PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

# Electrical Resistance Due to Nonmagnetic Localized State in Dilute Alloys

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(Received 21 December 1965; revised manuscript received 19 January 1966)

The electrical resistance due to a nonmagnetic localized state is examined in order to determine the possibility of observing a resistance minimum even when there is no local moment on an impurity. While Anderson's *s-d* mixing model is adopted to describe the impurity state in the metal, we go beyond the simple Hartree-Fock approximation. The lifetime of the conduction electrons at the Fermi surface is calculated by means of the double-time Green's function method, and the resulting electrical resistance is shown to have a maximum at a certain temperature. When this temperature is in a favorable region we may observe the resistance maximum as well as the minimum. The occurrence of a local moment is also discussed from our calculation of the lifetime of conduction electrons and it is associated with an instability of the system. A new criterion for the occurrence of a local moment is obtained which appears to be in accord with experiments.

## I. INTRODUCTION

RECENTLY Kondo[1] showed that the electrical resistance due to a paramagnetic impurity with a local moment in dilute alloys has a term proportional to $\log T$ at low temperatures, and with this fact he was able to explain the old problem of a resistance minimum. Since then a number of papers have been devoted to this problem.[2–6] On the other hand, a serious question has been raised regarding the strict correlation of a resistance minimum with the presence of local moments on impurities in dilute alloys[7,8] by the observation of resistance minima even when no local moment exists on the impurities. For example, Ti alloys containing 0.2 at.% of Fe or Cr show resistance minima, even though no local moment is detected by means of magnetic-susceptibility of magnetoresistance measurements.[8]

In this paper we present a possible mechanism for resistance minima in dilute alloys in which the localized impurity states are nonmagnetic. We adopt Anderson's model to describe a localized state of the impurity in a metal.[9] If we apply a simple Hartree-Fock approximation as Anderson did, the dynamical features of the system which might be contained in the strong Coulomb repulsion between localized electrons at the impurity is mostly lost, and nothing similar to Kondo's effect appears. What is essentially responsible for the appearance of the singularity in the scattering cross section is that the scatterer in the case of the *s-d* exchange interaction has an internal degree of freedom.[1,3] Therefore it is to be expected that if the internal structure and motion of the nonmagnetic localized state is considered properly one may obtain the same type of singularity in the scattering cross section. It is required to go beyond the simplest approximation for Anderson's Hamiltonian, as for the *s-d* exchange interaction. The improved treatment of the Coulomb repulsion at the impurity to be followed here is very similar to that used by Hubbard in the problem of electron correlation in narrow energy bands,[10] and is based on the double-time Green's-function method[11] recently used successfully by Nagaoka in the case of the *s-d* exchange interaction.[4]

In Sec. II we calculate the one-particle Green's function for conduction electrons and obtain the lifetime from the imaginary part of its pole. Electrical resistance is calculated in Sec. III from the lifetime, and related discussions are given in Sec. IV. According to our result the nonmagnetic localized state becomes unstable below a certain critical temperature $T_c$ and an anomaly in the conduction-electron lifetime, or scattering cross section, is associated with this instability. The origin of the instability may be understood as follows: The higher order effects considered here effectively change the parameter of the system so as to make a local moment appear at temperatures below the critical temperature. The scattering cross section, or inverse lifetime, of the conduction electron vanishes at $T_c$ and attains a maximum at a temperature $T_{\max}$ which is found to be above $T_c$. When $T_{\max}$ lies in a favorable temperature range one may observe the resistance maximum as well as the minimum. Knowing the magnitude of $T_c$ we may estimate whether the localized state is magnetic or nonmagnetic in the temperature region of interest. From this kind of consideration a new criterion for the occurrence of a local moment is obtained, which is in good agreement with experiment.

## II. CALCULATION OF THE GREEN'S FUNCTION

We adopt the model introduced by Anderson for the localized impurity state in a metal.[9] This model may

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[*] Part of this work was initiated while the author was at the Department of Physics, University of Tokyo.

[†] Supported by the U. S. Air Force Office of Scientific Research.

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be well understood from the following Hamiltonian:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\text{mix}}+\mathcal{H}_c, \tag{2.1}$$

$$\mathcal{H}_0=\sum_{k\sigma} \epsilon_k a_{k\sigma}^* a_{k\sigma}+\epsilon_d(n_\uparrow+n_\downarrow), \tag{2.2}$$

$$\mathcal{H}_{\text{mix}}=V\sum_{k\sigma}(a_{k\sigma}^* b_\sigma+b_\sigma^* a_{k\sigma}), \tag{2.3}$$

$$\mathcal{H}_c=Un_\uparrow n_\downarrow. \tag{2.4}$$

The first term in the Hamiltonian, $\mathcal{H}_0$, is the unperturbed energy of the system, where $a_{k\sigma}^*$ is the creation operator of a conduction electron in the state with wave number vector $k$, energy $\epsilon_k$, and spin $\sigma(\sigma=\uparrow$ or $\downarrow)$, and $n_\sigma=b_\sigma^* b_\sigma$ is the number operator of the localized state electron on the impurity with energy $\epsilon_d$ and spin $\sigma$. The energies $\epsilon_k$ and $\epsilon_d$ are measured from the Fermi surface. Here we assume that only one impurity is present in the metal supposing the case of very low impurity concentration in which the effect due to the interaction between impurities can be neglected. The second term in the Hamiltonian, $\mathcal{H}_{\text{mix}}$, describes the mixing of the conduction electron state and the localized electron state; the matrix element $V$ is assumed to be a real constant for simplicity. The third term, $\mathcal{H}_c$, represents the Coulomb repulsion between localized electrons.

As is seen from our Hamiltonian we simplified the structure of the impurity state by neglecting its orbital degeneracy. In any quantitative discussion for the transition metal impurities in which we are mainly interested, this may be considered to be a crude approximation.

Next we introduce the retarded double-time Green's function[11]

$$\begin{aligned}\langle\langle A\,|\,B\rangle\rangle_t&=-i\langle[A(t),B]_+\rangle \quad \text{for} \quad t>0,\\ &=0 \quad\quad\quad\quad\quad\quad\quad\, \text{for} \quad t<0,\end{aligned} \tag{2.5}$$

where $\langle\cdots\rangle$ denotes the statistical average, and we put $\hbar=1$. Its Fourier component is defined as

$$\langle\langle A\,|\,B\rangle\rangle_\omega=\int_{-\infty}^{\infty}\langle\langle A\,|\,B\rangle\rangle_t \exp(i\omega t-0^+t)dt, \tag{2.6}$$

and from its analytical property,

$$\langle BA\rangle=-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{1}{\exp\beta\omega+1}\operatorname{Im}\langle\langle A\,|\,B\rangle\rangle_{\omega+i0^+}d\omega. \tag{2.7}$$

As is usual to calculate the one-particle Green's function of conduction electrons under the Hamiltonian (2.2), we are required to solve a chain of equations of motion for Green's functions:

$$(\omega-\epsilon_{k'})\langle\langle a_{k'\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega=\delta_{kk'}+\text{V}\langle\langle b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega, \tag{2.8}$$

$$\begin{aligned}&(\omega-\epsilon_d)\langle\langle b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad=V\sum_m\langle\langle a_{m\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle+U\langle\langle n_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega,\end{aligned} \tag{2.9}$$

$$\begin{aligned}&(\omega-\epsilon_d-U)\langle\langle n_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad=-V\sum_m\langle\langle a_{m\downarrow}^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega+V\sum_m\langle\langle b_\downarrow^* a_{m\downarrow} b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+V\sum_m\langle\langle b_\downarrow^* b_\downarrow a_{m\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega.\end{aligned} \tag{2.10}$$

In previous treatments by Anderson and others,[9,12] only the first two of the above equations were considered by introducing the following approximation to the second term on the right-hand side of Eq. (2.9):

$$\langle\langle n_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\cong\langle n_\downarrow\rangle\langle\langle b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega. \tag{2.11}$$

In this approximation the Coulomb repulsion between localized electrons, $\mathcal{H}_c$, is replaced by an effective Hartree-Fock potential. In the present treatment, we do not introduce this approximation but use instead Eq. (2.10). Further, for each new Green's function appearing on the right-hand side of Eq. (2.10), we set up the equations of motion:

$$\begin{aligned}&(\omega-2\epsilon_d+\epsilon_m)\langle\langle a_{m\downarrow}^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad=-V\langle\langle b_\downarrow^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega+V\sum_n\langle\langle a_{m\downarrow}^* a_{n\downarrow} b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+V\sum_n\langle\langle a_{m\downarrow}^* b_\downarrow a_{n\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+U\langle\langle a_{m\downarrow}^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega,\end{aligned} \tag{2.12}$$

$$\begin{aligned}&(\omega-\epsilon_m)\langle\langle b_\downarrow^* a_{m\downarrow} b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad=-V\sum_n\langle\langle a_{n\downarrow}^* a_{m\downarrow} b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+\text{V}\langle\langle b_\downarrow^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+V\sum_n\langle\langle b_\downarrow^* \text{a}_{m\downarrow} a_{n\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega,\end{aligned} \tag{2.13}$$

$$\begin{aligned}&(\omega-\epsilon_m)\langle\langle b_\downarrow^* b_\downarrow a_{m\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad=\langle n_\downarrow\rangle\delta_{m,k}-V\sum_n\langle\langle a_{n\downarrow}^* b_\downarrow a_{m\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+V\sum_n\langle\langle b_\downarrow^* a_{n\downarrow} a_{m\uparrow}\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\\ &\quad\quad+V\langle\langle b_\downarrow^* b_\downarrow b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega.\end{aligned} \tag{2.14}$$

On the right-hand sides of the three equations above there again appear new Green's functions. In this paper, however, we terminate the hierarchy of Green's functions at this point by introducing certain approximations.[11] For example, in Eq. (2.12) we assume

$$\langle\langle a_{m\downarrow}^* \text{a}_{n\downarrow} b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\cong\langle a_{m\downarrow}^* a_{m\downarrow}\rangle\langle\langle b_\uparrow\,|\,a_{k\uparrow}^*\rangle\rangle_\omega\delta_{m,n}, \tag{2.15}$$

$$\begin{aligned}\delta_{mn}&=1 \quad \text{for} \quad m=n,\\ &=0 \quad \text{otherwise},\end{aligned} \tag{2.16}$$

and we neglect the third term on the right-hand side.

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Then Eq. (2.12) reduces to

$$(\omega-2\epsilon_d+\epsilon_m-U)\langle\langle a_{m\downarrow}{}^*b_\downarrow b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega$$
$$=-V\langle\langle b_\downarrow{}^*b_\downarrow b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega$$
$$+V\langle a_{m\downarrow}{}^*a_{m\downarrow}\rangle\langle\langle b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega. \quad (2.12')$$

The neglected Green's function may be approximated like Eq. (2.15) as

$$\langle\langle a_{m\downarrow}{}^*b_\downarrow a_{n\uparrow}|a_{k\uparrow}{}^*\rangle\rangle_\omega\cong\langle a_{m\downarrow}{}^*b_\downarrow\rangle\langle\langle a_{n\uparrow}|a_{k\uparrow}{}^*\rangle\rangle_\omega, \quad (2.17)$$

which can in principle contribute terms of the same order as those retained such as Eq. (2.15). Here, however, we are interested in the anomalous part which will result through the function $K(\omega)$, Eq. (2.21). In this respect the Green's function approximated as Eq. (2.17) contributes only a small correction at least for the nonmagnetic case, as will be shown in the Appendix.

Making the same kind of approximation in Eqs. (2.13) and (2.14) we obtain

$$(\omega-\epsilon_m)\langle\langle b_\downarrow{}^*a_{m\downarrow}b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega$$
$$=-V\langle a_{m\downarrow}{}^*a_{m\downarrow}\rangle\langle\langle b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega$$
$$+V\langle\langle b_\downarrow{}^*b_\downarrow b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega, \quad (2.13')$$

$$(\omega-\epsilon_m)\langle\langle b_\downarrow{}^*b_\downarrow a_{m\uparrow}|a_{k\uparrow}{}^*\rangle\rangle_\omega$$
$$=\langle n_\downarrow\rangle\delta_{m,k}+V\langle\langle b_\downarrow{}^*b_\downarrow b_\uparrow|a_{k\uparrow}{}^*\rangle\rangle_\omega. \quad (2.14')$$

Now the system of coupled equations (2.8), (2.9), (2.10), (2.12′), (2.13′), and (2.14′) may be solved to give

$$\langle\langle a_{k\uparrow}|a_{k\uparrow}{}^*\rangle\rangle_\omega=1/(\omega-\epsilon_k)+\frac{V^2}{(\omega-\epsilon_k)^2}\frac{1+[U/D(\omega)]\langle n_\downarrow\rangle}{\omega-\epsilon_d-V^2F(\omega)+UV^2\{[K(\omega)-K(2\epsilon_d+U-\omega)]/D(\omega)\}}, \quad (2.18)$$

where

$$D(\omega)\equiv\omega-\epsilon_d-U-2V^2F(\omega)+V^2F(2\epsilon_d+U-\omega), \quad (2.19)$$

$$F(\omega)\equiv\sum_k(\omega-\epsilon_k+i0^+)^{-1}=\sum_k P/(\omega-\epsilon_k)-i\pi\sum_k\delta(\omega-\epsilon_k)\equiv I(\omega)-i\pi\rho(\omega), \quad (2.20)$$

$$K(\omega)\equiv\sum_k f(\epsilon_k)/(\omega-\epsilon_k+i0^+)=\sum_k P[f(\epsilon_k)/(\omega-\epsilon_k)]-i\pi\sum_k\delta(\omega-\epsilon_k)f(\epsilon_k)\equiv R(\omega)-i\pi\rho(\omega)f(\omega). \quad (2.21)$$

In the above $\langle a_{k\sigma}{}^*a_{k\sigma}\rangle$ was replaced by a Fermi distribution function $f(\epsilon_k)$, and $\rho(\omega)$ is the unperturbed density of states of the conduction electrons.

At low temperatures the function $R(\omega)$ is calculated as

$$R(\omega)\cong-\rho(0)\ln|\omega/W|, \quad (2.22)$$

where we assumed the density of states $\rho(\omega)$ has the following simple form:

$$\begin{aligned}\rho(\omega)&=\rho(0) \quad \text{for} \quad -W<\omega<W,\\ &=0 \qquad \text{otherwise}.\end{aligned} \quad (2.23)$$

As is seen from Eq. (2.22), $R(\omega)$ diverges when $\omega$ approaches zero, namely the Fermi level, and this function in the expression of the lifetime gives rise to the $\log T$ term in the resistivity.[1]

Our solution, Eq. (2.18), may be rewritten as

$$[\langle\langle a_{k\uparrow}|a_{k\uparrow}{}^*\rangle\rangle_\omega]^{-1}\cong\omega-\epsilon_k-V^2\frac{D(\omega)+U\langle n_\downarrow\rangle}{[\omega-\epsilon_d-V^2F(\omega)]D(\omega)+UV^2[K(\omega)-K(2\epsilon_d+U-\omega)]}\equiv\omega-\epsilon_k-\Sigma(\omega), \quad (2.24)$$

where $\Sigma(\omega)$ is regarded as the self-energy of the conduction electron. The lifetime $\tau(\omega)$ is obtained as

$$\tau(\omega)^{-1}=-(2/\hbar)\,\mathrm{Im}\Sigma(\omega+i0^+), \quad (2.25)$$

with $\hbar$ appearing explicitly.

Here we remark the following important relation:

$$\Sigma(\omega)=V^2\langle\langle b_\uparrow|b_\uparrow{}^*\rangle\rangle_\omega, \quad (2.26)$$

or more explicitly,

$$\langle\langle b_\uparrow|b_\uparrow{}^*\rangle\rangle_\omega=\frac{1+U\langle n_\downarrow\rangle/D(\omega)}{\omega-\epsilon_d-V^2F(\omega)+UV^2\{[K(\omega)-K(2\epsilon_d+U-\omega)]/D(\omega)\}}. \quad (2.26')$$

The solution (2.18) is quite different from that of Anderson.[9,12] One feature of our solution is that it coincides with the exact solution in the limit of $V\rightarrow 0$, or $U\rightarrow 0$, in which limit the problem can be solved exactly. Anderson's Hartree-Fock approximation result does not coincide with the exact one in the limit $V\rightarrow 0$, though in the case of $U\rightarrow 0$ it does. In this respect our result is very similar to that of Hubbard[10] for the problem of ferromagnetism of narrow bands. As is seen from Eq. (2.26′) the density-of-states curve of a localized state of one spin direction is no longer described by a simple Lorentzian curve as in Anderson's solution, but by a more complicated curve composed of two overlapping peaks near $\epsilon_d$ and $\epsilon_d+U$. The shape of this curve is a sensitive function of the temperature in the low-temperature region.

## III. ELECTRICAL RESISTANCE

The electrical conductivity $\sigma$ is calculated from

$$\sigma=\tfrac{2}{3}e^2v_{\mathrm{F}}^2\int\rho(\omega)\tau(\omega)(-\partial f/\partial\omega)d\omega\,, \tag{3.1}$$

where $v_{\mathrm{F}}$ is the Fermi velocity. Noticing at low temperatures that $-\partial f/\partial\omega$ behaves like a delta function $\delta(\omega)$, we replace every $\omega$ in the expression for $\mathrm{Im}\sum(\omega)$ by zero, except for the function $R(\omega)$ which must be treated carefully near $\omega=0$. Thus we obtain

$$-\mathrm{Im}\Sigma(\omega+i0^+)$$

$$\cong V^2\frac{[\mathrm{Re}D(0)+\langle n_\downarrow\rangle U]B(0)-\mathrm{Im}D(0)A(\omega)}{A(\omega)^2+B(0)^2}\,, \tag{3.2}$$

where

$$\mathrm{Re}D(0)=-[\epsilon_d+U+2V^2I(0)-V^2I(2\epsilon_d+U)]\,, \tag{3.3}$$

$$\mathrm{Im}D(0)=\pi V^2[2\rho(0)+\rho(2\epsilon_d+U)]\,, \tag{3.4}$$

$$\begin{aligned}A(\omega)\equiv&-[\epsilon_d+V^2I(0)]\,\mathrm{Re}D(0)-\pi V^2\rho(0)\,\mathrm{Im}D(0)\\&+V^2U[R(\omega)-R(2\epsilon_d+U-\omega)]\,,\end{aligned} \tag{3.5}$$

$$\begin{aligned}B(0)=&\pi V^2\rho(0)\,\mathrm{Re}D(0)-[\epsilon_d+V^2I(0)]\,\mathrm{Im}D(0)\\&-\pi V^2U[\rho(0)f(0)+\rho(2\epsilon_d+U)f(2\epsilon_d+U)]\,.\end{aligned} \tag{3.6}$$

Now we impose the condition that the localized state has no local moment (then we call the localized state nonmagnetic):

$$\begin{aligned}\langle n_\uparrow\rangle=\langle n_\downarrow\rangle&=\tfrac{1}{2}n\\&=\tfrac{1}{2}\quad\text{for}\quad n=1\,.\end{aligned} \tag{3.7}$$

The condition $n=1$ is not necessary, but is made for simplicity. In this connection the following assumption may be reasonable:

$$\begin{aligned}\epsilon_d&<0\,,\\U+\epsilon_d&>0\,.\end{aligned} \tag{3.8}$$

Assumption (3.8) is also not necessary, but it may represent a most interesting situation. To make the expression for $\Sigma(\omega)$ simple, we assume further that all functions $I(\omega)$ appearing in Eq. (3.2) vanish. If we adopt such a band as that given in Eq. (2.23), then $I(\omega)=\rho(0)\times\ln|W+\omega/W-\omega|$ is by no means zero for $\omega\neq0$. For a quantitative discussion this kind of approximation should be avoided.

Under the above restrictions and approximations the lifetime is reduced to

$$\frac{1}{\tau(\omega)}=\frac{2}{\hbar}N_0\frac{3\pi V^4\rho(0)X}{Y^2}\,\frac{1-(UV^2/X)[R(\omega)-R(2\epsilon_d+U-\omega)]}{\{1-(UV^2/Y)[R(\omega)-R(2\epsilon_d+U-\omega)]\}^2+B(0)^2/Y^2}\,, \tag{3.9}$$

where we have introduced the number of impurity $N_0$, and

$$\begin{aligned}X&=\tfrac{1}{3}(\epsilon_d^2+\tfrac{1}{2}U^2+\tfrac{1}{2}\epsilon_dU)+3\pi^2V^4\rho(0)^2\quad\text{for}\quad 2\epsilon_d+U>0\,,\\&=\tfrac{1}{3}(\epsilon_d^2+\tfrac{3}{2}U^2+\tfrac{3}{2}\epsilon_dU)+3\pi^2V^4\rho(0)^2\quad\text{for}\quad 2\epsilon_d+U<0\,,\end{aligned} \tag{310}$$

$$Y=-\epsilon_d^2-\epsilon_dU+3\pi^2V^4\rho(0)^2\,, \tag{3.11}$$

$$\begin{aligned}B(0)&=-\pi V^2\rho(0)[4\epsilon_d+\tfrac{3}{2}U]\quad\text{for}\quad 2\epsilon_d+U>0\,,\\&=-\pi V^2\rho(0)[4\epsilon_d+\tfrac{5}{2}U]\quad\text{for}\quad 2\epsilon_d+U<0\,.\end{aligned} \tag{3.12}$$

Both $X$ and $Y$ are positive since we have assumed the conditions in Eq. (3.8). The function $R(\omega)$ diverges to positive infinity as the temperature and $\omega$ approach zero. Therefore, if

$$2\epsilon_d+U\neq0\,, \tag{3.13}$$

there is a critical temperature $T_c$ defined by

$$1-(UV^2/X)R(0)_{T=T_c}=0\,, \tag{3.14}$$

where $R(2\epsilon_d+U)$ was neglected compared to $R(0)$. Below this temperature the lifetime of the conduction electron at the Fermi surface becomes negative which means the system is unstable. At present we are not offering a fully self-consistent discussion, but we may limit our discussion to the situation where the localized impurity state is not magnetized, by assuming, for instance, a sufficiently large value for the parameter $V$. Our result is equivalent to saying that the perturbational approach to this state becomes invalid below a certain temperature. Therefore the temperature $T_c$ may be regarded as the transition point from the nonmagnetic to the magnetic state of impurity. In this respect the assumption (3.13) is important. If $2\epsilon_d+U=0$, the instability does not occur, and there is no transition to a state with a localized moment. In this case the nonmagnetic state is stable.

A possible physical explanation to associate the instability with the occurrence of a localized moment is as follows: when the temperature approaches $T_c$, as will be discussed below, the density of states of the localized state at the Fermi surface begins to increase [see Eqs. (2.26) and (3.15)], which favors the spin splitting of the state as is well known.

Restricting our calculation of electrical resistance to the temperature region above $T_c$, we insert Eq. (3.9) into Eq. (3.1) and obtain

$$R=1/\sigma$$

$$=\frac{3}{2e^2v_F{}^2\rho(0)}\frac{2}{\hbar}N_0\frac{3\pi V^4\rho(0)X}{Y^2}$$

$$\times\frac{1-(UV^2/X)g(T)}{[1-(UV^2/Y)g(T)]^2+B(0)^2/Y^2}\quad\text{for}\quad T>T_c, \tag{3.15}$$

where

$$g(T)\equiv\int R(\omega)(-\partial f/\partial\omega)d\omega$$

$$\cong-\rho(0)\ln(k_BT/W). \tag{3.16}$$

A simple way of obtaining Eq. (3.16) is to use Eq. (2.22) for $R(\omega)$ and then to replace the function $-\partial f/\partial\omega$ by a pulse function, $-\partial f/\partial\omega=1/2k_BT$, for $-k_BT<\omega<k_BT$, and $=0$, otherwise. This kind of integral was discussed more elaborately elsewhere.[1,4,5] The entire integral leading to Eq. (3.15) is carried out by assuming that we can expand the integrand in powers of $R(\omega)$, which is possible in the region $T>T_c$, and by noticing that

$$\int R(\omega)^m\left(-\frac{\partial f}{\partial\omega}\right)d\omega\cong g(T)^m,\ m\ \text{positive integer}, \tag{3.17}$$

which also is easily verified by the same procedure used in deriving Eq. (3.16). Also the relation

$$R(0)=g(T) \tag{3.18}$$

is proved by reducing the definition of $R(0)$, Eq. (2.21), to Eq. (3.16) by partial integration. This type of approximate calculation is justified in the temperature region $k_BT\ll W$, which is valid in our situation.

In the expression for the resistivity, Eq. (3.15), we can define another characteristic temperature $T_m$:

$$I-(UV^2/Y)g(T_m)=0, \tag{3.19}$$

or, using Eq. (3.16),

$$T_m=(W/k_B)\exp[-Y/UV^2\rho(0)]. \tag{3.19'}$$

Similarly, the explicit expression for $T_c$ is

$$T_c=(W/k_B)\exp[-X/UV^2\rho(0)]. \tag{3.14'}$$

In terms of $T_c$ and $T_m$ the resistivity is expressed as

$$R=\frac{3}{2e^2v_F{}^2\,\rho(0)}\frac{1}{\hbar}\frac{2}{}N_0\left(\frac{3\pi V^2}{U}\right)\frac{\ln(T/T_c)}{[\ln(T/T_m)]^2+G^2}, \tag{3.20}$$

where

$$G^2=\pi^2(\tfrac{3}{2}+4\epsilon_d/U)^2\quad\text{for}\quad 2\epsilon_d+U>0, \tag{3.21}$$
$$=\pi^2(\tfrac{5}{2}+4\epsilon_d/U)^2\quad\text{for}\quad 2\epsilon_d+U<0.$$

The resistance attains a maximum at the temperature $T_{\max}$:

$$T_{\max}=T_c\exp\{[\ln(T_m/T_c)]^2+G^2\}^{1/2}. \tag{3.22}$$

At a higher temperature, $T_{\min}(>T_{\max})$, a minimum also will be observed since that part of the resistance due to lattice vibrations increases monotonically with temperature.

For those maxima or minima to be observed in reality, however, it is required that $T_{\max}$ or $T_{\min}$ be sufficiently low, otherwise these small effects may not be distinguishable from the much larger terms in the resistance due to lattice vibrations. $T_{\max}$ or $T_{\min}$ which are too low will also be difficult to observe.

## IV. DISCUSSION

### 1. Occurrence of Localized Moment

In Figs. 1 and 2 we give a few examples of the calculation of $X/UV^2\rho(0)$ and $Y/UV^2\rho(0)$ as functions of $\rho(0)/N$ for several sets of parameters $U$, $V$, and $\epsilon_d$, where $N$ is the total number of lattice points in the system. From these we easily figure out the magnitude of $T_c$ and $T_m$ using Eqs. (3.14′) and (3.19′), or

$$\ln T_c=\ln(W/k_B)-X/UV^2\rho(0), \tag{4.1}$$

$$\ln T_m=\ln(W/k_B)-Y/UV^2\rho(0). \tag{4.2}$$

As a realistic example we consider the case of Fe as an impurity in Ti, Zr, and Hf which was recently investigated by Cape and Hake.[8] Let us fix parameters as $U=10$ eV, $V\sqrt{N}=2.5$ eV, and $\epsilon_d=-3$ eV, which are the most usual values.[9] Then noticing that $\rho(0)/N$ for Ti, Zr, and Hf are, from specific heat measurements, respectively 0.71, 0.59, and 0.46 in units of states per spin direction per eV per atom (see Table III of Ref. 8),

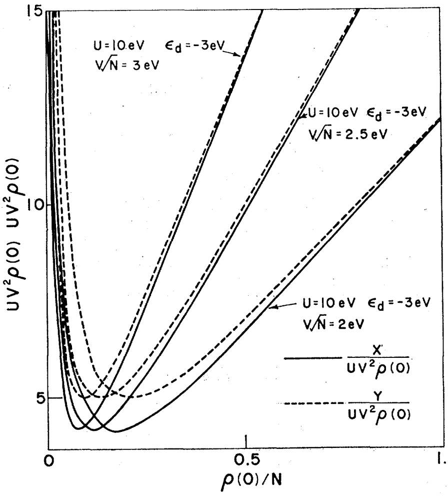

FIG. 1. The calculation of $X/UV^2\rho(0)$ and $Y/UV^2\rho(0)$ for $U=10$ eV and $\epsilon_d=-3$ eV, by changing $V\sqrt{N}$. $\rho(0)/N$ is given in the unit of states of one spin direction per eV per atom. This figure shows slight changes in $V\sqrt{N}$ produce large changes in $T_c$ and $T_m$ [see Eqs. (4.1) and (4.2)].

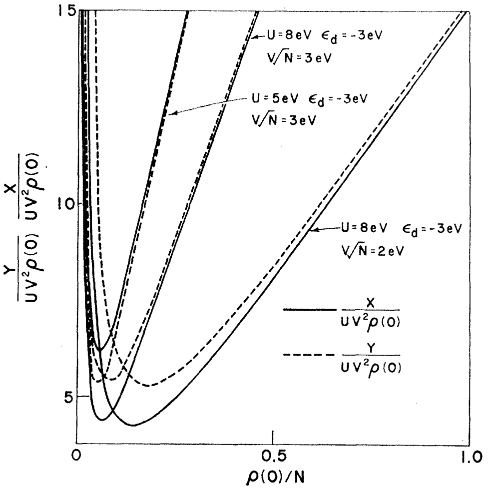

FIG. 2. The calculation of $X/UV^2\rho(0)$ and $Y/UV^2\rho(0)$ for $U=8$ eV and 5 eV. This figure, together with Fig. 1, shows how $T_c$ and $T_m$ change with $U$.

we read from the corresponding curve of Fig. 1 the magnitude of $X/UV^2\rho(0)$, respectively, as 13.5, 11.1, and 8.7. The magnitude of $W$ is determined from $4W\rho(0)=12$, which is required from the assumption Eq. (2.23) for the density-of-states curve and the assumption that the conduction-electron band of each matrix is composed of 12 states per atom since its electronic structure is of the form $nd^2(n+1)s^2$, with $n=3$, 4, and 5, respectively, for Ti, Zr, and Hf. Inserting these values into Eq. (4.1) we obtain the result for $T_c$ listed in Table I.

In the above estimate of $T_c$ we assumed, for simplicity, that the values of the three parameters $U$, $V$, and $\epsilon_d$ are common for the matrices Ti, Zr, and Hf. But comparing the similarity of the electronic structures of these matrices and that of the Fe impurity, the matrix element $V$ of the covalent mixing is expected to be larger in Ti and smaller in Hf. If we correct for these considerations in the result of Table I, the agreement of our theory with experiment is improved further. $T_c$ in Hf, for example, is raised by more than an order of magnitude assuming $V\sqrt{N}=2$ eV, instead of 2.5 eV. Thus we understand why a local moment due to an impurity Fe may be observed in Hf but not in Ti. Experimental data on Zr are not available.

Our method of predicting the occurrence of a local moment from the estimate of the magnitude of $T_c$ is apparently quite different from those of previous authors,[9,13,14,15] but it gives nearly the same explanation for the experimental data. We may understand the reason for this in the following way: When $\rho(0)/N$ is not too small, say $\rho(0)/N>0.1$, $X$, Eq. (3.10), can be approximated by the second term on the right-hand side of the equation since the first term is small by comparison. Then Eq. (3.14′) or (4.1) is approximated as

$$\ln(k_BT_c/W)\cong-(3\pi^2V^2/U)\rho(0)\,, \qquad (4.3)$$

and therefore $T_c$ is high when $(3\pi^2V^2/U)\rho(0)$ is small. This is the same conclusion as Anderson obtained in his Hartree-Fock treatment.[9] Large $U$, small $V$, and smaller $\rho(0)$ favors the occurrence of localized moment.

When $\rho(0)$ is very small, say $\rho(0)/N\ll 0.1$, however, the approximation used to obtain Eq. (4.3) is no longer valid, and instead we have

$$\ln\frac{k_BT_c}{W}\cong-\frac{\frac{1}{3}(\epsilon_d{}^2+\frac{1}{2}U^2+\frac{1}{2}\epsilon_dU)}{UV^2\rho(0)} \quad \text{for} \quad 2\epsilon_d+U>0\,,$$

$$\cong-\frac{\frac{1}{3}(\epsilon_d{}^2+\frac{3}{2}U^2+\frac{3}{2}\epsilon_dU)}{UV^2\rho(0)} \quad \text{for} \quad 2\epsilon_d+U<0\,. \qquad (4.4)$$

Thus we find that very small values of $\rho(0)$ are not favorable for the occurrence of a local moment, and that $T_c$ is now sensitive to the parameter $\epsilon_d$ whereas it is not sensitive when the approximation leading to Eq. (4.3) is valid.

Here we have the possibility of observing the transition of an impurity state from the nonmagnetic to the magnetic state. The case of Fe in Ir seems to show this transition at low temperatures since at higher temperature this alloy seems to have no local moment, but behaves at low temperature as if it has a local moment.[16]

Another important feature of our result, which is distinctly different from the Hartree-Fock result, is that the limit $U\to\infty$ does not imply the occurrence of a localized moment. In this limit for our treatment the available states of the localized electron with energies around $\epsilon_d+U$ can no longer participate in the dynamics of the system, and effectively one of the most important aspects of the role of $U$ is lost, as can be seen from Eq. (2.26′).

### 2. Resistance Anomaly

In the region where the approximation (4.3) is valid, namely when $\rho(0)/N>0.1$, we see that $T_c\cong T_m$ from

TABLE I. $T_c$ of Fe in Ti, Zr, and Hf. $U=10$ eV, $V/N=2.5$ eV, $\epsilon_d=-3$ eV.

| | Ti$(3d^24s^2)$ | Zr$(4d^25s^2)$ | Hf$(5d^26s^2)$ |
|---|---|---|---|
| $\rho(0)/N$ | 0.71[a] | 0.59[a] | 0.46[a] |
| $X/UV^2\rho(0)$ | 13.5 | 11.1 | 8.7 |
| $W$ | 4.24 eV | 5.20 eV | 6.53 eV |
| $T_c$ | 0.067°K | 0.89°K | 13°K |

[a] In units of states per spin direction per eV per atom. Taken from Ref. 8.

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Eqs. (3.10), (3.11), (3.14′), and (3.19′). In this case $T_{\max}$ is given by Eq. (3.22) as

$$T_{\max} \cong T_c \exp|G| \quad \text{for} \quad \rho(0)/N > 0.1. \tag{4.5}$$

In the case of the Ti-Fe alloy we estimate that $T_{\max} = 0.17$°K from Eq. (4.5) if we fix the parameters as in Table I, $G$ being 0.94. For clarity and emphasis we present, as an example, the calculation of electrical resistance for the Ti-Fe alloys by first adopting the parameters in Table I, and then modifying the parameters so as to fit the experimental result. If we assume the relations $\rho(0) = 3n_0/4\epsilon_F$, and $\mathrm{m}^* = (3\pi^2 n_0)^{2/3}\hbar^2/2\epsilon_F$, where $m^*$ is the effective mass of the conduction electrons and $n_0$ is the number of conduction electrons, we obtain from Eq. (3.20)

$$R = 2.32 \frac{\ln(T/T_c)}{[\ln(T/T_m)]^2 + G^2} \,\mu\Omega \text{ cm}, \tag{4.6}$$

where we assumed $n_0 = 4N$, $N_0/N = 0.002$. Further, inserting $T_c \cong T_m = 0.067$°K and $G^2 = 0.89$, we calculate the resistivity at 4.2°K and 16.7°K where the minimum is observed[8]:

$$\begin{aligned} &R(4.2°\text{K}) = 0.53 \,\mu\Omega \text{ cm}, \\ &\Delta R \equiv R(4.2°\text{K}) - R(16.7°\text{K}) = 0.12 \,\mu\Omega \text{ cm}, \\ &\Delta R/R(4.2°\text{K}) \cong 23\%. \end{aligned} \tag{4.7}$$

The corresponding experimental data are[8]

$$\begin{aligned} R_{\text{expt}}(4.2°\text{K}) = R_{\text{expt}}&(4.2°\text{K}, 0.2\% \text{ Fe-Ti}) \\ &- R_{\text{expt}}(4.2°\text{K}, \text{pure Ti}) = 1.20 \,\mu\Omega \text{ cm}, \end{aligned} \tag{4.8}$$

$$\begin{aligned} &\Delta R_{\text{expt}} \cong 0.054 \,\mu\Omega \text{ cm}, \\ &\Delta R_{\text{expt}}/R(4.2°\text{K}) \cong 5\%. \end{aligned}$$

Apart from the detailed examination of experimental data first we notice that the calculated value for $\Delta R/R(4.2°\text{K})$ is too large, namely that the temperature dependence for the resistance is too steep. This discrepancy, however, can be removed by a slight change in the values of parameters of the system. There are various possibilities of choosing the parameters to fit the experiment. If, for instance, we assume (a) $G^2 = 16$, and keep the values of the other parameters $U$ and $V$ as before, we obtain

$$\begin{aligned} &R(4.2°\text{K}) = 0.29 \,\mu\Omega \text{ cm}, \\ &\Delta R/R(4.2°\text{K}) \cong 5\%. \end{aligned} \tag{4.9}$$

Since $G^2$ is a very sensitive function of the parameter $\epsilon_d$, as can be seen from Eq. (3.21), such modification as (a) is easily produced.

Now, however, by fitting the calculated value of $\Delta R/R(4.2°\text{K})$ with experiment, the absolute magnitude of the calculated resistance, e.g., at 4.2°K, is smaller than that of experiment by nearly a factor of 4. Better agreement can be obtained by replacing the factor 2.32 in Eq. (4.6) by one about four times larger. This can be done by (b) assuming smaller $U$ and/or larger $V$, and/or (c) assuming a smaller number of conduction electrons. Since the value of $T_c$ is very sensitive to the procedure (b), if we are to leave $T_c$ unchanged to keep the result in Eq. (4.9) regarding $\Delta R/R$ valid, we are forced to adopt procedure (c). In obtaining the factor 2.32 in Eq. (4.6), we assumed that the number of conduction electrons is 4 per atom recalling that the Ti atom has 4 electrons outside the closed shells. If we assume, instead, that the conduction band of Ti is better approximated as Eq. (2.23) with the number of conduction electrons about 1.4 per atom, the absolute magnitude of the calculated resistance is increased to fit the experiment.

### 3. Concluding Remarks

All of our discussions have been carried out under some very simplifying assumptions. We have neglected the orbital degeneracy of the impurity state, notwithstanding that our main interest is in transition-element impurities. The concentration of impurities was assumed to be very low in order to neglect the interaction between impurities. The conduction electrons were treated as free with very small consideration paid to their band structures. To make our discussions more quantitative these deficiencies should be improved. Nevertheless, we have seen that even our simple discussion is able to give fairly satisfying explanations to various experimental results.

The discussions in this paper were essentially confined to the temperature region above $T_c$. In a future publication we extend our study to the region $T < T_c$ to improve the understanding of the nature of the instability.

Finally we may make an important remark. Though our interest has been concentrated on the case of the nonmagnetic localized state, our result can be interpreted in a quite different way. Namely, we can start our discussion from an impurity state with a local moment by assuming, for instance, a sufficiently small value for $V$. This modifies only assumption (3.7), which would not produce any serious change in the qualitative feature of the result obtained in this paper. Then the occurrence of the instability may be associated with the resonance coupling of the localized moment with the conduction electron spin, which was discussed by Nagaoka in the *s-d* exchange model.[4] Further investigation about this point would be interesting.

*Note added in proof.* Nagaoka (private communication) raised the following question: "If Eq. (2.26′) is expanded in both $V$ and $U$ the temperature-dependent anomalous terms appear in the expansion in order $UV^2$. On the other hand, however, if one calculates $\langle\langle b_\uparrow | b_\uparrow^* \rangle\rangle_\omega$ by a perturbation from the start no anomalous term appears to order $UV^2$." The above discrepancy is clearly due to our having neglected terms such as Eq. (2.17) in our result. We can formally include those terms in Eq. (2.17) into our solution for $\langle\langle b_\uparrow | b_\uparrow^* \rangle\rangle_\omega$ or $\langle\langle a_{k\uparrow'} | a_{k\uparrow}^* \rangle\rangle_\omega$

and if we expand this more complete solution up to the order $UV^2$ as Nagaoka suggests, the results does not contradict the result obtained by perturbation up to order $UV^2$. What we show in the Appendix of this paper is that, to higher orders, the effect of those terms such as Eq. (2.17) can be neglected for qualitative discussion in the temperature region sufficiently above $T_c$. The author thanks Dr. Y. Nagaoka for his valuable discussions on the manuscript of this paper.

In addition, as was stressed many times in this paper, the validity of our results is confined to the temperature region $T>T_c$. In this respect what is fully meaningful in our result is the part of initial increase of the resistivity, or the increase in the density of states of the localized electron at Fermi surface, with decreasing temperature. Therefore the temperature $T_c$ or $Tm$ only means that as the temperature approaches $T_c(\approx Tm)$ the temperature dependent effect can become large enough to destroy the stability of the system.

## ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. B. Lax and Dr. A. J. Freeman for the hospitality extended to him at the National Magnet Laboratory, MIT. It is a pleasure to thank Dr. A. J. Freeman and Dr. B. B. Schwartz for their valuable discussions about this work. Thanks are also due to Professor R. Kubo for his continual encouragement and valuable discussions.

## APPENDIX

In this Appendix we discuss in greater detail the approximations we adopted in calculating the Green's functions in Sec. II. We will concentrate on the velocity of reducing Eqs. (2.12), (2.13), and (2.14), respectively, to Eqs. (2.12′), (2.13′), and (2.14′).

(1) The reduction of Eq. (2.14) to Eq. (2.14′) may be justified without any problem. The second and third terms on the right-hand side of Eq. (2.14) may be approximated as

$$\begin{aligned} -V\sum_n\langle\langle a_{n\downarrow}{}^*b_\downarrow a_{m\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega+\mathrm{V}\sum_n\langle\langle b_\downarrow{}^*a_{n\downarrow}a_{m\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ \cong -V\sum_n\langle a_{n\downarrow}{}^*b_\downarrow\rangle\langle\langle a_{m\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ +V\sum_n\langle b_\downarrow{}^*a_{n\downarrow}\rangle\langle\langle a_{m\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \end{aligned} \tag{A1}$$

and vanishes because of the Hermiticity requirement

$$\langle a_{n\downarrow}{}^*b_\downarrow\rangle=\langle b_\downarrow{}^*a_{n\downarrow}\rangle\,. \tag{A2}$$

Thus we obtain Eq. (2.14′).

(2) Equation (2.13) is approximated as

$$\begin{aligned} (\omega-\epsilon_m)\langle\langle b_\downarrow{}^*a_{m\downarrow}b_\uparrow\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega\cong-\mathrm{V}\langle a_{m\downarrow}{}^*a_{m\downarrow}\rangle\langle\langle b_\uparrow\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ +V\langle b_\downarrow{}^*a_{m\downarrow}\rangle\sum_n\langle\langle a_{n\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ +V\langle\langle b_\downarrow{}^*b_\downarrow b_\uparrow\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega\,. \end{aligned} \tag{A3}$$

In Sec. II we neglected the second term on the right-hand side of Eq. (A3) compared to the first term. We justify this approximation by estimating the magnitude of the neglected term. As is well known,[11] the approximation used to obtain Eq. (A3) is valid when the quantity $\langle b_\downarrow{}^*a_{m\downarrow}\rangle$, as well as $\langle a_{m\downarrow}{}^*a_{m\downarrow}\rangle$, is given consistently with the obtained Green's functions. At present, however, we are unable to make a completely self-consistent calculation; therefore we have made the reasonable approximation of replacing $\langle a_{m\downarrow}{}^*a_{m\downarrow}\rangle$ by a Fermi distribution function of the unperturbed state. A similar approximation is also required to calculate $\langle b_\downarrow{}^*a_{m\downarrow}\rangle$.

From Eq. (2.7) and

$$(\omega-\epsilon_m)\langle\langle a_{m\downarrow}\,|\,b_\downarrow{}^*\rangle\rangle_\omega=V\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle\,, \tag{A4}$$

we obtain

$$\begin{aligned} \langle b_\downarrow{}^*a_{m\downarrow}\rangle=Vf(\epsilon_m)\,\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=\epsilon_m} \\ -\frac{V}{\pi}\int\frac{P}{\omega-\epsilon_m}\,\mathrm{Im}\langle\langle \mathrm{b}_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_\omega f(\omega)d\omega\,. \end{aligned} \tag{A5}$$

The value $\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_\omega$ to be used in the right-hand side of Eq. (A5) can be reasonably approximated by adopting Eq. (2.26′) and putting $T=\infty$ or by putting $K(\omega)=0$. From Eqs. (A5) and (2.8) the second term on the right-hand side of Eq. (A3) is rewritten as

$$\begin{aligned} V\langle b_\downarrow{}^*a_{m\downarrow}\rangle\sum_n\langle\langle a_{n\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ \cong V^2f(\epsilon_m)\,\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=\epsilon_m}[1/(\omega-\epsilon_k+i0^+)] \\ +V^3f(\epsilon_m)\,\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=\epsilon_m}F(\omega)\langle\langle b_\uparrow\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega\,, \end{aligned} \tag{A6}$$

where we retained only those terms which contain the Fermi distribution function $f(\epsilon_m)$ [namely we neglected the second term on the right-hand side of Eq. (A5)] since we know that the terms retained contribute the anomalous parts through the function $R(\omega)$. If Eq. (A3) is inserted into the right-hand side of Eq. (2.10), the term due to Eq. (A6) contributes

$$\begin{aligned} V^2\sum\frac{\langle b_\downarrow{}^*a_{m\downarrow}\rangle}{\omega-\epsilon_m}\sum_n\langle\langle a_{n\uparrow}\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega \\ \cong V^3\,\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=0}K(\omega)\frac{1}{\omega-\epsilon_k+i0^+} \\ +V^4\,\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=0}F(\omega)K(\omega)\langle\langle b_\uparrow\,|\,a_{k\uparrow}{}^*\rangle\rangle_\omega\,, \end{aligned} \tag{A7}$$

where we have assumed $\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_\omega$ (at high temperatures) is a smooth function of $\omega$.

If we estimate the magnitude of $\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=0}$ from Eq. (2.26′) with $K(\omega)=0$, as mentioned above, for ordinary values[9] of $V$, $U$, $\rho(0)$, and $\epsilon_d$ it turns out that $\mathrm{Re}\langle\langle b_\downarrow\,|\,b_\downarrow{}^*\rangle\rangle_{\omega=0}\equiv\alpha/U$, $|\alpha|\ll1$. Therefore, the contribution due to the second term on the right-hand side of Eq. (A6), which is the second term on the right-hand side of Eq. (A7), may be safely neglected compared to that due to the first term on the right-hand side of Eq. (A3). Finally, if we include the effect of the first term on the right-hand side of Eq. (A6), then $\langle n_\downarrow \rangle$ in Eq. (3.2) must be replaced by $\langle n_\downarrow \rangle + V^2 \operatorname{Re}\langle\langle b_\uparrow | b_\uparrow^* \rangle\rangle_{\omega=0} R(\omega)$, and accordingly the factor $1-(UV^2/X)g(T)$ in Eq. (3.15) is changed to

$$1-\frac{UV^2}{X}\left[1+\frac{B(0)}{3\pi V^2\rho(0)}\operatorname{Re}\langle\langle b_\uparrow | b_\uparrow^* \rangle\rangle_{\omega=0}\right]g(T)\,.$$

It is easy to see, however, that the correction

$$[B(0)/3\pi V^2\rho(0)](\alpha/U)\,,$$

with $|\alpha| \ll 1$, is small compared to 1 and may be neglected.

There remains one more point to be discussed concerning Eq. (A3). In the first term on the right-hand side of Eq. (A3) we introduced the following approximation:

$$\sum_n \langle a_{n\downarrow}{}^* a_{m\downarrow} \rangle \cong \langle a_{m\downarrow}{}^* a_{m\downarrow} \rangle \cong f(\epsilon_m)\,.$$

However, if we calculate $\sum_n \langle a_{n\downarrow}{}^* a_{m\downarrow} \rangle$ from Eqs. (2.7) and (2.8), there appear other terms besides $f(\epsilon_m)$ which are similar to those due to the second term on the right-hand side of Eq. (A3). These contributions, however, may be ignored for the same kinds of reasons given above for qualitative discussions.

(3) As to the nature of the approximation included in Eq. (2.12′), we can use arguments quite similar to those given above in order to obtain Eq. (2.13′).

Thus we have shown that Eqs. (2.12′), (2.13′), and (2.14′) are good approximations for Eq. (2.12), (2.13), and (2.14) and do not destroy the essential feature of the system at temperatures above $T_c$. Our calculation of the Green's function is organized so as to give a self-consistent solution at high temperatures ($T \gg T_c$) and to retain the lowest order anomalous temperature dependence correctly.

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PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

# Low-Temperature Specific Heat of Palladium Containing Interstitial Hydrogen

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(Received 31 January 1966)

Specific-heat measurements in the 1.2 to 4.2°K range have been carried out on four H-Pd specimens having H/Pd atomic ratios of 0.57, 0.70, 0.81, and 0.88. Corresponding values of $\gamma$ (the electronic-specific-heat coefficient) are 2.52, 1.38, 1.40, and 1.61 mJ/deg² *per g atom of palladium;* values of $\Theta_D$ (the Debye temperature) are 282, 273, 276, and 267°K, respectively. A "dynamic" method of measurement was necessarily employed because of the occurrence of an exothermic process in these alloys. The interpretation of the data was complicated by the interstitial character of these alloys, but the present results for the electronic specific heat appear to offer unusually direct support for the usual simple band picture of Pd and H-Pd alloys. Special care must be exercised in the interpretation of the Debye temperatures in this case.

## INTRODUCTION

ALTHOUGH there have been many investigations of the H-Pd system, a satisfactory understanding of its electronic structure has not been achieved. An important problem concerns the disposition of the electrons from the absorbed hydrogen. Although neutron-diffraction measurements[1] on $\beta$-phase[2] alloys at room temperature have shown that the protons from the absorbed hydrogen occupy octahedral interstitial positions of the slightly expanded fcc palladium lattice, the disposition of the electrons can not be determined by similar measurements and must, in fact, be inferred from other data.

The most pertinent data are those for the magnetic susceptibility[3] and specific heat[4] of Ag-Pd alloys and for the magnetic susceptibility[5] of H-Pd alloys. The results of these (and of other somewhat less direct) measurements are usually interpreted on a simple rigid-band model as indicating (i) that pure palladium has roughly 0.6 holes per atom in the $d$ band and (ii)

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[2] For H/Pd atomic ratios greater than about 0.6, the H-Pd alloys consist of a single ($\beta$) phase. For lower concentrations, the alloys consist of two phases, $\alpha$ and $\beta$; the hydrogen content of the $\alpha$ phase is small, perhaps even zero [see J. Cohen and F. de Bergevin, Compt. Rend. **246**, 3055 (1958)].

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