psi}$$

$$= -\frac{1}{c+bq^2+\bar{\epsilon}q_z^2}\frac{\partial}{\partial\beta}\left[-\ln\beta - \ln(c+bq^2+\epsilon q_z^2) - \ln\int_0^\infty d\xi e^{-\xi}\right]$$

$$= \frac{k_BT}{c+bq^2+\bar{\epsilon}q_z^2}.$$

In the vicinity of Curie point this is reduced to

$$\chi_{+-}(\mathbf{q}) = \frac{k_BT_c}{c+bq^2+\bar{\epsilon}q_z^2}.$$

Defining ϵ, C, C_0, C_2, B, B_0, and B_2 as

$$\epsilon \equiv \bar{\epsilon}/k_BT_c, \quad C \equiv c/k_BT_c,$$

$$C_0 \equiv c_0/k_BT_c, \quad \cdots, \quad B_2 \equiv b_2/k_BT_c,$$

we get the result shown in the text. Although some of the quantum effects would be thrown away by the above semiphenomenological treatment, these effects are not essential in the final results.

APPENDIX C

In the vicinity of the Curie point, overwhelming contribution to $\partial^2\Lambda_+/\partial H^2$ comes from the $\chi_{+-}(\mathbf{q})$ with small q. Then the Ornstein and Zernike form may be used for $\chi_{+-}(\mathbf{q})$. Thus

$$\frac{\partial^2\Lambda_+}{\partial H^2} \cong \frac{\partial^2}{\partial H^2}\sum_{\mathbf{q}} |J(q)|^2 \frac{1}{c+bq^2+\epsilon q_z^2} k_BT_c$$

$$= -\sum_{\mathbf{q}} |J(q)|^2 \frac{c_2+b_2q^2+\epsilon_2 q_z^2}{(c_0+b_0q^2)^2} k_BT_c.$$

Since the main contribution comes from the terms with small q, the following approximation may be used

$$\frac{\partial^2\Lambda_+}{\partial H^2} \cong -|J(0)|^2 C_2 \sum_{\mathbf{q}} \frac{1}{(C_0+B_0q^2)^2}$$

$$= -\frac{4\pi V|J(0)|^2C_2}{(2\pi)^3}\int_0^\infty \frac{q^2dq}{(C_0+B_0q^2)^2},$$

where V is the volume of the system.

The integral above can be evaluated by means of the Cauchy contour integral;

$$\int_0^\infty \frac{q^2dq}{(C_0+B_0q^2)^2} = \frac{1}{2}\int_{-\infty}^\infty = \frac{\pi}{4B_0^{3/2}C_0^{1/2}}.$$

Therefore

$$\frac{\partial^2\Lambda_+}{\partial H^2} = -\left(\frac{V|J(0)|^2C_2}{8\pi B_0^{3/2}}\right)\frac{1}{C_0^{1/2}}.$$

As $T \to T_c$, C_0 goes to zero, while B_0 and C_2 remains finite. Thus the result mentioned in the text has been obtained.