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# A Phenomenological Model for Semiconductor–Metal Transition in Mixed Conductors

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A phenomenological model for mixed conductors which includes interaction between mobile ions and mobile electrons was studied. The model predicts that an abrupt or gradual increase in the electronic carrier concentration accompanies the transition to the superionic phase. The magnitude of the jump in electronic carrier concentration at the superionic transition shows an increase with decrease in the valence and conduction bandwidths.

## 1. Introduction

In this paper, we extend the models proposed by Huberman (*1*) and Rice *et al.* (*2*), for transition to the superionic phase in pure ionic conductors, to mixed conductors. The models of Huberman and Rice *et al.* predict that in pure ionic conductors there is an abrupt or gradual increase in the mobile ion density with increase in temperature. In our model, besides thermally activated creation of mobile ions, we also consider thermally activated creation of electronic charge carriers and introduce an effective interaction between the two species. Hence, our model should be applicable to systems such as $Ag_2S$ which have small band gaps and also show a transition to the superionic phase (*3, 4*). Although we consider mainly intrinsic materials, our results are qualitatively correct for the case of extrinsic materials. In the next section we describe the model and in the last section we discuss the results of our model.

## 2. Model

Following Huberman and Rice *et al.*, we assume that the mobile ions are at the interstitial positions and are associated with a Frenkel energy of formation $U_i$. The mobile ions are effectively coupled to each other through a strain field associated with the displacement of ions from the "ideal" lattice positions to the interstitial positions. This coupling is assumed to be attractive with strength $U$. Assuming that for every "ideal" lattice position there are $g$ interstitial positions, the configurational entropy associated with the creation of interstitial ions is easily computed. There is also a vibrational contribution to the total entropy associated with the creation of interstitial ions and it arises due to the lower localized interstitial phonon frequency compared with the phonon frequency of the perfect crystal (*5*). This vibrational contribution has the form $3k_BN_i\ln\Gamma$, where $\Gamma$ is the ratio of interstitial phonon frequency to that of

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the perfect lattice and $N_i$ is the number of interstitial ions. The Helmholtz free energy density of the ions measured relative to the perfectly ordered state can now be written as

$$\mathscr{A}_{\text{ion}} = A_{\text{ion}}/N = n_i U_i - n_i^2 U + 2k_B T[n_i \ln n_i + (1 - n_i)\ln(1 - n_i) + n_i \ln g + \tfrac{3}{2} \ln \Gamma], \quad (1)$$

where $n_i$ is the fraction $N_i/N$ and $U_i$ and $U$ are positive.

To calculate the Helmholtz free energy of electrons in the solid, we assume that at $T = 0$ K there are no free electronic carriers and that at nonzero temperatures electronic carriers are created intrinsically through excitation across a band gap of magnitude $E_g$. Furthermore, following Adler and Brooks (6) we treat the electrons and holes as independent phases with chemical potentials $\mu_c$ and $\mu_v$, respectively. The Helmholtz free energy of the electronic carriers can therefore be written as

$$A_{\text{el.}} = N_e \mu_c + (N - N_e)\mu_v - (PV)_{\text{el.}} - (PV)_{\text{hole}}. \quad (2)$$

Since electrons and holes obey Fermi–Dirac statistics, Eq. (2) takes the form

$$A_{\text{el.}} = N_e \mu_e + (N - N_e)\mu_v - k_B T \int_{-\infty}^{\infty} \rho_c(E) \ln \left[1 + \exp\left(\frac{\mu_c - E}{k_B T}\right)\right] dE - k_B T \int_{-\infty}^{\infty} \rho_v(E) \ln \left[1 + \exp\left(\frac{\mu_v - E}{k_B T}\right)\right] dE, \quad (3)$$

where $\rho_c(E)$ and $\rho_v(E)$ are the density of states functions of the conduction and valence bands, respectively, and we have substituted expressions for $(PV)_{\text{el.}}$ and $(PV)_{\text{hole}}$ derived from the grand canonical ensemble formulation (7).

In the narrow band limit, the density of states functions can be approximated by Dirac delta functions, i.e., we can write

$$\rho_c(E) = N\delta(E - E_c), \quad (4a)$$

$$\rho_v(E) = N\delta(E - E_v), \quad (4b)$$

where $E_c$ and $E_v$ are the conduction band and valence band energies, respectively. In this approximation the electronic free energy can be written as

$$A_{\text{el.}} = N_e \mu_c + (N - N_e)\mu_v - k_B T\left\{\ln \left[1 + \exp\left(\frac{\mu_c - E_c}{k_B T}\right)\right] + \ln \left[1 + \exp\left(\frac{\mu_v - E_v}{k_B T}\right)\right]\right\}. \quad (5)$$

Minimizing $A_{\text{el.}}$ with respect to $\mu_c$ and $\mu_v$ and using the resulting expressions for $\mu_c$ and $\mu_v$ in $A_{\text{el.}}$, we can write

$$\mathscr{A}_{\text{el.}} = A_{\text{el.}}/N = n_e E_g + 2k_B T[n_e \ln n_e + (1 - n_e)\ln(1 - n_e)], \quad (6)$$

where $n_e$ is the fraction $N_e/N$ and $\mathscr{A}_{\text{el.}}$ is measured relative to the valence band edge. We should expect the mobile electrons and holes to interact with each other and so we include a quadratic term in $n_e$ in the expression for the free energy density and write

$$\mathscr{A}_{\text{el.}} = n_e E_g - n_e^2 V + 2k_B T[n_e \ln n_e + (1 - n_e)\ln(1 - n_e)], \quad (7)$$

where $V$ is the effective electron–electron interaction strength. It is reasonable to expect the effective electron–electron interaction to lower the free energy as these electronic carriers are mobile and lead to a net screening of the electron–electron repulsions.

The free energy density of electrons can also be computed in the effective mass approximation. In this approximation, we assume that $\rho_c(E)$ and $\rho_v(E)$ are given by

$$\rho_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(E - E_c)^{1/2}, \quad E \geq E_c, \tag{8a}$$

$$\rho_v(E) = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}(E_v - E)^{1/2}, \quad E \leq E_v, \tag{8b}$$

where $m_e^*$ and $m_h^*$ are the average effective masses of the electron and hole, respectively, and the number of states in each band is restricted to $N$. The electronic free energy in this approximation is given by

$$A_{\text{el.}} = N\bar{E}_v + N_e\mu_c + (N - N_e)\mu_v - \frac{4}{3\pi^{1/2}}k_B T^{5/2}\left[\alpha_e F_{3/2}\left(\frac{\mu_c - E_c}{k_B T}\right) + \alpha_h F_{3/2}\left(\frac{\mu_v - E_v}{k_B T}\right)\right], \tag{9}$$

where $\bar{E}_v$ is the mean valence band energy and $\alpha_e$, $\alpha_h$, and $F_n(y)$ are given by

$$\alpha_{e,h} = \frac{1}{4}\left(\frac{2m_{e,h}^* k_B}{\hbar^2\pi}\right)^{3/2}, \tag{10a}$$

$$F_n(y) = \int_0^\infty \frac{x^n}{\exp(x - y) + 1}\,dx. \tag{10b}$$

Minimizing $A_{\text{el.}}$ with respect to $\mu_c$ and $\mu_v$ and evaluating the integrals $F_n(y)$ in the Boltzmann limit, we can write

$$A_{\text{el.}} = N\bar{E}_v + N_e E_g + 2N_e k_B T \ln\left(\frac{N_e}{e\alpha^* T^{3/2}}\right), \tag{11}$$

where $\alpha^* = (\alpha_e\alpha_h)^{1/2}$ and $e$ is the natural number. Assuming that the electronic free energy density is measured relative to the mean valence band energy and invoking effective electron–electron interactions, we can write the free energy density $\mathscr{A}_{\text{el.}}$, in the effective mass approximation, as

$$\mathscr{A}_{\text{el.}} = \frac{A_{\text{el.}}}{N} = n_e E_g - n_e^2 V + 2k_B T \times \left[n_e \ln n_e + n_e \ln\left(\frac{N}{e\alpha^* T^{3/2}}\right)\right]. \tag{12}$$

The central assumption of the model is that the mobile electrons and the mobile ions have an effective attractive interaction leading to a lowering of the total free energy. This indeed is possible since creation of interstitial ions reduces the Madelung splitting of the bands. Furthermore, overlap of cation and anion orbitals is reduced due to the increased mean distance between the two species (*4*). This results in a reduction in the covalent splitting of the bands as well. Both these factors tend to decrease the band gap. Thus it is reasonable to assume that the creation of mobile ions favor creation of electronic carriers. It is also known that the mean cation–cation separation in the superionic phase is smaller than that in the normal phase (*4*). So, we should expect cation–cation repulsion to suppress creation of mobile ions, thus acting against the strain field. The electronic carriers, being mobile, tend to screen this repulsive interaction and hence in turn favor creation of mobile ions. This aspect of creation of mobile ions favoring creation of electronic carriers and vice versa can be incorporated into the total free energy expression through a term of the form

$$\mathscr{A}_{\text{el.-ion}} = -Wn_i n_e. \tag{13}$$

The total free energy density of the solid is given by the sum of all the three contributions, i.e.,

$$\mathscr{A}_{\text{tot.}} = \mathscr{A}_{\text{ion}} + \mathscr{A}_{\text{el.}} + \mathscr{A}_{\text{el.-ion}}. \tag{14}$$

The density of mobile ions and mobile electrons can be calculated as a function of temperature by minimizing the total free energy density with respect to the quantities $n_i$ and $n_e$. In the narrow-band approximation we have

$$n_i = \left\{1 + g^{-1/2}\Gamma^{3/2} \times \exp\left[\frac{1}{2k_B T}(U_i - 2Un_i - Wn_e)\right]\right\}^{-1}, \tag{15a}$$

$$n_e = \left\{1 + \exp\left[\frac{1}{2k_BT} \times (E_g - 2Vn_e - Wn_i)\right]\right\}^{-1}. \quad (15b)$$

In the effective mass approximation, $n_i$ is still given by Eq. (15a) but $n_e$ is given by

$$n_e = \frac{T^{3/2}\alpha^*}{N} \times \exp\left[-\frac{1}{2k_BT}(E_g - 2Vn_e - Wn_i)\right]. \quad (15c)$$

We have solved the above equations numerically for various reasonable values of the parameters to obtain $n_e$ and $n_i$ as functions of temperature.

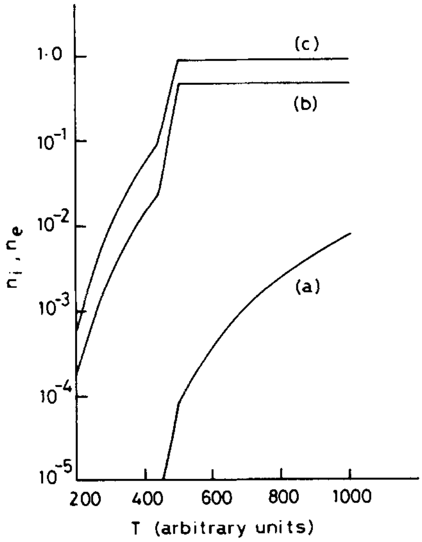

FIG. 1. Dependence of $n_e$ and $n_i$ on temperature in the narrow band limit. (a) $n_e(T)$ for $U_i = 0.3$, $U = 0.25$, $g = 1, \Gamma = 0.5, E_g = 1.0$, $V = 0.1$, $W = 0.2$. (b) $n_e(T)$ for $E_g = 0.3$, with the rest of the parameters remaining as in (a). (c) $n_i(T)$. This is very nearly the same for both sets of parameters (a) and (b).

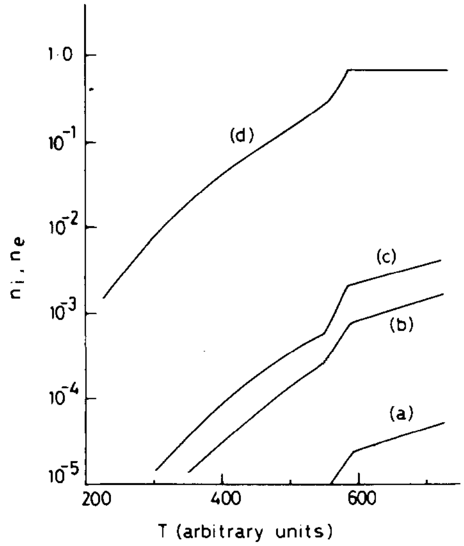

FIG. 2. Dependence of $n_e$ and $n_i$ on temperature in the effective mass approximation. (a) $n_e(T)$ for $m_e^* = 1$ $m_e$, (b) $n_e(T)$ for $m_e^* = 10$ $m_e$, (c) $n_e(T)$ for $m_e^* = 20$ $m_e$, and (d) $n_i(T)$ which is independent of $m$. The values of the remaining parameters are the same as in Fig. 1a.

## 3. Results and Discussion

Our model predicts a transition to the superionic phase, for suitable values of the parameters, as should be expected from earlier work. The superionic transition is accompanied by an electronic transition in both the narrow band limit and in the effective mass approximation. The change in electronic carrier concentration at the transition is abrupt if the ionic transition is abrupt and is gradual if the latter is gradual. For large band gaps, the electronic carrier concentration continues to increase beyond the transition, while for small band gaps the electronic carrier concentration saturates immediately above the transition (Fig. 1). The actual carrier concentration, in the broad band limit, besides being strongly dependent on $E_g$, is also found to depend strongly on the average effective mass or the bandwidths. The larger the effective mass, the higher is the electronic carrier concentrations at all temperatures (Fig. 2). This strong dependence of the electronic carrier concentration on the bandwidths is to be expected, as the electronic contribution to entropy, for a given $n_e$, decreases with increasing bandwidth. The transition temperature depends strongly upon $g$, the number of interstitial positions in the lattice available for every "ideal" lattice position. However, the transition does not depend strongly on the parameter $\Gamma$. We also find that the electron–electron interaction parameter, $V$, does not play an important role in the transition. This is to be expected since our choice of the parameters in $\mathcal{A}_{\text{ion}}$ have been such as to provide for a superionic transition. Given that a superionic transition does take place the term $Wn_i$ in Eq. (15b) dominates, forcing an electronic transition even if electron–electron interaction is weakly repulsive.

It is possible to extend our model to extrinsic materials exhibiting superionic transition and to predict the behavior of electronic carrier concentration near the superionic transition. Let us assume that our extrinsic material is doped only with donors (acceptors). The electronic free energy in the narrow-band approximation can be written as

$$\mathcal{A}_{\text{el.}} = n_e E'_g + k_B T \Big\{ [n_e \ln n_e + (1 - n_e)\ln(1 - n_e)] + x \Big[ \frac{n_e}{x} \ln \frac{n_e}{x} + \Big(1 - \frac{n_e}{x}\Big) \ln\Big(1 - \frac{n_e}{x}\Big) \Big] \Big\}, \quad (16)$$

where $E'_g$ is the energy gap between donor (acceptor) levels and the conduction (valence) band edge and $x$ is the ratio of number of donors (acceptors) to the number of states in the band. Assuming that the donor (acceptor) levels are rigidly fixed and that the conduction (valence) band shifts to lower (higher) energies with the creation of mobile ions (for reasons already discussed), we obtain qualitatively the same temperature dependence of $n_e$ near the superionic transition as in the case of intrinsic materials. However, we find two differences. First, the maximum carrier concentration in the extrinsic materials does not exceed $x$. Second, the nature of the electronic depends weakly on $x$, with the dependence becoming weaker as $x$ increases. The same similarities between intrinsic and extrinsic materials are found even in the effective mass approximation. The analysis becomes more complicated in compensated materials. Even so, it is reasonable to expect an electronic transition to accompany superionic transition (if these materials indeed exhibit the latter), since the same driving force should be present in this case as well. In conclusion, our model predicts that mixed conductors exhibit a superionic and an electronic transition, both at the same temperature, the latter being more pronounced for low activation energies and high effective mass.

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