PHYSICAL REVIEW B VOLUME 5, NUMBER 11 1 JUNE 1972

Effects of Impurities on the Metal-Insulator Transition

T. M. Rice and W. F. Brinkman
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 29 December 1971)

The effect of impurities on the critical interaction strength for the Mott transition has been investigated using an extension of the Gutzwiller approach to correlation in the metallic state. It is shown that the band narrowing due to impurities causes a reduction of the effective interaction necessary for the transition to the insulating state. The residual resistivity due to impurity scattering is considered and it is argued that the conductivity can be written as the product of the Fermi-surface area and the mean free path. Since the latter is limited by the average impurity separation the residual resistivity is bounded. This upper bound appears to be violated for Cr-doped V_2O_3.

I. INTRODUCTION

A number of metal-insulator transitions have been observed in the various oxides of the $3d$ transition series.[1] While none of the transitions observed are understood in any quantitative detail, it is generally accepted[2] that there are strong Coulomb interactions in these materials and that the Coulomb interactions play an essential role in determining many of their properties. In particular, one expects some rather strong effects due to correlation in the properties of the metallic state and it has been shown[3] that it is possible to make qualitative predictions of these effects by using an approach due to Gutzwiller[4] based on the Hubbard model. It is the purpose of this paper to examine the consequences of his approach further.

The metal-insulator transition in V_2O_3 has been studied extensively in the past few years.[1] One of the interesting results of these studies is the observed relationship between the effect of negative pressures and that of doping with Cr or Al.[1,5] Since both of these ions are stable trivalent ions one might as a first attempt regard them simply as deleting a site from the conduction band of pure V_2O_3. This deletion causes a band narrowing and, consequently, a reduction of the critical values of the interactions for the metal-insulator transitions. The relationship between negative pressure and Cr or Al doping simply arises because they both induce a band narrowing which drives the system more insulating. This result is explicitly worked out in Sec. II by generalizing Gutzwiller's approach to include the effect of impurities. This is accomplished by adding a term to the Hamiltonian which describes the energy difference between the impurity conduction level and the host level. We consider the case in which the number of electrons is equal to the number of host atoms and construct a trial wave function in which the amplitudes of those configurations with 2κ electrons on the impurities are reduced by $\theta^{2\kappa}$. At the same time we retain the reduction of the amplitude of configurations with doubly occupied sites and make the same type of approximation made by Gutzwiller in finding the energy. In this way we predict a critical value of the Coulomb interaction for the metal-insulator transition as a function of the impurity concentration and the separation of the impurity level and the host band. The above-mentioned relation between doping and pressure becomes explicit in this calculation.

One of the attractive features of the Gutzwiller approach is that the Fermi surface of the noninteracting Bloch state is retained as the interaction strength increases. The fact that the number of carriers (equal to the number of doubly occupied sites) becomes small as the metal-insulator transition is approached is represented by a large effective mass rather than a change in the volume enclosed by the Fermi surface. To the extent that the properties of such a metallic state are similar to those of a state with a small number of carriers, our picture is similar to that of Mott.[6] He visualizes the metallic state near the metal-insulator transition in terms of two overlapping Mott-Hubbard bands. In order to investigate the equivalences between the two views in Sec. III we derive expressions using Landau-Fermi-liquid theory for the frequency-dependent conductivity. We find that at fixed frequency the conductivity is inversely proportional to the effective mass and therefore goes to zero as the metal-insulator transition is approached. On the other hand it is possible to write the dc conductivity in the presence of a small number of impurities, in a form involving only the Fermi-surface area and the mean free path. A lower bound on the mean free path is obtained by assuming that a quasiparticle is completely scattered every time it encounters an impurity. Thus neither of the quantities entering the dc conductivity is expected to be strongly dependent on the interaction strength. This result suggests that in the dilute limit the increase in residual resistivity should not behave in an anomalous fashion near the Mott transition. On the other hand, recently McWhan *et al.*[7] have found a value of 140 $\mu\Omega$cm per at.% Cr for the residual resistivity in the metallic state of $(V_{1-x}Cr_x)_2O_3$ under pressure. This increase is more than an order of magnitude faster than can reasonably be expected from the formula of Sec. III. Possible explanations of this result are that series expansion in impurity concentration is breaking down in this case or that the Fermi-surface area is an order of magnitude smaller than anticipated from the large values observed for the susceptibility and the electronic specific heat. An alternative explanation is that our model does not apply to V_2O_3 and in this material the conduction processes are dominated by a small number of relatively light electrons possibly from the 4*s* band and the specific heat and susceptibility are governed by quasilocalized 3*d* electrons.

Finally we consider the Hall effect. Again using Landau-Fermi-liquid theory we find the Hall coefficient to be related to the area enclosed by the Fermi surface at low temperatures. At temperatures high compared to the renormalized Fermi temperature we expect the number of carriers to be equal to the number of doubly occupied sites leading to a temperature-dependent Hall coefficient. Recent experimental results of McWhan *et al.*,[7] however, show only a small difference between the values of the Hall coefficient of V_2O_3 at 1 atm and 300 °K and at 25 kbar and 4.2 °K.

II. REDUCTION OF CRITICAL INTERACTION

In this section we will consider the application of the Gutzwiller variational method to the problem of impurities in a single-band Hubbard Hamiltonian. We take as our model Hamiltonian

$$H=\sum_{ij\sigma} t_{ij}c^\dagger_{i\sigma}c_{j\sigma}+t_0\sum_{\sigma,i\in\{I\}} n_{i\sigma}+U\sum_i n_{i\uparrow}n_{i\downarrow}\;, \tag{2.1}$$

where $t_{ii}\equiv 0$, $c^\dagger_{i\sigma}$ is the creation operator for the Wannier state at site i and spin σ, and $n_{i\sigma}=c^\dagger_{i\sigma}c_{i\sigma}$. The second term represents the shift of the zero of energy on the impurity sites $\{I\}$. We assume for simplicity that the hopping integral t_{ij} and the Coulomb energy U are independent of whether the sites i and j are host or impurity sites.

In the Gutzwiller approximation to the Hubbard Hamiltonian in the absence of impurities, one constructs the matrix elements of the density operator as a product of two factors. One factor arises from phase relationships between the set of configurations where the electron positions are specified. For this factor one takes the value for the uncorrelated or noninteracting electron gas. The second factor comes from the correlation and is computed by summing over all possible configurations of the opposite-spin electrons with a weighting factor determined by the number of doubly occupied sites. In this procedure the kinetic energy of the opposite-spin electrons is neglected completely and they are treated as though they were infinitely heavy and random in position. It is straightforward therefore to generalize this second calculation to incorporate the effects of the impurities. The modification of the first factor due to the presence of impurities is a much more difficult matter. We shall make the simplest possible approximation and assume it is unmodified by the impurities. This leads to the unphysical consequence that the model has a sharp Fermi surface in momentum space even in the presence of the impurities. This approximation is only useful as a description of the coherent effects of impurities, e.g., the reduction of the average kinetic energy in the presence of strongly repulsive impurities. It neglects completely all the incoherent-scattering effects of the impurities. Thus it cannot describe such effects as the onset of Anderson localization.[8] We shall return to this point in Sec. III. In this section we will consider only the coherent-scattering effects of the impurities.

The details of calculation of the matrix elements are rather tedious and are given in the Appendix. The result obtained for the ground-state energy is

$$E_0=2m\bar{\epsilon}q(\nu,\kappa,\lambda)+\nu U+2\kappa t_0+\lambda U\;, \tag{2.2}$$

where m is the number of electrons of one spin, $\bar{\epsilon}\,[=m^{-1}\sum_{k<k_F}\epsilon(k)]$ is the average kinetic energy in band structure of the host. In writing Eq. (2.2) in this form we have made use of the exact relationship between the weighting factors and the numbers of appropriately occupied sites in the limit that the number of sites is very large. The symbols ν, κ, and λ denote the numbers of doubly occupied host sites, of electrons of one spin on the impurity sites, and of doubly occupied impurity sites, respectively. From Eq. (A13) of the Appendix we obtain the result

$$\begin{aligned} q(\bar{\nu},\bar{\kappa},\bar{\lambda})=\frac{1}{\bar{m}(1-\bar{m})}\,&\{(1-c)(\bar{\xi}-\bar{\nu})^{1/2}\\ &\times[(1-2\bar{\xi}+\bar{\nu})^{1/2}+\bar{\nu}^{1/2}]\\ &+c(\bar{\kappa}-\bar{\lambda})^{1/2}[(1-2\bar{\kappa}+\bar{\lambda})^{1/2}+\bar{\lambda}^{1/2}]\}^2\;, \end{aligned} \tag{2.3}$$

where c $(=I/L)$ denotes the concentration of impurity sites and $\bar{m}=m/L$, $\bar{\nu}\,[=\nu/(L-I)]$, $\bar{\kappa}$ $(=\kappa/I)$, and $\bar{\lambda}$ $(=\lambda/I)$ are the respective fractional occupation numbers. The quantity $\bar{\xi}$ denotes the ratio of the number of electrons of a single spin on the host sites to the number of host sites:

$$\bar{\xi}=(m-\kappa)/(L-I)\;. \tag{2.4}$$

Minimizing the total energy with respect to $\bar{\nu}$, $\bar{\kappa}$, and $\bar{\lambda}$ leads to the coupled set of equations

$$\frac{\partial q}{\partial \bar{\nu}} = (1-c)\left(\frac{U}{-2\bar{m}\bar{\epsilon}}\right) , \tag{2.5a}$$

$$\frac{\partial q}{\partial \bar{\kappa}} = c\left(\frac{t_0}{-\bar{m}\bar{\epsilon}}\right) , \tag{2.5b}$$

$$\frac{\partial q}{\partial \bar{\lambda}} = c\left(\frac{U}{-2\bar{m}\bar{\epsilon}}\right) . \tag{2.5c}$$

The solutions of these equations are in general rather involved and we shall restrict ourselves to two cases of interest. First let us take the case $U \equiv 0$. The Hamiltonian then reduces to the well-known alloy problem which has been considered by a number of authors. It is of interest to compare the results obtained by the Gutzwiller method and those obtained by other methods such as the coherent-potential approximation (CPA).[9,10] The second case is the metal-insulator transition in the presence of a set of repulsive impurities under the conditions that the number of electrons exactly equals the number of host sites.

In the limit $U \to 0$, Eqs. (2.5a) and (2.5c) reduce to

$$\frac{\partial q}{\partial \bar{\nu}} = \frac{\partial q}{\partial \bar{\lambda}} = 0 . \tag{2.6}$$

It is straightforward to show that the solutions of Eq. (2.6) are

$$\bar{\nu} = \bar{\xi}^2 ; \quad \bar{\lambda} = \bar{\kappa}^2 , \tag{2.7}$$

as one expects in the absence of correlations between the up- and down-spin electrons. Substituting from (2.7) in (2.3) one arrives at the result

$$q(\bar{\kappa}) = \frac{1}{\bar{m}(1-\bar{m})}[(1-c)\bar{\xi}^{1/2}(1-\bar{\xi})^{1/2} + c\bar{\kappa}^{1/2}(1-\bar{\kappa})^{1/2}]. \tag{2.8}$$

Let us now take the number of electrons equal to twice the number of host sites (i.e., $\bar{m} = 1-c$) and derive the condition for a metal-insulator transition. Such a transition will occur when the band centered at the average energy of the impurity sites (t_0) splits off from that centered at the average energy of the host sites. From Eq. (2.4), we have

$$\bar{\xi} = 1 - [c/(1-c)]\bar{\kappa} , \tag{2.9}$$

and substituting this value of $\bar{\xi}$ into Eq. (2.8) we arrive at the result

$$q(\bar{\kappa}) = \frac{\bar{\kappa}}{1-c}\,[(1-c-c\bar{\kappa})^{1/2} + c^{1/2}(1-\bar{\kappa})^{1/2}]^2 . \tag{2.10}$$

The metal-insulator boundary is determined by simultaneously solving Eq. (2.5b) and the condition $q(\bar{\kappa}) = 0$. After a little algebra we arrive at the result

$$\left(\frac{1}{(1-c)^{1/2}} + \frac{1}{c^{1/2}}\right)^2 = \left(\frac{t_0}{-\bar{m}\bar{\epsilon}}\right) . \tag{2.11}$$

Note this formula applies only for a less than half-filled band, i.e., $0.5 < c < 1$. For $0 < c < 0.5$ the results are obtained by using particle-hole symmetry by the substitution $c \to 1-c$. The detailed form of this condition depends on the band structure of the host material through the parameter $\bar{\epsilon}$. Velicky, Kirkpatrick, and Ehrenreich[10] have used the CPA to calculate the condition for band splitting for a band with a parabolic density-of-states function of the form

$$\begin{aligned} \eta(\epsilon) &= (2/\pi w^2)(w^2-\epsilon^2) , & |\epsilon| &\le w \\ &= 0 , & |\epsilon| &> w \end{aligned} \tag{2.12}$$

where w is the band width. In Fig. 1 we make a comparison between their results and those of Eq. (2.11). The general shape of the curves is similar but Eq. (2.11) leads to a value of t_0 which is larger by a factor of approximately 1.7. The dilute limit ($c \to 0$) is given exactly by the CPA and the failure of Eq. (2.11) in this limit shows that the detailed numerical predictions are not to be trusted to within a factor of at least 2.

We wish now to turn to the consideration of the combined effects of impurities and the intraatomic Coulomb repulsion U. We are again interested in the possible circumstances under which a metal-insulator transition occurs. Since the model we are considering only describes the coherent effects

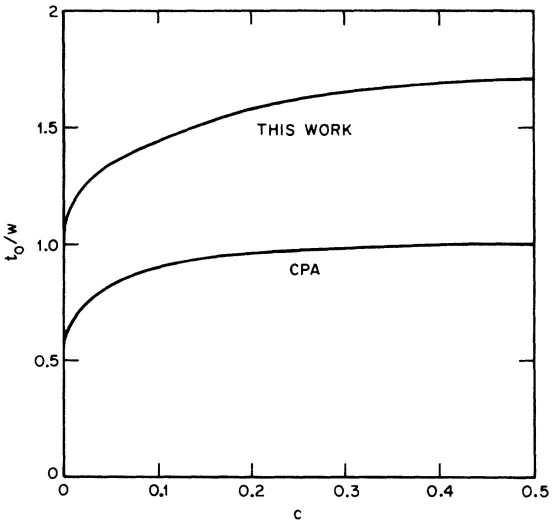

FIG. 1. Condition for an energy gap to develop between the band of states centered at the average energy (t_0) on the impurity sites and the band of states centered at the average energy of the host sites as a function of the concentration (c) of impurities. The upper curve shows the results obtained by using Eq. (2.11) and the lower curve those obtained in the coherent-potential approximation by Velicky, Kirkpatrick, and Ehrenreich (Ref. 10).

of impurities and ignores scattering effects it will not be applicable to situations where the impurity potentials are weak and the impurities have the same number of d electrons as the host. Instead we will restrict our attention to strongly scattering impurities with a different number of d electrons where we may hope that the coherent effects are largest. Therefore we take $t_0 > 0$ and the number of electrons equal to the number of host sites and examine the condition for a metal-insulator transition.

At the metal-insulator boundary both the fractional occupation numbers $\overline{\nu}$ (doubly occupied host sites) and $\overline{\kappa}$ (the number of electrons per impurity on the impurity sites) both go to zero. Clearly $\overline{\lambda}$ (the fraction of doubly occupied impurity sites) goes to zero faster and may be set equal to zero. Under these circumstances q may be written

$$q(\overline{\nu},\overline{\kappa})=\frac{4}{1-c^2}\{(1-c)(\overline{\zeta}-\overline{\nu})^{1/2}[(1-2\overline{\zeta}+\overline{\nu})^{1/2}+\overline{\nu}^{1/2}] + c\overline{\kappa}^{1/2}(1-2\overline{\kappa})^{1/2}\}^2 , \quad (2.13)$$

with

$$\overline{\zeta}=\tfrac{1}{2}-[c/(1-c)]\overline{\kappa} . \quad (2.14)$$

Substituting in Eq. (2.13) and expanding for small values of $\overline{\kappa}$ and $\overline{\nu}$, we find

$$q(\overline{\nu},\overline{\kappa})=\frac{4}{1-c^2}\left\{\frac{1-c}{2^{1/2}}\left[\left(\frac{2c}{1-c}\overline{\kappa}+\overline{\nu}\right)^{1/2}+\overline{\nu}^{1/2}\right]+c\overline{\kappa}^{1/2}\right\}^2 + O(\overline{\kappa}^2,\overline{\nu}^2,\overline{\kappa}\overline{\nu}) . \quad (2.15)$$

The metal-insulator transition boundary is found by solving the two coupled equations (2.5a) and (2.5b) using Eq. (2.15) for q. Taking the ratio of (2.5a) to (2.5b), we find

$$2t_0/U=x(2+2^{1/2}\alpha)/(x+\alpha) , \quad (2.16)$$

where $x^2=\overline{\nu}/\overline{\kappa}$ and $\alpha=[2c/(1-c)+x^2]^{1/2}$. We may rewrite Eq. (2.5b) as

$$\frac{t_0}{(-\overline{\epsilon})}=\frac{2}{1+c}\left(\frac{1-c}{2^{1/2}}(x+\alpha)+c\right)\left(2^{1/2}\alpha^{-1}+1\right). \quad (2.17)$$

First let us examine these equations in the two limits $U\rightarrow\infty$ and $t_0\rightarrow\infty$. In the latter case, $x\gg1$ and

$$\frac{2t_0}{U}=2^{-1/2}x \text{ and } \left(\frac{t_0}{-\overline{\epsilon}}\right)=2^{3/2}\frac{(1-c)}{1+c}x . \quad (2.18)$$

Solving for the critical value of U, we find

$$U_{\text{crit}}=\frac{8(1-c)}{(1+c)}(-\overline{\epsilon}) . \quad (2.19)$$

In the $U\rightarrow\infty$ limit, $x\ll1$ and

$$2t_0/U=2^{1/2}[(1-c)^{1/2}/c^{1/2}+1]\,x , \quad (2.20)$$

and one finds for the critical value

$$t_{0\ \text{crit}}=\frac{2}{1+c}(-\overline{\epsilon})[(1+c)^{1/2}+c^{1/2}]^2 . \quad (2.21)$$

For a general value of $2t_0/U$ it is straightforward to solve Eqs. (2.16) and (2.17) and we obtain the results shown in Fig. 2. At large values of t_0 and U the system is insulating and there are critical values for t_0 and U below which the system will not form an insulating phase.

It is interesting to compare these results with the recent experimental results on the addition of various impurities to V_2O_3.[1,5] There are two experimental points to be made. (a) Impurities which are very stable trivalent ions such as Cr^{3+}, Al^{3+} stabilize the insulating phase. (b) The effects of such impurities can be counteracted by applying pressure and there is a linear scaling relationship between the concentration of impurities and the pressure.

Consider first the addition of Cr to V_2O_3. Since Cr has an extra electron and a very stable Cr^{3+} configuration we can approximate it within our model Hamiltonian (2.1) by taking $t_0 < 0$ and $|t_0| \gg U$ and $\overline{m}=\frac{1}{2}(1+c)$. Because of the particle-hole symmetry we may rewrite the Hamiltonian in terms of hole operators. Thus the problem at hand is identical to the impurity problem with $t_0 \gg 0$ and $\overline{m}=\frac{1}{2}(1-c)$.

The critical value of U is then given by Eq. (2.19). Expanding for small values of c, one obtains

$$U_{\text{crit}}(c)=(-8\overline{\epsilon}_{(c=0)})\left[1-c\left(2-\frac{d\ln(-\overline{\epsilon})}{dc}\bigg|_{c=0}\right)\right] \quad (2.22)$$

and $\overline{\epsilon}$ is a function of c through the condition on the number of electrons. Assuming the second term in brackets is positive there is a linear reduction

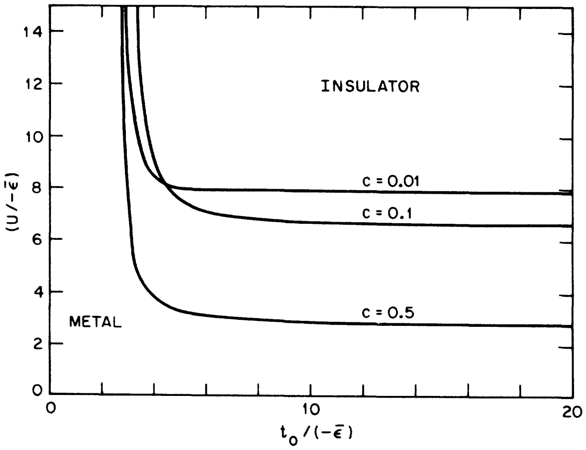

FIG. 2. Phase boundary between metallic and insulating behavior as a function of the intra-atomic Coulomb interaction U and the repulsive potential t_0 on the impurity sites for different values of the impurity concentration under the condition that the total number of electrons is equal to the number of host sites.

in the average and if U is held constant, the insulating phase is stabilized. On the other hand, the application of pressure broadens the bands and increases $(-\bar{\epsilon})$ so that

$$U_{\text{crit}}(c, P) = U_0\left[1 + P\frac{d\ln(-\bar{\epsilon})}{dP} - c\left(2 - \frac{d\ln(-\bar{\epsilon})}{dc}\bigg|_{c=0}\right)\right]. \tag{2.23}$$

If we make the reasonable assumption that U is only weakly dependent on pressure or composition we get a linear relation between applied pressure and concentration. The physical origin of the effect is clear. The effect of the pressure is to broaden the energy bands and to enhance the kinetic energy while the addition of Cr or Al because they are very stable trivalent ions reduces the itinerancy and therefore the average kinetic energy.

The situation as regards the addition of Ti and other types of doping is not clearcut experimentally. For some types of dopant there can be accompanying variations of the stoichiometry which complicates the situation. However, it is clear that within our model the introduction of impurities of different valence and small t_0 will tend to stabilize the metallic state. This is likely to be the case in Ti^{3+} doping.[11]

III. APPLICATION OF LANDAU-FERMI-LIQUID THEORY

As we noted in Sec. II the direct application of the Gutzwiller method to the impurity problem ignores all the effects of scattering. One can, however, make some progress towards understanding the transport effects by using the Gutzwiller approximation to give information on the Landau-Fermi-liquid parameters and thereby construct a Landau-Boltzmann transport equation. The present authors[3] have calculated the behavior of the effective mass, magnetic susceptibility, and screening constant near the Mott transition. Using the well-known relations of these quantities to the Landau parameters, one obtains the results

$$m/m^* = 1 - (U/U_0)^2 , \tag{3.1}$$

$$A_0 = U\rho(\epsilon_F)(1 + U/U_0)^{-1}(1 - U/U_0)^{-2} , \tag{3.2}$$

$$B_0 = U\rho(\epsilon_F)(1 + U/2U_0)(1 + U/U_0)^{-2} , \tag{3.3}$$

where A_0 and B_0 are the uniform averages of the singlet and triplet Landau interaction function, U_0 $(= -8\bar{\epsilon})$ is the critical value of U, and $\rho(\epsilon_F)$ is the band-structure density of states at the Fermi level. The Landau parameters whose order is greater than zero give a measure of the interaction energy when one has higher-order Fermi-surface distortions which do not change the total numbers of up- or down-spin electrons. Since within the Gutzwiller approximation the interaction energy depends only on the total numbers of up- and down-spin electrons it follows that within this approximation one has

$$A_n = B_n = 0 , \quad n \geq 1 . \tag{3.4}$$

This leads at once to the result for the current carried when the quasiparticle distribution function changes:

$$\vec{J} = \sum_{\vec{k}\sigma} e\,\vec{v}_{\vec{k}}\,\delta n_{\vec{k}\sigma} , \tag{3.5}$$

where $\vec{v}_{\vec{k}}$ is the velocity of a single quasiparticle which is renormalized by the effective mass. From this one finds that the conductivity at a frequency ω in the absence of scattering is given by

$$\sigma(\omega) = i\,\frac{e^2}{\omega}\sum_{\vec{k}\sigma}(\vec{v}_{\vec{k}}\cdot\vec{n})^2\,\delta(E_{\vec{k}\sigma} - \mu) , \tag{3.6}$$

where μ is the chemical potential and $\vec{n}$ is a unit vector parallel to the direction of the electric field. This can be written

$$\sigma(\omega) = \frac{ie^2 S_F v_F}{12\pi^3\omega} , \tag{3.7}$$

where S_F is the Fermi-surface area and v_F is an average quasiparticle velocity at the Fermi surface. Thus as the metal-insulator transition is approached S_F stays constant (at least for a simple model, see below) and $v_F \to 0$. The frequency-dependent conductivity decreases because of an increasing effective mass, while the effective number of carriers remains constant.

This is in contrast to translationally invariant systems where the conductivity at a fixed frequency is independent of the interaction strength. It is instructive to rederive Eq. (3. 5) by a different method which shows up the essential role played by the band structure. In the Gutzwiller approximation the bare particle-occupation number $m_{\vec{k}}$ has a simple form

$$m_{\vec{k}} = m_0 + q m^0(\vec{k}) , \tag{3.8}$$

where m_0 is a constant independent of $\vec{k}$ and $m^0(\vec{k})$ is the occupation number in the absence of interactions. In the presence of an electric field the current $\vec{J}$ is given by

$$\vec{J} = e\sum_{\vec{k}\sigma}\vec{v}^{\,0}_{\vec{k}\sigma}\,\delta m_{\vec{k}\sigma} , \tag{3.9}$$

where $\vec{v}^{\,0}_{\vec{k}}$ is the bare velocity determined by the band structure and $\delta m_{\vec{k}\sigma}$ is the change in the bare-particle distribution function. Since a full band carries no current we may assume that the constant term m_0 in (3. 8) plays no role, and we obtain the result

$$\vec{J} = e\sum_{\vec{k}\sigma} q\vec{v}^{\,0}_{\vec{k}\sigma}\,\delta m^0_{\vec{k}\sigma} . \tag{3.10}$$

Using the results that $qv^0_{\vec{k}} = v_{\vec{k}}$ and $\delta m^0_{\vec{k}\sigma} \equiv \delta n_{\vec{k}\sigma}$, we recover (3. 5). In general, as shown by Resibois,[12] there is a relation between the change in quasiparticle and bare-particle distribution functions of the form

$$\delta m_{\vec{k}\sigma} = q\,\delta n_{\vec{k}\sigma} + \sum_{\vec{k}'\sigma'} \gamma_{\vec{k}\sigma,\vec{k}'\sigma'}\,\delta m_{\vec{k}'\sigma'} \ , \tag{3.11}$$

where γ is the transformation function. Clearly within the framework of the Gutzwiller approximation, $\gamma \equiv 0$.

Up till this point we have considered the conductivity at a fixed frequency for a pure system. If we introduce a dilute set of scattering centers with a relaxation time τ then the change in quasiparticle distribution function caused by an electric field acting for a given time τ is

$$\delta n_{\vec{k}} = e\,\vec{E}\cdot\vec{v}_{\vec{k}}\,\tau\,\delta(E(\vec{k}) - \mu) \ . \tag{3.12}$$

In this formula there is a cancellation, for a fixed value of the time τ, between the enhanced density of states and the reduced velocity of the quasiparticles. However, in the presence of interactions the constant quantity is the mean free path $L = v_F\tau$. In the dilute limit clearly L must scale inversely with the concentration. Thus as the Mott transition is approached and the velocity v_F drops the relaxation time τ increases so as to keep the mean free path L constant. An examination of the detailed form of the renormalization of τ due to many-body effects given by Heine *et al.*[13] yields the same result. Thus we find that for a given set of impurities, the change $\delta n_{\vec{k}}$ in the quasiparticle distribution function becomes large as the Mott transition is approached. However, in the conductivity this is cancelled by the low velocity of the quasiparticles and we find

$$\sigma = e^2 S_F L / 12\pi^3 \ . \tag{3.13}$$

The conductivity therefore is independent of the strength of the interactions.

We had hoped in this work to investigate the possibility of an increased tendency towards Anderson localization[8] in the presence of strong correlations. This question has been discussed recently by Mott.[6] He has given an appealing description of this problem in terms of slightly overlapping Mott-Hubbard bands. He suggests that under such circumstances the effect of disorder scattering can be greatly enhanced and that Anderson localization will set in for a smaller amount of disorder. This point of view is supported by the recent experiments of McWhan *et al.*[7] on Cr-doped V_2O_3. In these experiments it was found that in the metallic phase at low temperature and high pressure, Cr impurities act as very strong scatterers. A rise in residual resistivity of ~ 140 $\mu\Omega$ cm per at.% Cr was measured and this is at least an order of magnitude larger than that observed for transition-metal alloys. This appears to conflict with the result we obtained in Eq. (3.12). Possible explanations for this dilemma are that the expansion in powers of $(k_F L)^{-1}$ breaks down very rapidly in this situation or that impurities nucleate a local insulating cluster leading to exceptionally large scattering centers.[14] However, it should be pointed out that the effect of the correlation is to decrease, not enhance, the scattering rate τ^{-1}.

The Hall effect should distinguish between the case of a small number of carriers and a large effective mass. It can be shown quite generally using Landau-Fermi-liquid theory[15] that at low temperature the number of carriers is related to the volume enclosed by the Fermi surface which is of course unaffected by the interaction. This suggests that for strongly correlated metals the Hall effect should be strongly temperature dependent. At temperatures high compared to the renormalized Fermi temperature (qT_F) one expects that all correlations caused by the Fermi surface should disappear and that the number of carriers entering the Hall effect should be related to ν, the number of doubly occupied sites. This latter statement has been proved, however, only in the atomic limit of the Hubbard model.[16]

Recently, McWhan *et al.*[7] have found that the Hall coefficient at high pressures and low temperatures is slightly larger than that observed at room temperature and 1 atm. This result argues against a heavy-mass model. However, an unambiguous interpretation of the Hall effect is not possible because of the multiple bands expected in V_2O_3.

It is clear from the above that the predictions of the strongly correlated model for conduction processes do not agree with experiment. This could be due to deficiencies in the theoretical treatment given in this section as discussed above. It could also mean that the model itself is inapplicable to the metallic state of V_2O_3. Possible alternative models are that V_2O_3 is a semimetal due to its band structure as suggested by Mott[6] or an *s*-*d* model where we assume electrons from different bands dominate the conduction processes and the density of states as measured by the susceptibility and specific heat. We shall not enter into a discussion here of the merits and demerits of these alternative models but refer the interested reader for such a discussion to Ref. 7.

ACKNOWLEDGMENTS

We would like to thank Professor N. F. Mott, P. W. Anderson, and D. B. McWhan for stimulating discussions.

APPENDIX

In this Appendix we derive the expression Eq. (2.3) for the coefficient $q(\bar{\nu}, \bar{\kappa}, \bar{\lambda})$ of the one-particle energy. In order to do this we follow Gutzwiller and assume that in the ground-state wave function the amplitude of a given configuration is reduced by an amount $\eta_H^\nu \eta_I^\lambda \theta^{2\kappa}$, where ν is the number of doubly occupied host sites, 2κ is the number of electrons on the impurities sites, and λ is the number of doubly occupied impurity sites. To obtain the norm of the wave function one calculates the number of configurations that can be obtained for given values of ν, λ, and κ and then sums over the possible values of these three variables.

Doing this one obtains for the normalization of the wave function the sum

$$N=\sum_{\substack{\nu\lambda\\ k}} \frac{(L-I)!\, I!\, \eta_H^{2\nu}\eta_I^{2\lambda}\theta^{4\kappa}}{\nu!\,\lambda!\,(m-\kappa-\nu)!\,(L-I-2m+2\kappa+\nu)!\,(m-\kappa-1)!}$$

$$\times\frac{1}{(\kappa-\lambda)!\,(I-2\kappa+\lambda)!\,(\kappa-\lambda)!}\ . \qquad \text{(A1)}$$

Here, as in Sec. II, L is the total number of sites, I is the number of impurity sites, and m is the total number of electrons of one spin. Since we will be interested in ratios of sums like (A1) we can replace these sums by their maximum term determined by setting the rates of change with respect to ν, λ, and κ equal to zero. In this way we can obtain an expression for η_H, η_I, and θ in terms of ν, λ, and κ. The results are

$$\eta_H^2=\nu(L-I-2m+2\kappa+\nu)/(m-\kappa-\nu)^2\ , \qquad \text{(A2)}$$

$$\eta_I^2=\lambda(I-2\kappa+\lambda)/(\kappa-\lambda)^2\ , \qquad \text{(A3)}$$

and

$$\theta^2=\frac{(\kappa-\lambda)(L-I-2m+2\kappa+\nu)}{(m-\kappa-\lambda)(I-2\kappa+\lambda)}\ . \qquad \text{(A4)}$$

In order to calculate $q(\bar\nu, \bar\kappa, \bar\lambda)$ we must calculate $\langle c_{i\uparrow}^\dagger c_{j\uparrow}\rangle$. Within the Gutzwiller approximation $\langle c_{i\uparrow}^\dagger c_{j\uparrow}\rangle$ is assumed to be of the form

$$\langle c_{i\uparrow}^\dagger c_{j\uparrow}\rangle = q(\bar\nu, \bar\kappa, \bar\lambda)\, w(i,j)\ , \qquad \text{(A5)}$$

where $w(i, j)$ is the unperturbed correlation function of the original Bloch state. The q is to be calculated by taking the random average over all configurations weighted according to the above prescription and normalized by dividing by N. In calculating this average one must carefully take into account the fact that j and i may be either host sites or impurity sites with or without a down-spin electron. Because the counting is symmetric in i and j this leads to ten distinct sums. After keeping only the maximum term and dividing by N, we obtain the following expressions for the various possibilities:

(i) i and j impurity sites with no down-spin electrons,

$$(\kappa-\lambda)(I-2\kappa+\lambda)/m(L-m)\ ; \qquad \text{(A6)}$$

(ii) i and j impurity sites with one site occupied by a down-spin electron,

$$\eta_I(\kappa-\lambda)^2/m(L-m)\ ; \qquad \text{(A7)}$$

(iii) i and j impurity sites both occupied by a down-spin electron,

$$\eta_I^2(\kappa-\lambda)^3/m(L-m)(I-2\kappa+\lambda)\ . \qquad \text{(A8)}$$

For contributions where i and j are both host sites the expressions are the same as above with $\eta_I \to \eta_H$, $\lambda\to\nu$, $I\to L-I$, and $\kappa\to(m-\kappa)$. There are four types of terms when i is an impurity site and j is not. These are

(iv) no down-spin electrons on either i or j,

$$\theta(m-\kappa-\nu)(I-2\kappa+\lambda)/m(L-m)\ ; \qquad \text{(A9)}$$

(v) a down-spin electron on j, the host site,

$$\frac{\theta\eta_H(m-\kappa-\nu)^2(I-2\kappa+\lambda)}{m(L-m)[L-I-2(m-\kappa)+\nu]}\ ; \qquad \text{(A10)}$$

(vi) a down-spin electron on i, the impurity site,

$$\theta\eta_I(\kappa-\lambda)(m-\kappa-\nu)/m(L-m)\ ; \qquad \text{(A11)}$$

(vii) a down-spin electron on both sites,

$$\frac{\theta\eta_H\eta_I(m-\kappa-\nu)^2(\kappa-\lambda)}{m(L-m)[L-I-2(m-\kappa)+\nu]}\ . \qquad \text{(A12)}$$

By adding all of these contributions together, substituting the values of η_H, η_I, and θ, and after some algebra, we arrive at the result

$$q(\nu,\kappa,\lambda)=\frac{1}{m(L-m)}\ \Big((m-\kappa-\nu)^{1/2}$$

$$\times\{\nu^{1/2}+[L-I-2(m-\kappa)+\nu]^{1/2}\}$$

$$+(\kappa-\lambda)^{1/2}[\lambda^{1/2}+(I-2\kappa+\lambda)^{1/2}]\Big)^2\ , \qquad \text{(A13)}$$

which is the same as (2. 3).

---

[1] D. B. McWhan and J. P. Remeika, Phys. Rev. B 2, 3734 (1970), and references therein.

[2] N. F. Mott and Z. Zinamon, Rept. Progr. Phys. 33, 881 (1970).

[3] W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 4302 (1970); also T. M. Rice and W. F. Brinkman, in *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills, E. Ascher, and R. I. Jaffe (McGraw-Hill, New York, 1971), p. 593.

[4] M. C. Gutzwiller, Phys. Rev. 137, A1726 (1965).

[5] D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Letters 23, 1384 (1969).

[6] N. F. Mott, J. Phys. Radium 32, 11 (1971).

[7] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice (unpublished).

[8] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[9] P. Soven, Phys. Rev. 156, 809 (1967).

[10] B. Velicky, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[11] D. B. McWhan, J. P. Remeika, T. M. Rice, W. F. Brinkman, J. P. Maita, and A. Menth, Phys. Rev. Letters 27, 941 (1971).

[12] P. Resibois, Phys. Rev. 138, B281 (1965).

[13] V. Heine, P. Nozières, and J. W. Wilkins, Phil. Mag. 13, 741 (1966).

[14] This possibility has been suggested to the authors by J. Friedel and J. R. Schrieffer.

[15] R. E. Prange, Phys. Letters 12, 181 (1964).

[16] W. F. Brinkman and T. M. Rice, Phys. Rev. B 4, 1566 (1971).

PHYSICAL REVIEW B VOLUME 5, NUMBER 11 1 JUNE 1972

Critical-Field Curve of Superconducting Lead[†]

G. Chanin and J. P. Torre
Service d'Aéronomie du Centre National de la Recherche Scientifique,
Verrières-le-Buisson, France

(Received 20 January 1972)

The critical field of pure monocrystalline lead has been measured throughout its range. A vibrating phase-boundary technique was used, permitting continuous observation of the boundary between the normal and superconducting phases within the sample. Because of the coexistence of both phases at all times, supercooling and superheating effects are avoided. Departures from thermodynamic equilibrium are small, as is indicated by the very weak hysteresis (as low as several parts in 10 000). The deviation curve is strongly positive, as expected for strong-coupling superconductors. The measured values of the usual superconductive parameters are $T_c = (7.195 \pm 0.006)\,^\circ\text{K}$, $H_0 = 803.4 \pm 0.3$ Oe, $dH_c/dT\,|_{T_c} = 237.3 \pm 1.1$ Oe/°K.

I. INTRODUCTION

The very low Debye temperature (~ 96 °K) and high critical temperature (7.2 °K) of lead class it as an extreme strong-coupling superconductor. In contrast to the negative values for the deviation from parabolic behavior that characterize the critical field curves of the weak-coupling superconductors, lead shows a positive deviation curve. While the Bardeen-Cooper-Schrieffer[1] (BCS) theory of superconductivity is in very close agreement with the deviation curves of weak-coupling superconductors such as aluminum,[2] intermediate- and strong-coupling superconductors remain difficult to treat theoretically. An extension of the BCS theory shows promise of handling this class of metals.[3]

The critical field curve of lead merits study because, in addition to its being a strong-coupling superconductor, no recent measurements have been made which determine the curve throughout its range, obtaining both H_0 and T_c for the same specimen. Since calorimetric measurements of the heat capacity are dominated by the lattice contribution, the electronic heat capacity cannot be accurately determined except from thermodynamic analysis of the critical field curve.

II. EXPERIMENT

A. Sample

The sample, a cylindrical single crystal of lead 2 mm in diam, 12 cm long, and nominal purity 99.999%, was supplied by Monocrystals Inc. of Cleveland, Ohio. It was selected from among three specimens of different manufacture for its surface regularity and smoothness. A chemical etch confirmed its single-crystal structure and freedom from surface defects. The sample quality may best be judged from its residual-resistance ratio. After the completion of the magnetic measurements, its electrical resistance was measured at room temperature and at 4.2 °K. For the latter, a series of resistance values at different field strengths from 560 to 780 Oe were extrapolated to zero field in order to obtain the normal-state resistance corrected for magnetoresistance effects. The residual-resistance ratio thus obtained was $R_{273}/R_{4.2} = 15\,000$ indicating a very high sample purity.

B. Apparatus

The cryogenic apparatus was designed to permit operation in three temperature ranges: He^3, He^4, and above 4.2 °K, without disassembly or warmup of the sample. The double-walled cryostat of Fig. 1 was mounted within conventional glass Dewars for liquid nitrogen and liquid helium. All materials used were nonmagnetic and nonsuperconductive in order to avoid perturbing the magnetic field near the sample. Two pairs of Helmholtz coils surrounding the outer Dewar were used to cancel the horizontal and vertical components of the Earth's magnetic field to less than 10^{-2} Oe over the region occupied by the sample. Within the liquid-nitrogen Dewar a solenoid provided the magnetic field for the superconductive transition. Its