PHYSICAL REVIEW B VOLUME 25, NUMBER 4 15 FEBRUARY 1982

New models for the positive and negative temperature coefficients of resistivity for TiO$_{0.80-1.23}$ metallic oxides

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(Received 17 August 1981)

A reexamination is made of previous resistivity data of the TiO$_{0.80-1.23}$ metallic oxide system, in which very large positive and negative temperature coefficients of resistivity α are observed. TiO$_{0.80-1.23}$ samples contain a large number of stoichiometric vacancies which can be thermally ordered and disordered, drastically changing the residual resistivity, without seriously affecting the superconducting T_c. Fitting the results to the two-level model shows that any resistivity due to the two-level system must operate in parallel with the normal electron-phonon interactions. A phenomenological formula, based on the ideas of incipient localization in very-high-resistivity materials, is introduced. This formula fits all the data for the TiO$_{0.80-1.23}$ system in a semiquantitative way. It also predicts that a zero α (the Mooij criterion) occurs when the elastic mean free path and the weak localization coherence length are approximately equal.

I. INTRODUCTION

It is well known, but not completely understood why, the electrical resistivity of many disordered and noncrystalline metallic conductors increases with decreasing temperature over a wide range of temperatures before becoming essentially temperature independent at relatively low temperatures. As was first pointed out by Mooij[1] $\alpha(T)$ (where $\alpha(T)$, or the temperature coefficient of resistance equal to $[1/\rho(T)][d\rho(T)/dT]$) is generally positive for metals with $\rho(0) < 100$ $\mu\Omega$ cm and usually negative for metals where $\rho(0) > 200$ $\mu\Omega$ cm. A number of theoretical models for this effect, some of which will be discussed later, have been proposed. However, the only certain criterion for a negative α remains the Mooij criterion, which means that the electron mean free path ($l = V_F\tau$ if the conductivity is calculated using the classical Boltzman approach) is one to several interatomic spacings. In order to obtain these ultrashort mean free paths it is necessary that the system must be highly disordered. In many instances, the exact nature of the disorder and how the electrons interact with the disordered lattice are not yet clear. A recent review of the electrical properties of disordered materials has been given by Tsuei.[2]

A less well-known fact is that many strong scattering conductors show saturation effects in their resistivity with increasing temperature. For instance, Fisk and Webb[3] have observed the resistivity of some $A15$ materials saturates with increasing temperature at about 135 $\mu\Omega$ cm, presumably where the mean free path l in the $A15$ compounds becomes comparable with the interatomic spacing. The Ioffe-Regal criteria[4] for the upper value of the resistivity states that the electron mean full path cannot be shorter than the interatomic spacing. Another example of this phenomenon is α manganese, the resistivity of which is 121 $\mu\Omega$ cm at 80 K,[5] after which it increases slowly to about 170 $\mu\Omega$ cm at 900 K, before dropping sharply at the α-β phase boundary.[6] Again, the mean free path of the electron would appear to be limited by the interatomic spacing.

The purpose of this paper is to analyze the resistivity data of the TiO$_{0.80-1.25}$ (or TiO$_x$) metallic transition-metal oxide system as a function of temperature. This system exhibits all the previously described phenomenon, having both very large negative and positive temperature coefficients of resistance α (Denker,[7] Suzuki and Takeuchi,[8] Banus *et al.*,[9] Hulm *et al.*[10]). The maximum value of $\rho(0)$ would appear to be about 500 $\mu\Omega$ cm and the criterion for a negative α would appear that $\rho(0)$ be larger than about 290 $\mu\Omega$ cm. The saturation resistivity at high temperatures, for samples with a positive α, is somewhat above 320 $\mu\Omega$ cm (Gamolshwalov and Rastamov,[11] Suzuki and Takeuchi[8]). All these values are about twice those observed for crystalline and amorphous metals. Another interesting feature of this system is

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that the primary sources of electron scattering at low temperature are clearly identifiable as nonstoichiometric oxygen and titanium vacancies, which occur in large numbers (approximately 15 at. %) in this system and which can to some extent be ordered and disordered by thermal annealing. Thermal annealing can even produce both a positive and negative α in the same specimen without significantly changing the number of vacancies.[10] All the above features combine to make TiO_x an ideal system to study the many perplexing features associated with the resistivity of highly disordered materials and the saturation of the resistivity of both positive and negative α materials at higher temperatures.

II. THE STRUCTURE AND ELECTRICAL RESISTIVITY OF TiO_x

The $TiO_{0.80-1.25}$ system[12,9] has statistically the NaCl structure at high temperatures, is stable over a wide composition range, and contains a large proportion of vacancies of both titanium and oxygen. The relative number of each type of vacancy depends strongly on the composition but the total number is approximately constant. For $TiO_{1.0}$ 15% of both kinds of sites are vacant, while $TiO_{1.25}$ has all the oxygen sites full but 22% of the titanium sites are empty. Below about 990 °C $TiO_{0.90}$ to $TiO_{1.10}$ can exist as an ordered monoclinic superlattice phase with vacancy ordering on every third atomic plane normal to the [110] direction. The above structures, both ordered and disordered, can be frozen in at temperatures below about 500 K.

Detailed theoretical calculations of the band structure of TiO have been carried out by Ern and Switendich,[13] while Goodenough[14] has also addressed the problem of the modification of the electrical properties of TiO_x by the vacancies. Overlap of the d bands of the Ti ions give rise to a narrow metallic d band. Lattice vacancies are stable as they reduce the effective density of conduction electrons and lower the Fermi energy by 2.2 eV. (To maintain the charge distribution of the NaCl structure it would appear that each titanium vacancy is occupied by two holes and each oxygen vacancy by two electrons.) The fact that the conduction is primarily via the titanium ions is supported by the fact that the residual resistance per titanium vacancy is 11.5 times that of an oxygen vacancy.[10]

While many experimental results have been published on the resistivity of the TiO_x system, really extensive work has been done only by Denker,[7] Suzuki and Takeuchi,[8] Banus *et al.*,[9] and Hulm *et al.*[10] As the results of Banus *et al.* do not extend below 77 K this paper will concentrate on the work of Denker, Suzuki and Takeuchi, and Hulm *et al.* Further, because the resistivity of some of Denker's samples show peculiarities at very low temperatures, the only samples discussed from his paper discussed are a single crystal of $TiO_{1.22}$ and some annealed TiO_1 samples. However, the features of Denker results in the temperature range 30–300 K agree with those of Hulm *et al.* and Suzuki and Takeuchi. Figure 1 shows the main results of Hulm *et al.*[10] for their quench cast TiO_x samples, while Fig. 2 shows the effect on the resistivity of annealing some of these samples. Figure 3 shows Denker's[7] results for annealed $TiO_{1.0}$. Figure 4 shows the $\rho(T)$ curve for a single crystal[7] of $TiO_{1.22}$ over a very large temperature range plotted using a $\log_{10}T$ scale. Figure 5 shows the results of Suzuki and Takeuchi[8] also plotted using a $\log_{10}T$ scale. The saturation or upturn in $\rho(T)$ around 300 K observed in Figs. 2 and 3 are not reproduced in the results shown in Figs. 4 and 5. It is, therefore, assumed that the resistivity of negative α TiO_x usually decreases below 295 $\mu\Omega$ cm at temperatures above 400–500 K. Partial annealing towards the ordered monoclinic structure may account for the increase in resistivity observed by Hulm *et al.*[10]

Small increases in the resistivity at low temperatures for samples with positive α's could possibly be accounted for by the Kondo effect, as these al-

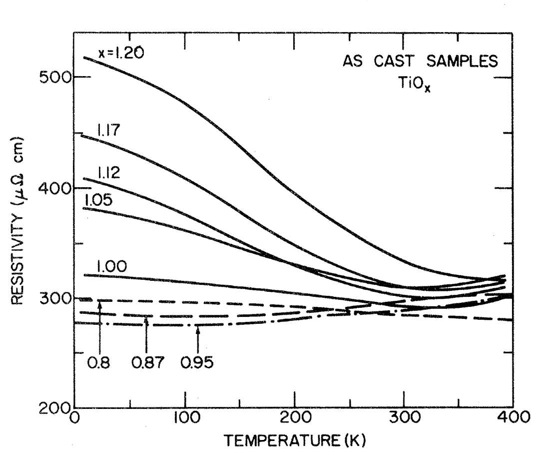

FIG. 1. The experimental results of Hulm *et al.* on as-cast TiO_x samples. These samples are referred to as H080, H087, H095, H100, H105, H112, H117, and H123. $\rho(0)$ is obtained by an extrapolation to $T=0$ K.

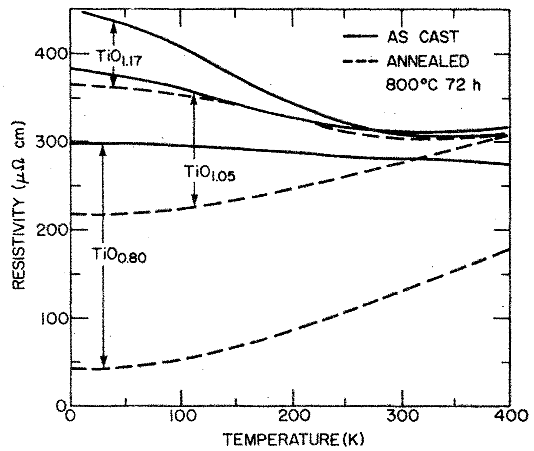

FIG. 2. The experimental results of Hulm *et al.* on as-cast and annealed TiO_x samples. These samples are referred to as H080, HA080, H105, HA105, H117, and HA117. The annealed samples have the prefix HA.

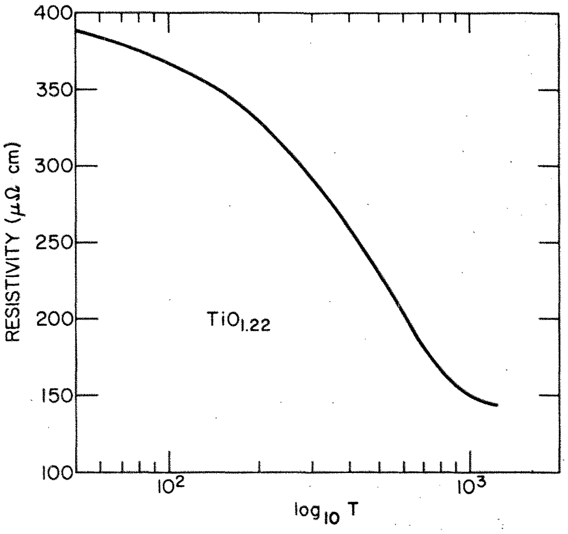

FIG. 4. The experimental results for a single crystal of $TiO_{1.22}$. Note the large range and magnitude of the negative temperature-dependent resistivity and the low resistivity value at $T = 1200$ K.

loys typically contained 50–100 ppm of iron.[7] It should be noted that any of the Kondo effect occurring in the TiO_x system is in a system in which all the conduction electrons are in the d band. The Kondo effect may also be present in materials with strong negative α's but, as at this stage, it cannot be separated from other resistive mechanisms, possible contributions due to the Kondo effect are henceforth ignored. The sharp increases in the resistivity at about 4 K, seen in some of Denkers negative α materials,[7] may also be attributable to the Kondo effect.

Hall effect measurements on the TiO_x system

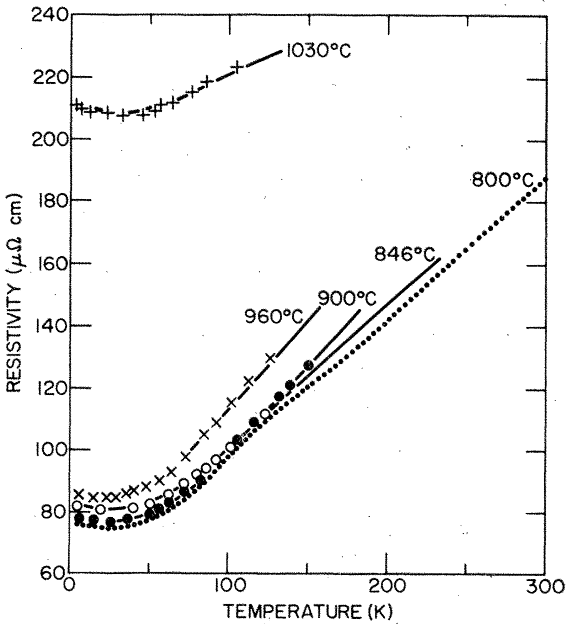

FIG. 3. The experimental results of Denker on ordered and partially ordered TiO. $\rho(\Theta_D)$ for $\rho(0) \approx 80$ $\mu\Omega$ cm is about 200 $\mu\Omega$ cm. For $\rho(0) \approx 210$ $\mu\Omega$ cm $\rho(\Theta_D)$ is 80 $\mu\Omega$ cm. The annealing temperatures are given in the figure.

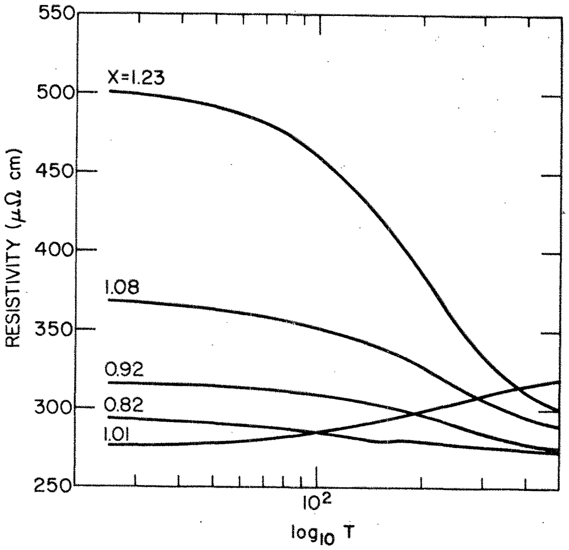

FIG. 5. The experimental results of Suzuki and Takeuchi. These samples are referred to as S082, S093, S101, S108, and S123. In the original plots the data points are given and the data extends down to helium temperatures.

have been reported by Denker[7] and Suzuki and Takeuchi.[8] The available results are very limited and for the various TiO_1 specimens reported vary widely. However, none of the Hall coefficients show a strong temperature dependence, which is to be expected for a metallic oxide. A "typical" value of the Hall coefficient is $1-2\times10^{-4}$ cm^3/c or $3-6\times10^{22}$ carriers per cm^3 which, based on the lattice constant, is about equal to the number of Ti atoms (5.48×10^{22} per cm^3) in stoichiometric TiO_1. Denker reports reflectivity data which is used to determine $N/m^*\epsilon_\infty$ for TiO_1 and $TiO_{1.22}$. Due to the lack of agreement in the Hall coefficients, these will not be used in the further interpretation of the data.

Specific-heat measurement at low temperatures have been reported by Okaz and Keesom.[15] Their results show the density of states to be a minimum (0.8 − 1.0 states/eV atom) for $x=1$ and to increase more rapidly for $x>1$ than $x<1$. The greatest observed change is $+40\%$ for $x=1.17$. The density of states also appears to depend upon the method of preparation.

Measurements of T_c have been made on as prepared (cast or quenched) samples and ones annealed at various temperatures at ambient pressure. The transition temperature lies between 0.5 and 1 K for x between 0.95 and 1.18, dropping sharply to 0 on either side. The results of Hulm *et al.*[10] and Reed *et al.*[16] show T_c to be essentially the same for ordered (annealed) or disordered (quenched) specimens. Therefore, the various parameters determining T_c appear not to be greatly affected by the ordering or disordering of the vacancies while the resistivity which, at least in the clean limit, depends on the same parameters is strongly affected by the order or disorder of the vacancies. It is also of interest to note that nearly stoichiometric TiO which is formed by annealing at high temperatures (1650 °C) and pressures (90 kbar) has a transition temperature of 2.3 K.[17]

III. DISCUSSION

Before discussing the results in detail, it is interesting to note that annealing the sample or ordering the vacancies into a superlattice can lower the residual by as much as 250 $\mu\Omega$ cm. This phenomenon can be understood in terms of the Bloch electron wave functions rearranging themselves to fit the new more ordered lattice. In ordered TiO_x (see Fig. 3), at least to a first approximation, Matthiessen's rule is obeyed and a residual resistivity plus phonon and other temperature-dependent resistivities would appear to account for the results. In terms of localization theory,[18–20] the ordering of the vacancies causes the energy levels of the adjacent blocks of side L to align with each other thereby allowing electrons to diffuse freely between blocks, destroying any tendency for the electrons to localize and thereby lowering the residual resistivity.

There are two basic approaches to the problem of negative resistivity coefficients in structurally disordered materials. The first is to make extrapolations from the highly conductive metallic side using Boltzman-type theory, even though the Boltzman approach is not valid for materials where the mean free path l is of the order of several atomic spacings or less. The two major models using this approach are the Ziman-type theory and the two-level model. The second approach is to make extrapolations from the insulating or Anderson localization regions towards the more metallic regions. Recent theories[21–24] have suggested that incipient localization is responsible for negative α's and the Mooij[1] criteria. A phenomenological formula based on the above ideas but which bridges the incipient localization region and the region where Matthiesen's rule is obeyed, while semiquantitatively predicting the Mooij criteria, will be proposed. This formula accounts in a semiquantitative way for most of the observed TiO_x resistivity data.

At this point, the correlation between the high-temperature resistivity and the residual resistivity at which the α changes sign should be noted. (This is of the order of 300 $\mu\Omega$ cm for TiO_x and 100 − 200 $\mu\Omega$ cm for metallic systems.[1,3,6]) From these results, it is clear that if the Ioffe-Regel[4] criterion determines the maximum resistivity at $T=0$ then it cannot also determine the saturation resistivity at high temperatures. However, if the Ioffe-Regal criterion is the limiting factor at high temperatures, then effective mean free paths of less than a lattice spacing must occur at low temperatures.

The correlation of the data for the TiO_x system with the two different approaches mentioned above will now be dealt with below. See Tsuei[2] for a more detailed review of the Ziman and the Kondo or two-level approach.

A. Ziman theory

The Ziman theory,[25] which was originally developed for liquid metals, predicts that the total resistance of an amorphous material can be expressed as follows:

$$\rho(T)=\rho(0)+AS(2k_F,T) \, . \tag{1}$$

Here A is a constant and the temperature dependence of the resistance follows that of the structure factor $S(2k_F,T)$. Based on a Debye approximation and an assumption that the Ziman condition for a negative α, $2k_F \approx k_p$, is satisfied, Nagal[26] has predicted that the temperature dependence should be $C_1-C_2T^2$ for $T<\Theta_D$ and C_3-C_4T for $T \gtrsim \Theta_D$ where Θ_D is the Debye temperature and C_1 to C_4 are constants.

The results shown in Figs. 1, 2, 4, and 5 do indeed show a $C_1-C_2T^2$ behavior at low temperatures (see below under two-level system) but do not show a linear temperature dependence over any extended region (Θ_D for TiO_x from the results shown in Fig. 3 is about 400 K). As TiO_x has a disordered NaCl crystalline structure with an approximately constant lattice spacing the RDF's are much sharper than for an amorphous material. With the varying Ti, and hence electron concentration, it is almost impossible that the condition $2k_F \approx k_p$ be maintained over the entire composition range. Further, the Ziman theory was never intended to account for a decrease in the resistivity by a factor of 2 as sometimes is seen in the TiO_x system. For these reasons, it is felt that the Ziman theory will not account for even the negative α's observed, much less the positive α's which are obtainable by a mere ordering of the vacancies. How the small changes in T_c observed in ordered and disordered TiO_x would be accounted for by this theory is also not clear.

B. The Kondo-type or two-level approach

The "structural Kondo" model was first proposed by Cochrane *et al.*[27] for explaining low-temperature resistance minima in metallic glasses but can be extended[28] to explain the occurrence of a negative α over a wide temperature range. The essential feature of this model is that there is an attractive interaction between the electrons and certain localized excitations. The localized excitations are approximated by a two-level system. This will then, in analogy with the magnetic Kondo effect, lead to an equation for the resistivity given by

$$\rho(T)=A-C\ln(T^2+T_\Delta^2) \, , \tag{2}$$

where A is a constant $[\rho(0)=A-C\ln T_\Delta^2]$, C is a measure of the "strength" of the two-level system, and k_BT_Δ is the energy difference between the levels characterizing the two-level system. For $T<<T_\Delta<\Theta_D$ Eq. (2) takes the form

$$\rho(T)=C_1-C_2T^2 \, . \tag{3}$$

Therefore, for $T<<T_\Delta<\Theta_D$ the Ziman and two-level theories are indistinguishable.

In Tsuei[28] the constant C was thought to be a measure of the abundance of two-level configurations. In the TiO_x system, as the number of vacancies is approximately constant, C can only be a measure of the disorder of the system, the best measure of which is the residual resistance.

The data for the samples with negative α's in the accompanying figures have been fitted to Eq. (2) using a computer program which minimizes

$$F=\{[\rho(\text{obs})-\rho(T)]^2\}^{1/2}/\mathscr{D} \, , \tag{4}$$

where $\mathscr{D}$ represents the number of data points and the results are listed in Table I. Figure 6 shows a plot C against $\rho(0)$ where, as one might expect, C extrapolates to 0, in the region where the α's change sign. There is no distinguishable trend in the values of T_Δ but they are well below the Θ_D which is about 400 K from resistivity measurements.[7]

However, as one cannot expect the two-level mechanism to shut off abruptly where the α is zero, one might suspect that the two-level mechanism is operating over and above the normal resistive mechanisms. These, at least at higher temperatures, are dominated by the electron-phonon interaction, usually represented by the Grüneisen function $G(T/\Theta_D)$. That the normal electron-phonon interaction is still operative is borne out by the fact that the superconducting transition temperature, which is extremely sensitive to changes in the electron-phonon interaction, is virtually unchanged by the ordering or disordering of the vacancies. This contention is supported by the work of Gurvitch *et al.*[19] who find that the transition temperature of Mo_3Ge increases with α-particle damage, while the α decreases and approaches 0 in the extreme case. The increase in T_c is attributed mainly to a change in the density of states $n(E_F)$ while the electron-phonon interaction, and hence the phonon density of states, is thought to be relatively constant. For this reason, the results have also been fitted using the same program and Eq. (4) with

TABLE I. Values of C and T_Δ obtained by fitting the experimental data to Eqs. (2) and (5). The quantity F is defined in Eq. (4). The letters H and HA refer to the samples of Hulm *et al.* while S refers to samples of Suzuki and Takeuchi.

Sample	$\rho(0)$	Eq. (2) C	Eq. (2) T_Δ	Eq. (2) F	Eq. (5) C	Eq. (5) T_Δ	Eq. (5) F
H080	297	−17.3	275	0.17	−147	165	2.4
H087	288				−108	137	1.5
H095	277				−108	139	1.6
H100	321	−8.12	69.6	0.79	−132	141	2.4
H105	382	−19.4	56.1	1.3	−135	121	2.1
H112	410	−30.2	58.3	1.6	−144	113	2.4
H117	447	−42.6	67.5	1.9	−157	112	2.4
H120	519	−79.7	106	1.5	−204	130	2.4
HA080	42.3				−44.5	90.2	1.9
HA105	216				−69.5	118	1.7
HA117	364	−19.5	74.8	1.6	−140	132	2.0
S082	296	−51.7	768	1.1	−145	157	2.4
S093	317	−14.1	109	0.28	−160	165	2.4
S101	277				−142	197	2.5
S108	370	−24.3	89.6	0.43	−166	152	2.6
S124	503	−61.3	82.2	1.9	−193	125	2.9

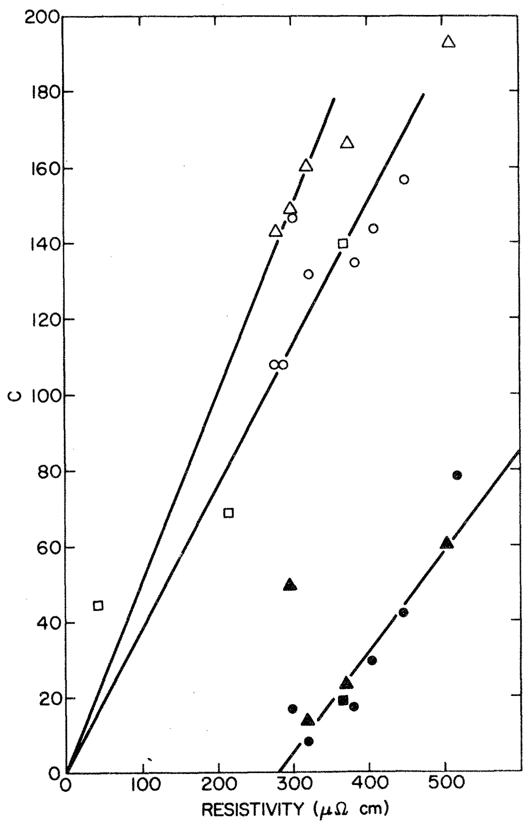

FIG. 6. The results obtained for the coefficient $|C|$ by fitting the data using Eq. (2) (closed ▲, ●, ■) and Eq. (5) (open △, ○, □). [Suzuki and Takeuchi (▲ and △), Hulm *et al.* (● and ○ as cast) and (■ and □ annealed)]. Note Eq. (5) enables values of $|C|$ to be obtained for samples with positive α's.

$$\rho(T)=A-C\ln(T^2+T_\Delta^2)+250G(T/400)\,, \tag{5}$$

where $G(T/400)$ is the Grüneisen function. Fixed values of the Debye or Grüneisen temperature Θ_D (400 K) and $\rho(\Theta_D)$ (250 $\mu\Omega$ cm) have been assumed. These values are obtained from Denker,[7] the value of 250 $\mu\Omega$ cm being obtained by extrapolating his values of $\rho(\Theta_D)$ to $\rho(0)=0$. Θ_D and $\rho(\Theta_D)$ could be made variable but with five variables $[A,C,T_\Delta,\rho(\Theta_D),\Theta_D]$ the program gave inconsistent results and at this stage of our knowledge principles are more important than exact results. The values of C, T_Δ, and F obtained in this manner are also shown in Table I and C is plotted in Fig. 6. Sample HA080 is extremely sensitive to the choice of $\rho(\Theta_D)$ and Θ_D and so the values obtained can be disregarded.

The values of F obtained using Eq. (5) are higher than for Eq. (2) indicating that Eq. (5) does not fit the data as well as Eq. (2). However, it should be realized that the Grüneisen function and the values of $\rho(\Theta_D)$ and Θ_D may not accurately account for the non-two-level temperature-dependent part of the resistivity. The important point is that the values of $|C|$ obtained using Eq. (5) can be extrapolated to O for $\rho(0)=O$, which must be the case for a perfect crystal. The values of T_Δ from Eq. (5) are closer to Θ_D than for Eq. (3).

Based primarily on the fact that $|C|$ should tend to zero for a perfect crystal and that T_c is not strongly dependent on disorder, it is concluded that the two-level mechanism, if it is relevant, must be in parallel with the normal electron-phonon mechanism.

Reference to Figs. 4 and 5 shows that, although there is a linear region when the data are plotted against $\log_{10}T$ the results also deviate from linearity at high temperatures. This indicates either the two-level mechanism plays no major role in determining the α or that Eqs. (2) and (5) are an inadequate description of the resistivity due to the two-level mechanism in TiO_x.

However, TiO_x still provides an ideal system for further testing the two-level (and other models) as the α's are large and can be changed by simple annealing while the number of clearly identifiable scattering centers remains almost constant. The verification of the two-level model would then depend on whether additional experiments or theoretical calculations are able to show that disordered stoichiometric vacancies can give rise to temperature-dependent resistivities of the observed magnitudes. As the energy levels of the electrons and/or holes trapped in the vacancies are almost certainly below the Fermi energy, electronic transitions will probably not be the appropriate two-level system. This would appear to leave localized phonons or distortions of the vacancies as the most probable two-level system. It is doubtful if localized phonons or distortions can give rise to resistivities as large or larger than the normal phonons unless, due to the short mean free paths, there is some kind of resonance or cooperative effect.

As it is crystalline, TiO_x also provides a possible material in which a critical experiment looking for the correlation between α and the phonon density of states can be performed, using inelastic neutron scattering.

C. Incipient localization

The scaling theory of localization,[18,19] which was constructed by Abrahams *et al.*[20] to deal with the Anderson transition in a noninteracting electron gas, leads to a formula

$$\sigma_0 = Ag_c e^2/\hbar\xi \tag{6}$$

which relates the localization, or perhaps better, coherance length ξ and the conductivity in a three-dimensional highly disordered material. Ag_c is expected to be of the order of or somewhat greater than unity. This equation is also consistent with results obtained earlier by Wegner.[30] The above results hold in the limit $l_{\mathrm{in}}(T) > \xi$, where $l_{\mathrm{in}}(T)$ is the temperature-dependent inelastic mean free path. If $l_{\mathrm{in}}(T) < \xi$ Eq. (6) becomes[22]

$$\sigma = Bg_c e^2/\hbar l_{\mathrm{in}} \ . \tag{6'}$$

A convenient interpolation formula between Eqs. (6) and (6′) is[23,24]

$$\sigma = (Ce^2/\hbar)[1/l_{\mathrm{in}}(T) + 1/\xi] \ . \tag{7}$$

At sufficiently low temperatures $[l_{\mathrm{in}}(T) > \xi]$ and assuming $\rho_{\mathrm{in}}(T) = K/l_{\mathrm{in}}(T)$ Eq. (7) can be inverted and expanded to give

$$\rho(T) = (\hbar\xi/Ce^2) - (\hbar\xi/Ce^2)(\xi/K)\rho_{\mathrm{in}}(T) \ . \tag{8}$$

Identifying $\hbar\xi/Ce^2$ as $\rho(0)$ and assuming $K/\rho(0) = \lambda$ (which is probably of the order of l_{el}) Eq. (8) becomes

$$\rho(T) = \rho(0) - (\xi/\lambda)\rho_{\mathrm{in}}(T) \tag{8'}$$

Note this equation predicts only negative α's. However, if the constant λ is incorporated so that the equation becomes

$$\rho(T) = \rho(0) + [(\lambda - \xi)/\lambda]\rho_{\mathrm{in}}(T) \ . \tag{9}$$

Both positive and negative α's are possible. In effect, what has been done is to add the temperature-dependent resistivity to Eq. (8′). This is similar to what was done to Eq. (2) in order to obtain Eq. (5) in the preceding section. The remarks made in justifying this step in that section are also applicable here.

Assuming that the correct expression for $\rho_{\mathrm{in}}(T)$ is known, the above equation predicts the following.

(1) A negative α in highly resistive materials where $\xi > \lambda$.

(2) The Mooij criterion for $\lambda = \xi$.

(3) The decreasing positive α, with increasing residual resistivity, observed in many materials.

(4) Mattheissen's rule for low-residual-resistivity materials.

In all localization theories, the only situation dealt with is the one where the conductivity is of a diffusive nature with $\xi >> l_{\mathrm{el}}$ and negative α's are predicted. It is, therefore, not unreasonable that the Mooij criteria ($\lambda = \xi$) in Eq. (9) should occur where $\xi \sim l_{\mathrm{el}}$.

The free-electron-type equation[31] which is often used to obtain the mean free path in disordered materials[2] can be expressed in Å as

$$\lambda = Dl_{\mathrm{el}} = 92D(r_s/a_0)^2\rho(0)^{-1} \ , \tag{10}$$

where r_s/a_0 is the radius of the free-electron sphere r_s in units of the Bohr radius a_0 and the resistivity $\rho(0)$ is in $\mu\Omega\,\mathrm{cm}$. D is of the order of unity if one identifies λ with l_{el}. Equating λ and ξ, given by $(Ce^2/\hbar)\rho(0)$, one obtains for the Mooij criterion

$$\rho_m=\sqrt{D/C}\,(r_s/a_0)61.4 \tag{11}$$

in units of $\mu\Omega\,\mathrm{cm}$. As for most metals r_s/a ranges from ~ 2 to 3.5, Eq. (11) gives ρ_m in the range $122(D/C)$ to $214\sqrt{D/C}$ $\mu\Omega\,\mathrm{cm}$ which for $\sqrt{D/C}\sim 0.8$ is the Mooij criteria. The corresponding value of $\lambda=\xi=7.2\sqrt{CD}$ Å. That ρ_m for TiO_x lies at about 300 $\mu\Omega\,\mathrm{cm}$ can easily be accounted for by the fact that only the Ti atoms donate carriers to the conduction band (i.e., large r_s/a_0). In addition, the carriers have to percolate around the oxygen ions when carrying an electric current. Multiplying $(\lambda-\xi)/\lambda$ in Eq. (9) by $Ce^2/\hbar$ allows one to express Eq. (9) as

$$\rho(T)=\rho(0)+\{[\rho_m-\rho(0)]/\rho_m\}\rho_{\mathrm{in}}(T)\;. \tag{12}$$

At this state, it is not possible to say whether Eq. (9), Eq. (12), or neither is of basic physical importance. The fitting of the data will be done using Eq. (12). To convert to lengths as in Eq. (9), the factor $Ce^2/\hbar$ may be used.

If an appropriate expression for $\rho_{\mathrm{in}}(T)$ is known, the prediction of Eqs. (9) and (12) can be compared with the results for TiO_x. As these equations reduce to Matthiessen's rule for low $\rho(0)$, the most appropriate first approximation for $\rho_{\mathrm{in}}(T)$ for low $\rho(0)$ materials might be the Grüneisen function $G(T/\Theta_D)$, especially if the temperature range over which the comparison is done is fairly large. However, for high-residual-resistivity materials localization theories predict temperature dependences of the form ET^n, where E is a constant and n depends on the type of inelastic scattering the electrons are experiencing. As in the temperature range 1 – 125 K the dominant inelastic scattering is probably due to phonons $n=1.5$.[32] On the other hand, over a more extended range of temperature, based on the premise that $\rho_{\mathrm{in}}(T)\alpha(l_{\mathrm{in}}l_{\mathrm{el}})^{1/2}$, another possible temperature dependence is $[G(T/\Theta_D)]^{1/2}$.

To test Eq. (12) [and (9)], the data from Figs. 1, 2, and 5 are fitted to Eq. (12) [substituting $Bf(t)$ for $\rho_{\mathrm{in}}(T)$] using a program which minimizes

$$F=[\rho(\mathrm{obs})-\rho(T)]^{1/2}/\mathscr{D} \tag{13}$$

(where $\mathscr{D}$ represents the number of data points) by varying B for a given $f(T)$ in the temperature range 1 – 125 K. Here ρ(obs) is the experimental data and $f(T)$ is either $G(T/400\ \mathrm{K})$, $G^{1/2}(T/400\ \mathrm{K})$, or $T^{1.5}$. The results of these fits are shown in Table II. In Fig. 7 B is plotted against $\rho(0)$ for $f(T)=G(T/400\ \mathrm{K})$ thereby determining ρ_m and $\rho(\Theta_D=400\ \mathrm{K})$. The values of ρ_m and $\rho(\Theta_D)$ would appear to lie between 250 and 270 and 300 and 350 $\mu\Omega\,\mathrm{cm}$, respectively. A similar plot for $f(T)=T^{1.5}$ (Fig. 8) gives ρ_m and B between 250 and 280 and 0.045 and 0.048, respectively. The results using $G^{1/2}(T/400\ \mathrm{K})$ when plotted against $\rho(0)$ look very similar. The fit using $f(T)=T^{1.5}$ gives lowest values fo F (Table II). Note these results are based primarily on the low-temperature resistivity data. The values of $\rho(\Theta_D=400\ \mathrm{K})$ would appear to be somewhat higher than previously supposed i.e., 300 – 350 instead of 250 $\mu\Omega\,\mathrm{cm}$).

Note that the use of the Gruneisen function implies a phonon density of states and an electron-phonon interaction which are unaltered by the disorder of the vacancies. The diffusive-type of conductivity leading to the $T^{1.5}$ temperature dependence is based on a typical phonon density of states and, therefore, presumably does not predict T_c to be a strong function of disorder.

The results of Suzuki and Takeuchi[8] and also Gamolchvalov and Rustamov[11] show that the resistivity of TiO_1, with a positive α, tends to saturate with increasing temperature at a value somewhere between 320 and 350 $\mu\Omega\,\mathrm{cm}$. Figures 1, 2, 4, and 5 show that at high temperatures the resistivity of negative α samples in general lies lower than that of positive α samples. Whether the resistivity always continues to decrease with temperature as shown in Figs. 4 and 5 or can start to increase again as shown in Fig. 1 is not yet clear. These high-temperature saturation effects may be incorporated in Eq. (9) or (12) by defining a suitable temperature dependent $\lambda(T)$ and $\xi(T)$ or $\rho_m(T)$. At the moment, no justification exists other than phenomenologically fitting the data. One, and perhaps the simplest, possibility is to redefine ξ as

$$\xi(T)=(Ce^2/\hbar)\rho(T)\;. \tag{14}$$

If this is done and ρ_∞ substituted for ρ_m Eq. (12) becomes

$$\rho(T)=\frac{\rho(0)[1+Bf(T)/\rho(o)]}{1+Bf(T)/\rho_\infty}\;. \tag{15}$$

TABLE II. Values of B and ρ_∞ obtained by fitting the experimental data to Eqs. (12) and (15), respectively. The quantity F is defined in Eq. (13).

		Eq. (12)						Eq. (15)	
		$BG^{1/2}(T/400\text{ K})$		$BG(T/400\text{ K})$		$BT^{1.5}$		$BT^{1.5}$	
Sample	$\rho(0)$	B	F	B	F	B	F	ρ_∞	F
H100	321	−20.9	0.204	−50	0.054	−0.0071	0.15	254	0.29
H105	382			−157	1.67	−0.0220	0.44	246	1.55
H112	410	−104.8	1.14	−252	2.86	−0.0356	0.85	214	1.80
H117	447	−118.2	0.88	−288	2.78	−0.0401	0.49	204	1.85
H120	519	−137.3	1.33	−334	3.41	−0.0466	0.84	196	1.81
HA080	42.3	+33.9	0.41	+127	0.37	+0.0115	0.35		
HA105	216	+25.0	0.27	+63	0.34	+0.0085	0.21	375	1.68
HA117	364	−37.3	0.25	−92	0.72	−0.0127	0.11	252	1.67
S082	296	−33.0	0.71	−77	1.49	−0.0112	0.74	254	0.99
S093	317	−26.0	0.32	−61	0.87	−0.0088	0.32	252	0.27
S101	277	+22.3	0.68	+58	0.31	−0.0076	0.69	351	0.43
S108	370	−55.0	0.38	−134	1.62	−0.0187	0.34	245	0.37
S123	503	−123.4	1.28	−310	1.95	−0.0419	1.08	205	2.04

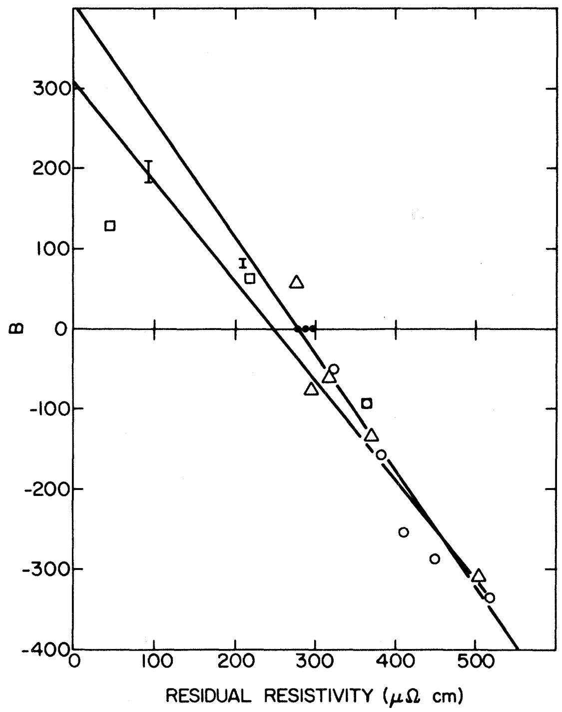

FIG. 7. Values of B, obtained by fitting the data using Eq. (13) with $f(t)=G(T/400\text{ K})$, plotted against the residual resistivity $\rho(0)$. The notation for the points is the same as in Fig. 6 except that the values of B from Fig. 3 are included as (I) and the samples H080, H087, and H095 are assumed to have a zero α and are marked (●).

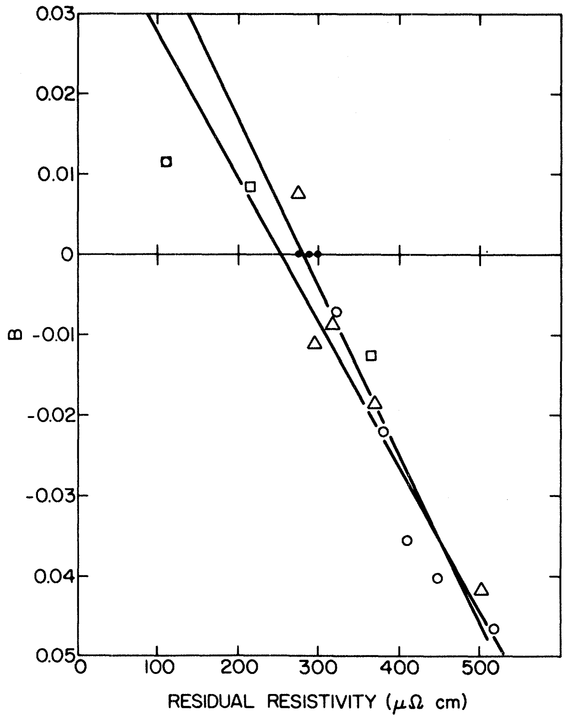

FIG. 8. Values of B, obtained by fitting the data using Eq. (13) with $f(t)=T^{1.5}$, plotted against the residual resistivity $\rho(0)$. The notation for the points is the same as in Figs. 6 and 7.

As T and hence $f(T)$ tend to infinity $\rho(T)$ tends to ρ_∞; therefore, ρ_∞ is now not so much the Mooij resistivity but rather the limit of $\rho(T)$ as T tends to infinity. The interesting correlation between the Mooij resistivity and $\rho(T \to \infty)$ or ρ_∞ has already been pointed out.

Fitting the data over the entire temperature range using Eqs. (14) and (15) with $f(T)$ equal to $0.045T^{1.5}$ and $0.048T^{1.5}$ and varying ρ_∞ results in the last values of F and ρ_∞ shown in Table II. The values of ρ_∞ plotted against $\rho(0)$ are shown in Fig. 9.

Figure 9 confirms what might be suspected from Figs. 4 and 5, which is that ρ_∞ decreases with increasing residual resistivity. In fact, Fig. 9 represents a "phase diagram" with $\rho(0)$ given on the X axis and ρ_∞ on the Y axis. This shows all samples with $\rho(0) < \rho_\infty$ to have positive α's while for $\rho(0) > \rho_\infty$ negative α's are observed. If the above extension of Eq. (12) is true, ρ_m is not a constant for the $TiO_{0.80-1.23}$ system and ρ_∞ is ρ_m for that particular sample. This leads to the interesting possibility that negative α's occur when the elastic mean free path (l_{el}) is shorter than the minimum inelastic mean free path (l_{in}) or minimum phonon wavelength (see next paragraph). A very similar plot is obtained if B is set constant at 300 $\mu\Omega$ cm and $G(T/400\text{ K})$ is used for $f(t)$ in Eq. (15). Another very similar plot is obtained using $B=170$ and $f(T)=G^{1/2}(T/400\text{ K})$. The average F value is lowest for $T^{3/2}$ followed by $G(T/400\text{ K})$.

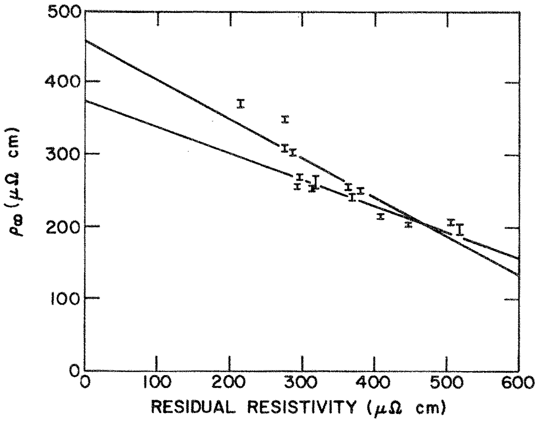

FIG. 9. Values of ρ_∞ obtained by fitting the data over the entire temperature range using Eqs. (14) and (15) with $Bf(t)$ equal to $0.045T^{1.5}$ and $0.048T^{1.5}$. The tops and bottoms of the data points (I) are the actual values obtained for the two different coefficients of $T^{1.5}$.

In Fig. 9 extrapolation based on all the points gives $\rho_\infty \approx 450$ $\mu\Omega$ cm for $\rho(0)=0$ and for $\rho_\infty=0$ a value for $\rho(0)$ (or a maximum metallic resistivity) of ~ 850 $\mu\Omega$ cm. Using Eq. (10) to determine the mean free path l at the intercepts gives ~ 4.7 and ~ 2.5 Å, respectively. In TiO_x, the Ti-Ti distance is 3.0 Å and the Ti-O distance is 2.1 Å. Therefore, the above mean free paths could well correspond to the minimum phonon wavelength $(l \approx 2a)$ for the lattice and the minimum interatomic spacing (a), respectively. The value of 850 $\mu\Omega$ cm is, therefore, in accord with the Ioffe-Regel criterion $(l \approx a)$ for the maximum metallic resistivity. Based on the negative α points, which lie in a better straight line, and for which the $T^{1.5}$ temperature dependence is more likely to hold, the intercepts would be ~ 380 and ~ 1050 $\mu\Omega$ cm, respectively. For the temperature dependences $300G(T/400\text{ K})$ and $170G^{1/2}(T/400\text{ K})$ the intercepts are very similar and lie in the range 400 to 500 $\mu\Omega$ cm and 780 to 880 $\mu\Omega$ cm, respectively.

While the validity of Eq. (15) is doubtful, it certainly does allow reasonable extrapolations to be made to high temperatures and allows one to conclude ρ_∞ depends strongly on $\rho(0)$ and contrary to what might be expected lies lower for higher values of $\rho(0)$. Equation (15) will not work in materials where the resistivity first decreases and then increases with temperature.

Based on the above experimental results, it would appear that the regular lattice waves (or vibrations) in the ordered lattice can, with increasing temperature, give rise to a saturation resistivity where the electron mean free path is comparable to the minimum phonon wavelength. On the other hand, the irregular lattice vibrations on a disordered lattice main role would appear to be the delocalization of the electrons by thermal excitations, leading to a continual decrease in the resistivity with temperature of a highly disordered material. The results also imply that lattice vibrations or phonons in highly disordered materials are unable to cause the ultrashort phonon limited electron mean free paths observed in ordered materials. One has here something of a paradox in that, as far as the electrons are concerned, a disordered system with phonons is more ordered than an ordered system with phonons.

However, it is important to note that as $\rho(0) \to O$ Eq. (15) reduces to the phenomenological parallel resistor formula,

$$\frac{1}{\rho}=\frac{1}{\rho_{\text{ideal}}}+\frac{1}{\rho_{\text{sat}}} \text{ or } \frac{1}{\rho_{\text{in}}}+\frac{1}{\rho_{\infty}} \qquad (16)$$

proposed by Wiesman *et al.*[33] Therefore, much of the data (see, for instance, Gurvitch,[34] Refs. 6–14) fitted using the parallel resistor formula could also be accounted for by Eq. (15). Gurvitch[34] has recently given an interpretation of ρ_{sat} in Eq. (16) as the resistivity where $l=a$. If this is the case, then in many of the $\text{TiO}_{x>1}$ specimens the effective mean free path must be less than the interatomic spacing. This sort of physical situation can only be visualized as some form of localization. The fact that the electrons have to percolate around the oxygen ions, or to some extent are trapped in a cage of oxygen ions, may be why very small effective mean free paths and large negative α's are observed in the TiO_x system. It should also be noted that ρ_∞ or (ρ_{sat}) decreases with increasing electron (or relative Ti) concentration, this is in accord with Gurvitch's[34] predictions.

The authors of Refs. 7–10 never specifically looked for very low-temperature electron-electron interaction resistivity of the type observed by Rosenbaum *et al.*[32] Therefore, a small contribution of this nature to the observed low-temperature resistivity cannot be ruled out. The cusps observed at the lowest temperatures by Denker[7] may be a manifestation of the effects described in Rosenbaum *et al.*[32]

IV. SUMMARY

If, based on the nonvariance of T_c with disorder and the consistency of the results, one can conclude that in the TiO_x system the major changes, due to ordering and disordering the vacancies, are in the residual resistivity and not in the electron and phonon density of states or the electron-phonon interaction, the following conclusions can be made:

(1) The Ziman-type theory will not account for the results.

(2) A two-level-type resistivity is not ruled out but it must operate in parallel with the normal electron-phonon mechanisms.

(3) The TiO_x system is an almost ideal one for further calculations and experiments to test the two-level model and to show whether or not it is able to give effects as large as those observed in TiO_x.

(4) Using reasonable temperature dependences for the inelastic resistivity, it is shown that the absolute magnitude of the α is proportional to $|\rho(0)-\rho_m|$. (This also applies to the simple two-level model [Eq. (2) and Fig. 6].)

(5) A new class of phenomenological formulas have been introduced which account, at least a semiquantitative way, for all the resistivity results observed in the TiO_x system with a minimum of parameters, all of which have some physical basis. For high-residual-resistivity materials at low temperatures these formulas incorporate current ideas on localization resistivity. At low residual resistivities, Mattheisen's rule is recovered.

(6) These formulas show that for both metallic systems and the TiO_x metallic oxide system the residual resistivity at which the elastic mean free path (l_{el}) is approximately equal to the weak localization coherence length (ξ) is equivalent to the Mooij resistivity (ρ_m). This ansatz also predicts how the Mooij resistivity (ρ_m), for a zero α, changes with carrier concentration.

(7) It is also clearly demonstrated that the high-temperature saturation resistivity ρ_∞ for high $\rho(0)$ samples is lower than for low $\rho(0)$ samples.

ACKNOWLEDGMENTS

The author would like to acknowledge the valuable assistance of C. C. Tsuei, who not only introduced him to this subject but also provided many stimulating discussions and critically read the manuscript. Y. Imry is thanked for his suggestion that incipient localization may be causing the negative temperature coefficients of resistance.

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