waves, we can also derive all the above results for metals, with ϵ replaced by the generalized dielectric constant $\epsilon - i\sigma/\omega$. A difficulty to be kept in mind is the increased effectiveness of screening, which increases the importance of higher-order perturbation terms and requires a consideration of the wave-number dependence of the dielectric constant. We expect that the latter effect will largely cancel out, owing to the fact that the weight of an unperturbed plane wave $|\vec{q}\rangle$ in a perturbed wave $|\vec{k}\rangle$ generally equals that of the unperturbed plane wave $|\vec{k}$ in the perturbed wave $|\vec{q}\rangle$.

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Metal-Insulator Transitions: A Simple Theoretical Model

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A simple theoretical model for metal-insulator transitions is presented. It is based on the existence of both localized (ionic) and band (Bloch) states. It differs from other theories in that it assumes the one-electron states to be essentially unchanged by the transition. The electron-hole interaction is responsible for the anomalous temperature dependence of the number of conduction electrons. The model is studied in detail for several specific band models, in particular, for an *s*-like tight-binding cubic structure. The conditions for the presence of metallic and insulating phases at all temperatures as well as for the existence of first-order and higher-order transitions are given. The possibility of formation of bound-exciton states and the scattering mechanism responsible for the resistivity are also discussed.

I. INTRODUCTION

Transition-metal as well as rare-earth oxides, sulfides, and borides constitute a large group of substances which exhibit an unusually wide variety of electrical and magnetic properties.[1] Among these substances there are (i) excellent conductors, such as TiO, ReO_3, and CrO_3, with resistivities[2] as low (for ReO_3) as 4×10^{-7} Ω cm at 77 °K; (ii) insulators[3] such as MnO and CoO with room-temperature resistivities of $10^{8}-10^{15}$ Ω cm; and (iii) some substances whose resistivities show an unusually large variation with temperature. Of this third group, some materials present a first-order transition in the resistivity as a function of temperature; the transition temperature[1,4] ranges from 119 °K for Fe_3O_4 to 1070 °K for NbO_2 and the change in resistivity at the transition ranges[5,6] from a factor of about 20 for Ti_6O_{11} to a factor of 10^8 for V_2O_3 (see Fig. 1). In most cases there is a simultaneous change in crystal structure, as for instance in V_2O_3 which goes from rhombohedral (corundum structure) at high temperatures ($\gtrsim 150$ °K) to monoclinic in the low-temperature phase ($\lesssim 150$ °K).

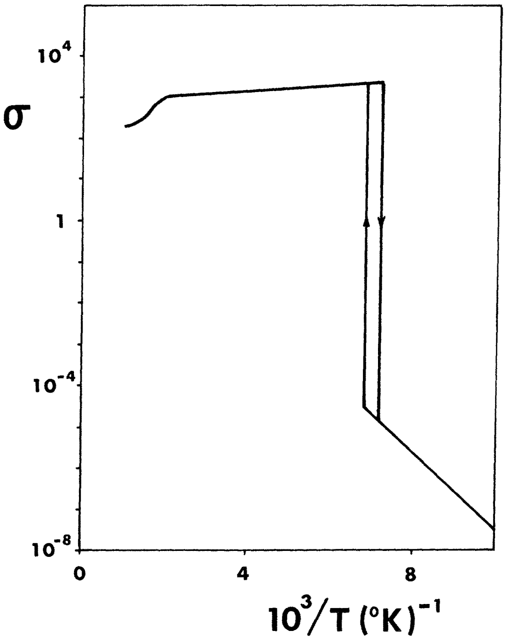

FIG. 1. Conductivity of V_2O_3 in $(\Omega\,\mathrm{cm})^{-1}$ as a function of T^{-1} (after Feinleib and Paul, Ref. 6).

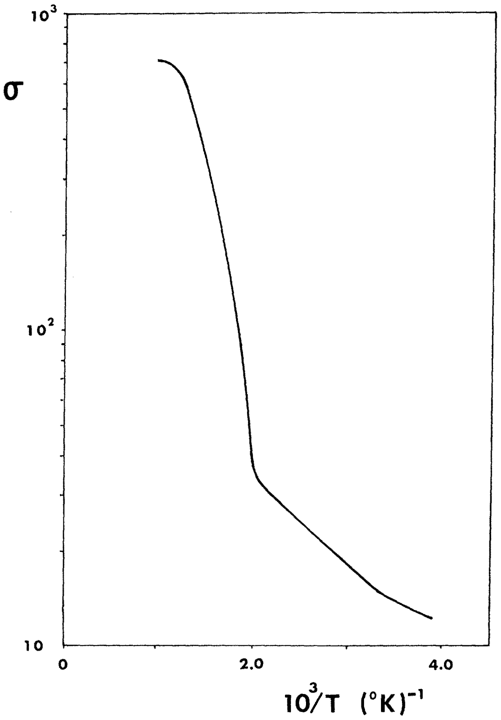

FIG. 2. Conductivity of Ti_2O_3 in $(\Omega\,\mathrm{cm})^{-1}$ as a function of T^{-1} (after Abrahams, Ref. 7).

A second subgroup of substances in this third group exhibits a fairly large but smooth change in resistivity as a function of temperature. The usual exponential behavior to be expected from a semiconductor changes in a rather abrupt way to a major decrease in resistivity followed by an almost constant metal-like value at high temperatures. A typical example in this subgroup is Ti_2O_3, shown in Fig. 2; here[7] the resistivity drops by a factor of 40 as the temperature is raised from 300 to 750 °K.

A third subgroup of substances corresponds to those where the resistivity undergoes a very gradual transition as the temperature is changed by a large factor. As an example of this type of material,[8] we can cite SmB_6; here the resistivity changes in a smooth semiconductorlike fashion from 4 to 20 °K with an effective energy gap of 0.046 eV, and after a somewhat steeper decrease between 20 and 50 °K, it saturates to a metal-like value between 50 °K and room temperature (see Fig. 3).

With respect to magnetic properties, these materials also behave in a variety of ways. There are several antiferromagnets among them, for instance, Fe_2O_3, FeO, and Cr_2O_3, as well as ferrimagnets (e.g., Mn_3O_4) and ferromagnets (e.g., CrO_2). The resistivity properties are not necessarily correlated with any long-range magnetic order. For example,[1] VO_2, V_2O_3, Fe_3O_4, and NiS all present similar first-order transition in the resistivity, with transition temperatures of 340 150, 119, and 264 °K, respectively. However, VO_2 shows no long-range magnetic order,[1] NiS is an antiferromagnet with a Néel temperature equal to its metal-insulator transition temperature, Fe_3O_4 is a ferrimagnet[9] with a Néel temperature of 850 °K, and there is still a controversy over whether V_2O_3 is an antiferromagnet in its insulating phase.[1,10]

While band theory has been successfully used in explaining the electrical properties of some of the materials of the first group (conductors), it has strikingly failed in many other cases. As an ex-

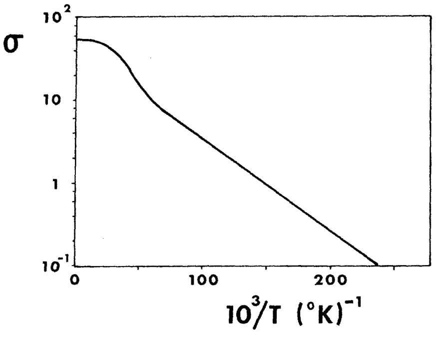

FIG. 3. Conductivity of SmB_6 in arbitrary units as a function of T^{-1} (after Menth *et al*, Ref. 8).

ample we quote the case of MnO mentioned by Adler.[11] Here we have a d band with ten states per cation which the crystalline field and spin-orbit coupling could split at most into two fourfold and one doubly degenerate band. Now since MnO has five $3d$ electrons per unit cell, we conclude from band theory that MnO is metallic, in contradiction with the experimental fact that this oxide is a very good insulator.[2]

The assumption that these substances have a d band which is too narrow to support conductivity (an assumption that would explain the properties of MnO) also fails in some cases, such as that for ReO_3, which has one $5d$ electron outside the filled bands; then, according to this assumption this material should be an insulator. However, ReO_3 is a very good conductor with a conductivity of 10^5 $(\Omega\,\text{cm})^{-1}$.

Several models have been also proposed to explain the insulator-to-metal transitions that occur in these substances. The simplest way to obtain a transition from an insulator at low temperatures to a metal at high temperatures is by means of a temperature-dependent band structure which shows a band gap at the Fermi level at low temperatures and a band overlap at higher temperatures. However, this mechanism would not be applicable to the many cases where the transitions are sharp, since, being a continuous parameter theory, it can only produce a second-order phase transition. A sharper transition could be obtained if an excitonic insulator[12] state were formed just before the gap vanishes. It appears, nevertheless, that this model produces a somewhat gradual transition[12] and it is not likely to yield a first-order one.

Another possibility is to start from the metallic state and find a mechanism that would produce a low-temperature insulator. One possible mechanism is a crystalline-structure distortion[13] which could give rise to a reduction of symmetry resulting in additional splittings of the bands; then, if these band splittings produce a gap in the density of states at the Fermi energy, a low-temperature insulator is obtained. A similar effect can occur if the material became antiferromagnetic below the transition temperature since the antiferromagnetic order corresponds to doubling the periodicity of the lattice and therefore to a reduction of the Brillouin zone to one-half of the original size. Then the spin-dependent part of the exchange interaction would produce a gap at the surface of the reduced magnetic Brillouin zone,[14] and in this way a material with a half-filled band would become a low-temperature insulator. The first of these mechanisms, however, cannot explain transitions where no structural change occurs (e.g., Ti_4O_7, see Ref. 5) and the second one is not applicable in those cases where the low-temperature phase is not antiferromagnetic (e.g., VO_2, see Ref. 1).

A quite different mechanism for explaining the insulator-conductor transition was proposed by Mott.[15] In this model two different situations are considered. First, if only one free electron and one hole are present in the material, they would attract each other by a Coulomb interaction $V_C = -e^2/\kappa r$ and they would form a bound exciton; in such a case neither of them could participate in conduction. In the second situation, there are a large number of free carriers and therefore the attraction between electrons and holes would be a screened Coulomb interaction $V_s = -(e^2/\kappa r)\exp(-r/\lambda)$. Then in this case electrons and holes would not form bound-exciton states and they could participate in conduction. In the first situation we have an insulator and in the second a metal. If we start from a low-temperature insulator in the first situation and then increase the temperature, the number of carriers will go from a small to a large number, and an insulator-metal transition will be produced. This type of transition will always be sharp because it is not possible to have a small number n of free carriers since the energy increases with n near $n = 0$; therefore, if the state with a large number of carriers is energetically favorable above certain temperatures, a sharp transition will be produced.

Mott argued that the state with a large number of carriers is energetically favorable at high temperatures if the lattice constant is smaller than a certain critical value. A requirement that the lattice constant must pass through this critical value can be considered as a main condition for the existence of this type of transition.

The main objection to this theory is that real crystals have a lattice constant which can vary only by small amounts with temperature, and therefore it is very unlikely that their values are near the critical one. The main criticism we can make to all these models is that every one of them is applicable to only certain members of an otherwise homogeneous family of substances, and therefore their general validity is very questionable. In this respect it has become very important to have a more general mechanism that would be capable of explaining the wide variety of behaviors which are found in these substances. It is therefore important to isolate the relevant parameters and to formulate a model which allows for the various behaviors as the parameters are changed. Such a model is presented here.[16] We describe it in Sec. II, where the various parameters are defined and estimated. Section III is concerned with the possibility of exciton formation. In Sec. IV, we present the thermodynamics of the model and the possibility and range of existence of a stable insulator, a stable metal, a first-order phase transition between the two phases, or a higher-order gradual transition. In Sec. V, we discuss the scattering mechanism which might contribute to the resistivity. Section VI contains the conclusions.

II. MODEL

The anomalous temperature dependence[17] of the magnetic susceptibility of many of the materials under discussion (e.g., SmB_6) suggests that localized moments play an important part in the mechanism of the transition. We propose here a model which assumes that in the insulating phase (if present) the electrons move in highly correlated atomic-like orbitals which strongly resemble the orbitals of the corresponding free ions. They therefore produce a well-defined total-angular-momentum quantum number J_0. One of these localized electrons can be promoted to a delocalized band state. In this fashion, it can contribute to the conductivity and it can leave behind an ion with one extra positive charge and a total-angular-momentum quantum number J. For example, $V^{++}(J_0=\frac{3}{2}) \rightarrow V^{+++}(J=2)$; $Sm^{++}(J_0=0) \rightarrow Sm^{+++}(J=\frac{5}{2})$.

In this model, therefore, both localized and itinerant quasiparticle states are present. Under these circumstances we have two different types of single-electron states: (a) bands of extended Bloch functions, and (b) a set of localized states centered at the sites of the metallic ions in the crystal. The insulating ground state of this system corresponds to the case where the localized states are fully occupied by electrons. Therefore, quasiparticle excitations correspond to either localized holes or itinerant electrons in the conduction band.[18]

In the language of second quantization, the one-quasiparticle terms of the Hamiltonian are written as

$$\mathcal{H}_0 = \sum_{\nu\vec{k}\sigma} \epsilon_\nu(\vec{k})\, a^\dagger_{\nu\vec{k}\sigma} a_{\nu\vec{k}\sigma} + \sum_{i\sigma} E b^\dagger_{i\sigma} b_{i\sigma} \quad , \tag{2.1}$$

where $a^\dagger_{\nu\vec{k}\sigma}$ creates an electron in the state $\vec{k}$, band ν, with spin σ; and $b^\dagger_{i\sigma}$ creates a hole with spin σ at site i. The energies $\epsilon_\nu(\vec{k})$ and E are positive definite and such that

$$\Delta \equiv \min[E + \epsilon_\nu(\vec{k})] > 0 \tag{2.2}$$

is the energy gap between the valence and the conduction band.

The quasiparticle interaction is assumed to be screened with a screening constant such that only intra-atomic terms need be considered. The sixteen kinds of terms that constitute the interaction part of the Hamiltonian can be arranged into six groups, each of them characterized by different interactions G. In this way we are left with the following six basically different terms:

$$G_1 b^\dagger_{i\sigma} b^\dagger_{i\bar{\sigma}} b_{i\bar{\sigma}} b_{i\sigma} \quad , \tag{2.3}$$

$$G_2 b^\dagger_{i\sigma} b^\dagger_{i\bar{\sigma}} c^\dagger_{\nu i\bar{\sigma}} b_{i\sigma} \quad , \tag{2.4}$$

$$G_3 b^\dagger_{i\sigma} b^\dagger_{i\bar{\sigma}} c^\dagger_{\nu i\bar{\sigma}} c^\dagger_{\nu' i\sigma} \quad , \tag{2.5}$$

$$G_4 b^\dagger_{i\sigma} c^\dagger_{\nu i\sigma'} c_{\nu' i\sigma'} b_{i\sigma} \quad , \tag{2.6}$$

$$G_5 c^\dagger_{\nu i\sigma} c^\dagger_{\nu' i\sigma'} b^\dagger_{i\sigma'} c_{\nu'' i\sigma} \quad , \tag{2.7}$$

$$G_6 c^\dagger_{\nu i\sigma} c^\dagger_{\nu' i\sigma'} c_{\nu'' i\sigma'} c_{\nu''' i\sigma} \quad , \tag{2.8}$$

where the operator $c^\dagger_{\nu i\sigma}$ creates a Wannier state at site i corresponding to the Bloch band $(\nu\sigma)$ and is related to $a^\dagger_{\nu\vec{k}\sigma}$ by the transformation

$$c^\dagger_{\nu j\sigma} = N^{-1/2} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_j} a^\dagger_{\nu\vec{k}\sigma} \quad . \tag{2.9}$$

The largest terms in the interaction are (2.3), where G_1 corresponds to the hole-hole repulsion. The values of G_1 are of the order of 10–20 eV for this type of material. For example, in the case of V_2O_3, the V^{2+} ion becomes V^{3+} as one electron is promoted into the conduction band. The difference in ionization potential for V^{2+} and V^{3+}, which is 18 eV,[19] is a reasonable estimate of G_1 in this case. Even when corrected by screening effects, these values are much larger than the energy gaps found for these substances. For example, for V_2O_3 the measured[6] energy gap is 0.1 eV and in general is at most of the order of 1 eV. Therefore, the hole-hole repulsion is the dominant term in the Hamiltonian. Configurations which involve more than one hole per ion are energetically very unfavorable and need not be considered in our arguments. In other words, in the limit as $G_1 \rightarrow \infty$, two holes can never coexist in one ion, and such a state can be eliminated from all calculations. In this way in the manifold of states with no more than one hole per ion, terms of the form (2.3), (2.4), and (2.5) give identically zero contribution; they have, therefore been projected out. The most important remaining terms are of the form (2.6) and represent the electron-hole attraction. Interaction (2.7) and (2.8) are smaller since they involve three or four extended wave functions instead of only two; these interactions are ignored in this model.[20] In this fashion, the final Hamiltonian is reduced to

$$\mathcal{H} = \sum_{\nu\vec{k}\sigma} \epsilon_\nu(\vec{k})\, a^\dagger_{\nu\vec{k}\sigma} a_{\nu\vec{k}\sigma} + \sum_{i\sigma} E b^\dagger_{i\sigma} b_{i\sigma} - G \sum_{i\sigma\sigma'\nu\nu'} b^\dagger_{i\sigma} c^\dagger_{\nu i\sigma'} c_{\nu' i\sigma'} b_{i\sigma} \quad , \tag{2.10}$$

where we have assumed $G > 0$ corresponding to an attractive electron-hole interaction independent of spin and band index. The model therefore includes as parameters the effective interaction G and the band-energy function $E + \epsilon_\nu(\vec{k})$. This last function has an absolute minimum Δ (which is one of the most important features of the band structure) and a bandwidth

$$W = \max\epsilon_\nu(\vec{k}) - \min\ \epsilon_\nu(\vec{k}) \ . \tag{2.11}$$

We can also define the corresponding density of states $D(\epsilon)$ and restrict ourselves to either a finite bandwidth or an infinite one. In either case, it is also useful to define a density-of-states bandwidth W_1 such that the total number of available states between $[\min\epsilon_\nu(\vec{k})]$ and $[W_1 + \min\epsilon_\nu(k)]$ is equal to one electron of each spin per metallic ion. For the cases in which there is one electron of each spin per unit cell, we obtain $W = W_1$.

III. POSSIBILITY OF EXCITON FORMATION

It is important to examine under what conditions in the present model the electron-hole interaction leads to the formation of a bound exciton. We know that in the cases in which we are mostly interested excitons do not occur since, being bound states, they cannot contribute to the conductivity of the substances. We therefore must restrict the parameters to take on only those values which do not lead to the formation of an exciton.

In order to study this possibility, let us first consider the system in its insulating ground state where there are no localized holes and no electrons in the conduction band; $\mathcal{H}$ is then identically zero. Now we take one electron from the ion at the lattice position 0, leaving a localized hole there. The Hamiltonian (2.10) reduces now to

$$\mathcal{H} = \sum_{\nu\vec{k}\sigma} \epsilon_\nu(\vec{k})\, a^\dagger_{\nu\vec{k}\sigma} a_{\nu\vec{k}\sigma} + E - G \sum_{\nu\nu'\sigma} c^\dagger_{\nu 0\sigma} c_{\nu' 0\sigma} \ . \tag{3.1}$$

If we restrict this calculation for the case of only one conduction band and choose the energy scale such that $E = 0$, then Eq. (3.1) further reduces to

$$\mathcal{H} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}\sigma} a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} - (G/N) \sum_{\vec{k}\vec{k}'\sigma} a^\dagger_{\vec{k}\sigma} a_{\vec{k}'\sigma} \ , \tag{3.2}$$

where we write $\epsilon_{\vec{k}} \equiv \epsilon(\vec{k})$ and we have made the transformation

$$a_{\vec{k}} = N^{-1/2} \textstyle\sum_j e^{i\vec{k}\cdot\vec{R}_j} c_j \ . \tag{3.3}$$

The Hamiltonian (3.2) is diagonalized by making the transformation

$$\alpha_{n\sigma} = \textstyle\sum_{\vec{k}} u_{n\vec{k}} a_{\vec{k}\sigma} \tag{3.4}$$

such that

$$\mathcal{H} = \sum_{n\sigma} E_{n\sigma}\, \alpha^\dagger_{n\sigma} \alpha_{n\sigma} \ ,$$

where $E_{n\sigma}$ are the new eigenvalues of the system.

The equation of motion

$$[\mathcal{H}, \alpha_{n\sigma}] \equiv \mathcal{H}\alpha_{n\sigma} - \alpha_{n\sigma}\mathcal{H} = -E_{n\sigma}\alpha_{n\sigma} \tag{3.5}$$

gives the result

$$(E_{n\sigma} - \epsilon_{\vec{k}\sigma}) u_{n\vec{k}} + (G/N) \sum_{\vec{k}'\sigma} u_{n\vec{k}'} = 0 \ . \tag{3.6}$$

If we now consider the case in which the electron and the hole form an excitonic bound state, the energy $E_{n\sigma}$ of this state will be outside the band $\epsilon_{\vec{k}\sigma}$. This means that $E_{n\sigma} \neq \epsilon_{\vec{k}\sigma}$ for all $\vec{k}$ and σ, and Eq. (3.6) can be reduced to

$$(1/N) \textstyle\sum_{\vec{k}} [1/(E_{n\sigma} - \epsilon_{\vec{k}\sigma})] = -1/G \ . \tag{3.7}$$

From this equation, we can find the exciton energy level $E_{n\sigma}$. We consider now several types of conduction bands. Let us first consider a conduction band made out of an s electron in a simple-cubic lattice. The lattice parameter is a and the unit cell volume is equal to a^3. Then in a tight-binding approximation with nearest-neighbor interactions only, $\epsilon_{\vec{k}\sigma}$ can be written as

$$\epsilon_{\vec{k}\sigma} = \Delta + \tfrac{1}{2}W - \tfrac{1}{6}W(\cos k_x a + \cos k_y a + \cos k_z a) \ , \tag{3.8}$$

where Δ is the energy gap at $\vec{k} = 0$. Equation (3.7) now reduces to

$$\frac{1}{G} = \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{dx\, dy\, dz}{\epsilon_0 - E_n - f(x, y, z)} \ , \tag{3.9}$$

where

$$\epsilon_0 = \Delta + \tfrac{1}{2}W, \tag{3.10}$$

$$f(x, y, z) = \tfrac{1}{6}W(\cos x + \cos y + \cos z) \ . \tag{3.11}$$

We notice that the right-hand side of Eq. (3.9) has its maximum value at $E_n = \Delta$, which is also the maximum value that a *bona fide* exciton energy might take. The result of the integral (3.9) for that value of E_n is known[21] and yields $(\beta W)^{-1}$, where

$$\beta(\text{simple cubic}) = 0.329\,73 \ . \tag{3.12}$$

Consequently, excitons exist if and only if

$$G \geqslant \beta W \ , \tag{3.13}$$

or in other words, if the electron-hole interaction is greater than about one-third of the bandwidth.

Similar calculations can be made for a s-like tight-binding band in the fcc and bcc structures. Equations (3.9), (3.10), and (3.13) still hold, but Eq. (3.11) has to be replaced by

$$\begin{aligned} f(x, y, z) &= \tfrac{1}{4}W(\cos x \cos y + \cos y \cos z \\ &\quad + \cos z \cos x - 1) \ , \qquad \text{fcc} \\ &= \tfrac{1}{2}W \cos x \cos y \cos z \ , \quad \text{bcc} \end{aligned} \tag{3.14}$$

and the values of β in (3.13) are[21]

$$\beta(\text{fcc}) = 0.557\,76 \ , \tag{3.15}$$

$$\beta(\text{bcc}) = 0.358\,89 \ . \tag{3.16}$$

If an electron-hole exchange interaction

$$G'\sum_{i\sigma\sigma'} b^\dagger_{i\sigma} c^\dagger_{i\sigma} c_{i\sigma'} b_{i\sigma'} \tag{3.17}$$

is considered in addition to the direct term (2.10), the excitons that we have considered thus far, whose energy is independent of the electron and hole spins, split into a singlet and a triplet excitonic state, with different binding energies. It is easily shown that the results (3.13), (3.12), (3.15), and (3.16) still hold if the interaction G is replaced by $G-G'(1+s)$ where $s=1$ for the singlet and $s=-1$ for the triplet excitonic state.

It is also instructive (although not consistent with any physically reasonable band) to consider a truncated free-electron approximation, such that

$$\epsilon_{\vec{k}\sigma}=\Delta+Wk^2/k_0^2\ , \quad |\vec{k}|<k_0\ , \tag{3.18}$$

where

$$k_0=(6\pi^2)^{1/3}/a\ , \tag{3.19}$$

a^3 is the volume of the primitive unit cell, and the Brillouin zone has been approximated by a sphere of radius k_0. In this case, the condition for the existence of an exciton is still given by Eq. (3.13), but now we have

$$\beta(\text{truncated free electron})=\tfrac{1}{3}\ . \tag{3.20}$$

In order to investigate the exciton-exciton interaction, we have studied the possibility of exciton formation when two electrons are promoted from the ionic sites 1 and 2 into the conduction bands, leaving two holes behind. If we restrict ourselves to only one conduction band, (2.10) takes the form

$$\mathcal{H}=\sum_{\vec{k}\sigma}\epsilon(\vec{k})a^\dagger_{\vec{k}\sigma}a_{\vec{k}\sigma}+2E-G\sum_{\sigma}(c^\dagger_{1\sigma}c_{1\sigma}+c^\dagger_{2\sigma}c_{2\sigma}). \tag{3.21}$$

If as before we choose $E=0$, use the transformations (3.3) and (3.4), and choose the origin such that $\vec{R}_2=-\vec{R}_1=\vec{R}$, Eq. (3.5) yields

$$(E_{n\sigma}-\epsilon_{\vec{k}\sigma})U_{n\vec{k}\sigma}+(G/N)\sum_{\vec{k}'\sigma}\gamma_{\vec{k}\vec{k}'}U_{n\vec{k}'\sigma}=0\ , \tag{3.22}$$

where

$$\gamma_{\vec{k}\vec{k}'}=2\cos[(\vec{k}'-\vec{k})\cdot\vec{R}]. \tag{3.23}$$

The solution for the "molecular" excitonic state is now obtained following the same line of argument as for the "atomic" case. It is found that an excitonic (discrete) solution exists only if Eq. (3.13) is satisfied, but β is now given by

$$\beta^{-1}=\beta_0^{-1}+[\beta_1(\vec{R})]^{-1}\ , \tag{3.24}$$

where β_0 is the value for the "atomic" exciton [(3.12), (3.15), (3.16), or (3.20)] and

$$[\beta_1(\vec{R})]^{-1}=\frac{W}{N}\sum_{\vec{k}}\frac{\cos(2\vec{k}\cdot\vec{R})}{\epsilon_0-\epsilon_{\vec{k}}}\ , \tag{3.25}$$

where ϵ_0 is the value of $\epsilon_{\vec{k}}$ at the bottom of the band $\vec{k}=0$. The integral in the right-hand side of (3.25) is very complicated in most cases. It is, however, quite simple for the truncated free-electron model and yields

$$[\beta_1(R)]^{-1}=(3/4\pi)^{2/3}(a/R)\,\mathrm{Si}(2k_0R)\ , \tag{3.26}$$

where Si is the integral sine function

$$\mathrm{Si}(x)=\int_0^x\frac{\sin y}{y}\,dy$$

and k_0 is defined by (3.19). For the nearest-neighbor distance, we find $R=\frac{1}{2}a$:

$$[\beta_1(\tfrac{1}{2}a)]^{-1}=1.37\ , \tag{3.27}$$

which yields

$$\beta=0.228\ . \tag{3.28}$$

This calculation, however, is not to be taken too seriously since it does not take into account the electron-electron interaction for the two electrons in the conduction band. Such an interaction is in this case very important since we must place two electrons in the same orbital. The interaction, if properly taken into account, would push the value of β up to values quite close to the value of original "atomic" value, implying that "molecular" excitations do not exist. We therefore consider the one-electron exciton condition (3.13), with β given by (3.12), (3.15), (3.16), and (3.20), as the boundary line between excitonic and normal states.

If $G<\beta W$, it can be easily proved that (3.6) yields no bound state and that the energy eigenvalues $E_{n\sigma}$ are corrected from their unperturbed value $\epsilon_{\vec{k}\sigma}$ by an infinitesimal amount of order (G/N). For N_0 excitations, that correction is of order (GN_0/N), in which case the Hartree mean field approximation is a sensible one to make.

IV. THERMODYNAMICS

In this section we study the behavior of the model as a function of temperature when the Hartree (mean field) approximation is made. This means that the interaction Hamiltonian

$$\mathcal{H}_{\mathrm{int}}=-G\sum_{i\sigma\sigma'\nu\nu'}b^\dagger_{i\sigma}c^\dagger_{\nu i\sigma'}c_{\nu' i\sigma'}b_{i\sigma} \tag{4.1}$$

is replaced by its mean field value

$$\langle\mathcal{H}_{\mathrm{int}}\rangle=-Gn_T\int_\Delta^\infty D(\epsilon)n(\epsilon)\,d\epsilon\ , \tag{4.2}$$

where n_T is the average number of holes per ion, $D(\epsilon)$ is a density of electron states, and $n(\epsilon)$ is the average occupation of electron states of energy ϵ.

The internal energy of the system in this self-consistent field approximation is therefore given by

$$\mathcal{E}=\int_\Delta^\infty D(\epsilon)(\epsilon-Gn_T)n(\epsilon)\,d\epsilon\ . \tag{4.3}$$

Equation (4.3) is subject to the constraint

$$Nn_T = \int_\Delta^\infty D(\epsilon) n(\epsilon)\, d\epsilon \quad , \tag{4.4}$$

which simply states that the number of electrons is equal to the number of holes. In (4.4), N is the total number of ions in the crystal, and, as in Sec. III, we have taken E (the hole energy) to be zero.

The free energy of the system is obtained by (a) writing the internal energy, (b) substracting the entropy term, and (c) minimizing the whole expression with respect to $n(\epsilon)$, subject to the constraint (4.4). The expansion to be minimized is

$$\mathfrak{F} = \mathcal{E} - T\mathcal{S} = \int_\Delta^\infty D(\epsilon)\,(\epsilon - Gn_T) n(\epsilon)\, d\epsilon + k_B T \times \int_\Delta^\infty D(\epsilon) \{n(\epsilon) \ln n(\epsilon) + [1 - n(\epsilon)] \ln[1 - n(\epsilon)]\} d\epsilon + Nk_B T(1 - n_T) \ln(1 - n_T) + Nk_B T n_T \ln(n_T/q) , \tag{4.5}$$

where $q \equiv (2J+1)/(2J_0+1)$ is the ratio of the spin multiplicities of the ions with and without a hole, respectively. The three entropy terms in (4.5) correspond, respectively, to the electrons, the holes, and the ion spins. Minimizing (4.5) with respect to $n(\epsilon)$ yields

$$n(\epsilon) = \left[a_T \exp\left(\frac{\epsilon - 2Gn_T}{k_B T}\right) + 1\right]^{-1} , \tag{4.6}$$

where

$$a_T = n_T / q(1 - n_T) \tag{4.7}$$

and (4.4) should also be satisfied. Replacing (4.6) and (4.7) in (4.4), we obtain a transcendental equation for n_T, the solution of which depends explicitly on $D(\epsilon)$ and G. For given values of these quantities, and as a function of temperature T, the transcendental equation may give one or more solutions for n_T. In the case of multiple solutions (usually three appear), the absolute minimum of Eq. (4.5) has to be determined. (In the case of three solutions, two are relative minima and one is a relative maximum; the values of the minima have then to be computed to determine which one of them is the absolute minimum.)

In what follows, we discuss in detail the special case of a simple-cubic lattice in which $q = 2$ and the density of states $D(\epsilon)$ is approximated by

$$\begin{aligned} D(\epsilon) &= 0 , && \epsilon < \Delta \\ &= D_0\left[1 - \frac{1}{\pi}\cos^{-1}\left(\frac{6(\epsilon - \Delta)}{W} - 1\right)\right] , && \Delta < \epsilon < \Delta + \tfrac{1}{3}W \\ &= D_0 , && \Delta + \tfrac{1}{3}W < \epsilon < \Delta + \tfrac{2}{3}W \\ &= \frac{D_0}{\pi}\cos^{-1}\left(\frac{6(\epsilon - \Delta)}{W} - 5\right) , && \Delta + \tfrac{2}{3}W < \epsilon < \Delta + W \\ &= 0 , && \epsilon > W + \Delta , \end{aligned} \tag{4.8}$$

where

$$D_0 = 3N/W \quad . \tag{4.9}$$

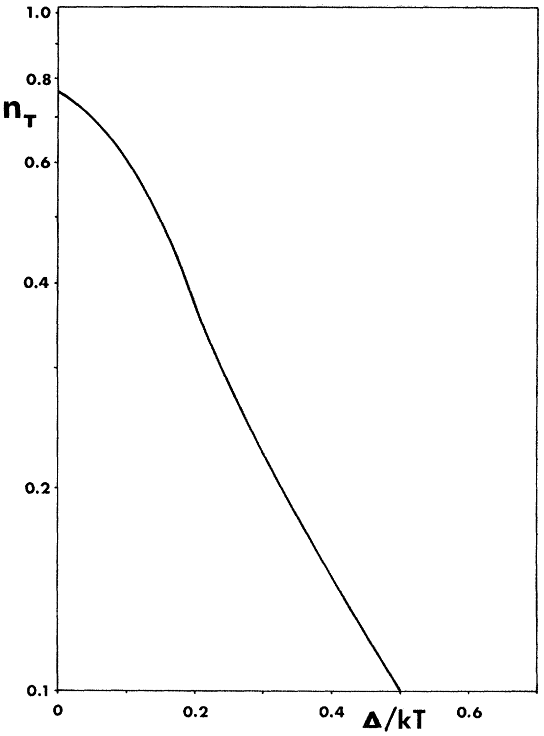

FIG. 4. Occupation of the conduction band as a function of T^{-1} for an insulating phase. The parameters are $W = 70\Delta$, $G = 17.5\Delta$.

The model thus specified contains only three parameters: the band gap Δ, the bandwidth W, and the electron-hole interaction G. If we measure energies in units of Δ, the only two parameters are $G' = G/\Delta$ and $W' = W/\Delta$. In the $G' - W'$ plane there will be, therefore, several regions in which the system will exhibit different behavior: (i) Excitonic phases appear when conditions (3.13), (3.12) are satisfied:

$$G' > 0.329\,73\, W' \quad . \tag{4.10}$$

(ii) The solution of n_T as a function of $\Delta/k_B T$ for a given set of parameters might take the five general shapes shown in Figs. 4–8. Of these, Fig. 4 is the only one which shows only one solution as $T \to 0$. We call this an insulating behavior. The existence of three solutions as $T \to 0$ corresponds to

$$\left(\frac{\partial \mathcal{E}}{\partial n_T}\right)_{n_T = 1} < 0 \quad , \tag{4.11}$$

and consequently the boundary line for the insulating behavior is given by

$$G' = 0.25\, W' + 0.5 \quad . \tag{4.12}$$

(iii) Figure 8 corresponds to what we call a metallic

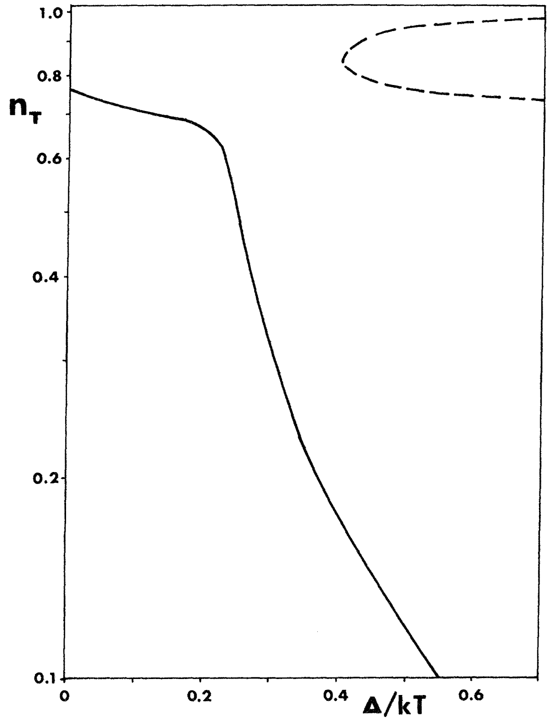

FIG. 5. Occupation of the conduction band as a function of T^{-1} for a system that exhibits a smooth transition. The parameters are $W = 70\Delta$, $G = 20.6\Delta$.

behavior, i.e., as $T \to 0$, there are three solutions, but the absolute minimum corresponds for all values of T to the higher value of n_T. This means that a metal is obtained whenever

$$\mathcal{E}(n_T = 1) < 0 \quad . \tag{4.13}$$

The boundary for the metallic case is therefore given by

$$\int_{\Delta}^{\Delta + 1/2W} \epsilon D(\epsilon) d\epsilon = NG \quad , \tag{4.14}$$

which yields

$$G' = 0.3125 W' + 1 \quad . \tag{4.15}$$

(iv) Figure 6, which is a limiting behavior between Figs. 5 and 7, corresponds to the boundary between a first-order phase transition (Fig. 7) and a smooth insulator-metal transition (Fig. 5). If we define the quantity

$$\Delta' = \Delta / k_B T \quad , \tag{4.16}$$

the condition for critical behavior, i.e., the existence of a curve of the type shown in Fig. 6, is that

$$\left(\frac{\partial \Delta'}{\partial n_T} \right)_{W,G} = 0 \, , \quad \left(\frac{\partial^2 \Delta'}{\partial n_T^2} \right)_{W,G} = 0 \tag{4.17}$$

are both satisfied simultaneously. In other words, n_T as a function of $\Delta / k_B T$ has a "long" vertical slope. We have calculated the implicit equations (4.17) numerically and we find that they are satisfied (approximately) whenever

$$G' = 0.294 W' + 0.633 \quad . \tag{4.18}$$

(v) All these curves are summarized in Fig. 9. In the $G' - W'$ plane, there are five well-defined regions: (a) insulator, (b) a region of smooth insulator-to-metal transitions, (c) a region of first-order metal-to-insulator transitions, (d) a metallic region, and (e) a region where excitons can occur (which we have not analyzed in detail).

It is interesting (although physically meaningless) to consider the limit $W \to 0$, ignoring at the same time the possibility of exciton formation. In this case, all calculations can be made analytically (they have been reported in a previous paper from two of the present authors[16]). For the present example, in such a limit we find (a) insulating behavior for $G < 0.5\,\Delta$, (b) smooth transitions for $0.5\,\Delta < G < 0.633\,\Delta$, (c) first-order transitions for $0.633\,\Delta < G < \Delta$, and (d) a metallic phase at all temperatures for $\Delta < G$.

For this model, and in the region where first-order transitions take place, the transition temperature is well approximated by

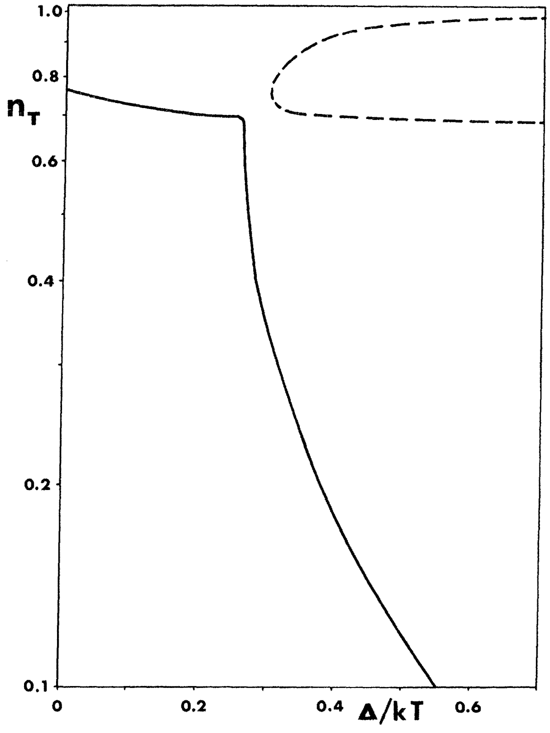

FIG. 6. Occupation of the conduction band as a function of T^{-1} for a system showing critical behavior. The parameters are $W = 70\Delta$, $G = 20.92\Delta$.

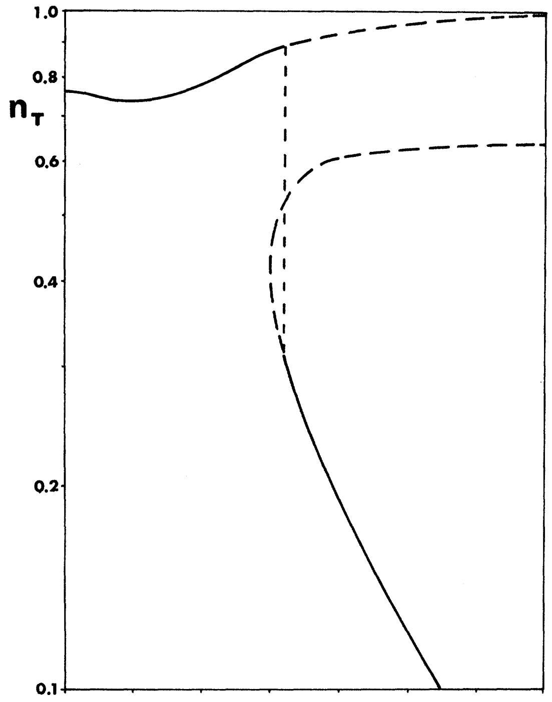

FIG. 7. Occupation of the conduction band as a function of T^{-1} for a system that exhibits a first-order transition. The parameters are $W=70\Delta$, $G=21.4\Delta$.

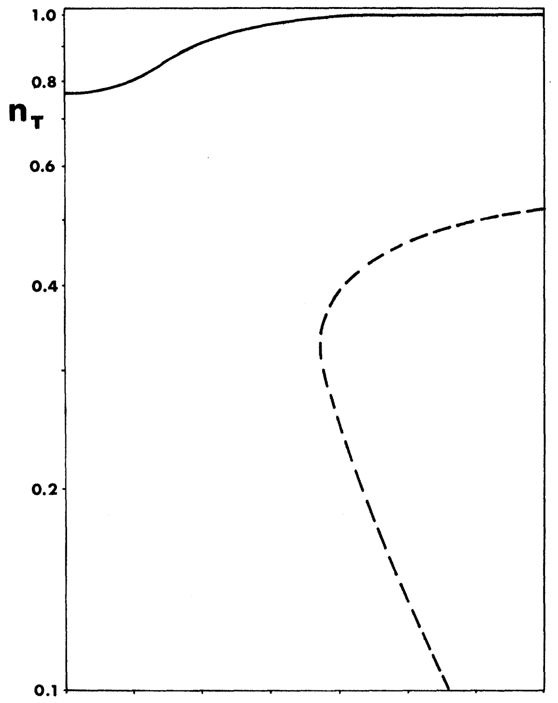

FIG. 8. Occupation of the conduction band as a function of T^{-1} for a metallic phase. The parameters are $W=70\Delta$, $G=23.0\Delta$.

$$k_B T_c = 0.481\,(\Delta - G) \quad , \tag{4.19}$$

which gives a maximum value of

$$k_B T_{cM} = 0.177\,\Delta \quad . \tag{4.20}$$

For the general case, an approximate formula for the maximum possible transition temperature is given by

$$k_B T_{cM} = 0.177\,\Delta + 0.052\,W \quad , \tag{4.21}$$

which allows for higher values of the transition temperature in the case of wide bands.

V. LOCALIZED HOLE SCATTERING

In Sec. IV, we have discussed the equilibrium value at various temperatures of the number of electrons in the conduction band. The curves (Figs. 4–8) shown in Sec. IV strongly resemble[22] the conductivity curves (Figs. 1–3) as determined experimentally. However, the proportionality between carrier density and conductivity is only valid if a constant mobility, i.e., a constant relaxation rate, is obtained. Most of the data (with some notable exceptions, e.g., those shown in Figs. 1 and 2) reported in the literature are taken on powders and dirty samples. Therefore, impurity and imperfection scattering should dominate at most temperatures.

In our model, however, the electrons excited from the localized states into the conduction band leave behind a set of randomly distributed holes which, in principle, might produce some contribution to the scattering rate. We have therefore calculated the contribution from such a scattering process to the reciprocal relaxation time and found the contribution to be negligible in all cases.

In the insulating limit, the standard procedure

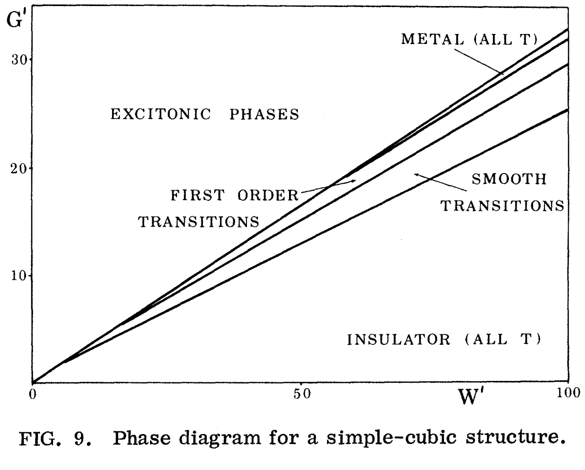

FIG. 9. Phase diagram for a simple-cubic structure.

for calculating relaxation mechanism in semiconductors[23] was applied. The same attractive term in the Hamiltonian which gives rise to the phase transition produces a relaxation rate given by

$$1/\tau(\epsilon) = (2^{1/2} m_e^{3/2}\, \Omega_0/\pi \hbar^{7/2})\, n_T G^2 (\epsilon - \Delta)^{1/2}\,, \qquad (5.1)$$

when m_e is the effective mass at the bottom of the conduction band, $(\epsilon - \Delta)$ is the electron energy measured from the bottom of the conduction band, and Ω_0 is the specific volume (volume per ion). In all cases, (5.1) should be much smaller than the impurity relaxation rate, due to the factor n_T.

The situation is not so clear in the metallic range, and in principle the localized ions may be responsible for Kondo-type[24] scattering at very low temperatures. Such an effect may be of interest and deserves a special study in itself. There is, in addition, the straightforward scattering produced by the same interaction term which we have considered thus far. In the limit in which $n_T \rightarrow 1$, the scattering rate at the Fermi level for a free-electron-like band[23] is given by

$$1/\tau(\epsilon_F) = (m^* k_F\, \Omega_0/\pi \hbar^3)\,(1 - n_T)\, G^2 \quad , \qquad (5.2)$$

where k_F is the Fermi wave vector. Such an effect again is negligible.

We therefore conclude that, with the possible exception of those substances which are metallic at very low temperatures in which some spin-dependent scattering may be important, the temperature dependence of the conductivity, as reported experimentally, can be interpreted in our model as describing the carrier density at equilibrium.

VI. CONCLUSIONS

We have presented here a very simple model for the metal-insulator transition in transition-metal and rare-earth oxides, sulfides, and borides. It is based on a mean field approximation applied to quasiparticles, which of course may have some important many-body corrections.

The main feature of this model is the presence in the same substance of two kinds of electronic states: (a) localized highly correlated states, which strongly resemble the configuration of the corresponding ions and in which the interionic effects are negligible and (b) bona fide Bloch-like states, which extend throughout the crystal and in which the electron correlations are only of secondary importance.

The residual interactions between localized and extended states (which in the mean field approximation are proportional to the square of the carrier concentration) are responsible for the changes in occupation of these states. The relative position of the localized levels with respect to the extended ones is therefore strongly dependent on the occupation of both.

The model is flexible enough to allow for all varieties found in the substances under consideration: good insulators, good metals, first-order transitions, and smooth transitions. In the way presented here, however, it is not complete, because (a) it does not include higher-order many-body corrections; (b) it does not allow a self-consistent rearrangement of the parameters (which should be very important in the case of first-order transition with their concomitant change in crystal structure, unit cell volumes, band structures, etc.); (c) it neglects smaller effects, like spin-spin interaction which are responsible for the very interesting magnetic properties found throughout the family.

The most serious criticism which can be applied to the model is the assumption of a short-ranged interaction G which is independent of n_T, the concentration of electron in the localized level. The long-range Coulomb interaction cannot be completely screened off in the insulating limit, and corrections due to the long-range tail may become important. If the short-range assumption is taken at face value, however, the dependence of G on n_T should be small, since only short distances are involved and screening is therefore not important. The problem, however, deserves more study and further thought.

In conclusion, we would like to point out that similar models can be built for substances which are not necessarily insulators but which have both well-defined localized and extended states. Such a case can be made for the rare-earth metals, and some of the interesting phase transitions found in them[25] can probably be explained along lines similar to those presented here.

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Thermally Stimulated Conductivity and Luminescence in KBr Due to γ Irradiation at 10°K

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The annealing behavior of KBr, γ-irradiated at 10 °K, was studied by means of simultaneous measurements of the thermally stimulated conductivity and luminescence and of the optical absorption. Over the investigated temperature range between 10 and 35 °K, the conductivity and luminescence behaved very similarly, and the latter did not change its spectral distribution. All observed peaks have been ascribed to the annealing of the irradiation-induced imperfections of the lattice structure. Four peaks, appearing at 14, 17, 20, and 24 °K with characteristic activation energies between 0.025 and 0.058 eV, which saturate in intensity after a moderate irradiation dose, are believed to be due to the generation of conduction electrons. A smaller peak at 22 °K, which was observed only in the conductivity data, may be due to ionic motion. The most prominent peak appeared at 27 °K, and it was shown by "thermal cleaning" experiments that this peak is caused by processes with activation energies of 0.062 and 0.100 eV. Here, too, the signals are believed to be caused by conduction electrons and their consecutive recombination with traps. The 0.062-eV process has "mixed-order" kinetics, i.e., there is an excess of recombination centers. At higher irradiation doses, the 0.100-eV process becomes dominant. This process seems to be associated with the first annealing stage of the *H* band, which had an activation energy of 0.097 eV. A tentative model of the *H*-center decay involves the dissociation of the *H* center followed by an interstitial-vacancy recombination.

I. INTRODUCTION

It is generally believed that the low-temperature annealing processes of the interstitial-type centers in irradiated KBr crystals are associated with the recombination of complimentary centers. Considerable light on the nature of the annealing of the Br⁻ interstitial has come from the kinetic studies of the α-band annealing carried out by Smoluchowski and his co-workers.[1,2] In particular, these workers suggest that the annealing event at 22 °K is due to a random migration of Br⁻ interstitials with a motion