ELECTRON TRANSPORT PROPERTIES OF TRANSITION METAL COMPOUNDS†

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INTRODUCTION

The experimental situation with regard to the electrical properties of the transition metal compounds is, on the whole, rather unsatisfactory. In the main this is due to the fact that single crystals are not readily prepared. Thus, to date, the vast majority of the data result from measurements on pressed and sintered or polycrystalline masses. As is well known, the intergranular structures can have a pronounced effect on the electrical properties. Thus such data are not necessarily representative of the bulk material itself. As a consequence, much time has been needlessly spent on devising theories or explanations of effects which turn out to be spurious.

The approach taken in the present paper will be somewhat the opposite. We will take a rather idealized model of a compound semiconductor and simply ask what are the various properties that one might reasonably expect. We will see that such an attack gives, at first glance, several unexpected results, which naturally lead to some new experimentation. In addition, we take the point of view that results not contained within the framework of this model should be carefully examined to ascertain that they are really representative of the bulk material under study.

In order to make this article easily accessible to those not familiar with the ideas of band theory, an attempt will be made to provide the necessary background. Furthermore, we will avoid unnecessary mathematical detail, keeping the chemical and physical basis of things in the foreground.

Since this article is to be devoted to a study of electrons, it is worthwhile to ask how we might best describe them. It is well known that we may assign an electron a wavelength λ given by

$$\lambda = \frac{h}{p} \tag{1}$$

where h is Plank's constant and p is the momentum of the electron. To get an order of magnitude let us ascertain the wavelength of an electron possessing thermal energy, $\boldsymbol{k}T$, where $\boldsymbol{k}$ is the Boltzman constant. Expressing p in terms energy $E(p = \sqrt{(2mE)})$ and setting $E \approx \boldsymbol{k}T$, we quickly find

$$\lambda = \frac{h}{(2m\boldsymbol{k}T)^{1/2}} \tag{2}$$

where m is the mass of the electron.

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Speaking very loosely we can take this wavelength as a measure of the spatial extent or size of the electron. If, for example, we now determine the wavelength of an electron where the thermal energy is evaluated at room temperature, we find this wavelength to be approximately 60 Å. That is, one might consider the electron as being spread over a volume approximately 60 Å on a side.

You will observe that we have used the mass of the free electron in our discussion thus far. We must examine this point. In fact, we now show that in solids the free electron mass should not be used. What is the mass of a particle? It is simply that property of a body which relates force, F, to acceleration, a, that is, it is simply the proportionality constant in Newton's second law. The most important thing to remember about this relation is that the force F must include *all* the forces acting on the electron. Consider two cases: (1) an electron in a vacuum acted on by an electric field and (2) an electron in a solid acted on by an electric field. In the first case the sole force acting on the particle is the electric field and m is, of course, the mass of the free electron. In the second case, however, we have a complication. Here the force must include not only the external electric field but also all the forces due to the other electrons and nuclei in the crystal. Thus we can write

$$F_{\text{crystal}} + F_{\text{electric field}} = ma \tag{3}$$

where F_{crystal} refers to the forces originating from the other electrons and nuclei of the solid. Again m is clearly the free electron mass. However, this equation is of little use to us as we would really like to have a relation between the acceleration of the electron and the applied *external force*, namely the electric field. Now it turns out that this can be done. We may write the preceding equation in a form resembling the free space equation

$$F_{\text{electric field}} = m^*a \tag{4}$$

where we have simply replaced the electron mass by m^*, the effective mass. In other words all the crystal forces have been lumped into the electron effective mass. It turns out that it is possible for this quantity to be either greater or less than the free electron mass. In fact, we will even see that it can be negative. We will find this concept of effective mass useful; however, we must keep in mind that although it is a concept which allows many discussions to be simplified, it is not an easy quantity to calculate. It is clear, in fact, that to do this one must evaluate the crystal forces.

Let us try to get some insight into the factors determining the effective mass. Suppose we consider a crystal of very large lattice spacing, and we put an extra electron on one atom. Since the lattice spacing is very large we know that it will be very difficult for the electron to move from one atom to another. Therefore, on applying an electric field we would expect the acceleration of the electron to be very small. Looking at our equation, we see that this means that the effective mass would be consequently very large. Thus we see that the effective mass is essentially a measure of how tightly bound an electron is to an atom. In a solid, the core electrons of an atom have very large effective masses, whereas the conduction electrons in a

metal, for example, have effective masses of the order of the free electron mass.

Looking back to equation (2) for the "size" of an electron, we see that it depends inversely on the square root of the mass. Thus as the mass, that is, the effective mass, of the electron increases, its size will decrease. It is convenient to remember that for an effective mass of approximately 100 electron masses the "size" of the electron is down to approximately one lattice constant. We will see presently that when the effective mass of the electron gets this large it is preferable to drop the concept of the wavelength for the electron and to treat it essentially as a classical particle localized on a given atom.

We now wish to see in what types of crystal each of these descriptions is proper and then we wish to see what electrical properties follow in each case. In order to do the former let us consider the following thought experiment (*Figure 1*). Consider a lattice in which we hold all the atoms rigidly

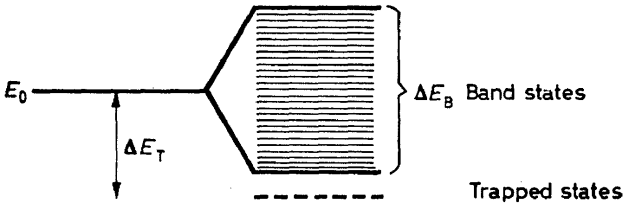

Figure 1

in position. Now add one additional electron to this crystal, placing it upon a given atom. We may designate the energy of the electron in this case by E_0. We now want to show that there are two alternate sets of energy levels available to the electron. We may see this as follows. Let us continue to hold all the atoms of the crystal fixed in place but let us free the electron from the constraint which forces it to remain on a given atom. Under these conditions we know that all the sites in the crystal are equivalent and that the proper quantum mechanical description for the electron is a state in which the electron has an equal probability of being on any given site. We know that when we solve this problem to find the energy of the electron, we find a whole series of states, the total number being equal to the total number of atoms in our solid. The average energy of these states is equal to E_0, and the spread in energy is equal to the band width ΔE_B.

To find the other set of states accessible to the electron we may reverse the above procedure and hold the electron fixed on a given atom but allow all other atoms of the lattice to move. We know that the additional charge on the given atom will distort the surrounding lattice. It can be shown that this distortion is able to trap the electron on the given site. The depth of this trap is denoted by ΔE_T.

Now if we are to ask what is the proper description of the electron we need only ask which are the lowest energy states available to the electron. From *Figure 1* we see that if the depth of the trapped state ΔE_T is greater than half

the band width ΔE_B, the electrons will find themselves in the localized trapped states. This is the situation shown in the figure. If the converse is true, namely, if half the band width is greater than the depth of the trap, the electrons will be found in the band states.

We might pause a moment to ask what physical factors determine the width of the band. The band width is determined essentially by the overlap of the wave function of an electron when centred on neighbouring atoms. Thus, if the spacial extent of the electronic wave function is large, that is, if the effective mass is small, we will find the overlap great and consequently the band width will be large. Conversely, a large effective mass will lead to a small band width.

Let us now state a few of the fundamental ideas with regard to the electron transport properties of crystals. First, we know that it is one of the results of quantum mechanics that a periodic lattice will not scatter electrons. Thus the resistivity of a perfectly periodic lattice is zero. The resistance comes about from structural defects, impurities, the vibrations of the atoms in the lattice, *etc.* It is easy to see the temperature dependence of the resistivity due to these atomic vibrations, for we know that as the temperature is increased the magnitude of the vibration, and therefore the deviation from perfect periodicity, increases. Thus we must expect the electrical resistivity to increase with temperature. These ideas are proper when using a band description for the conductivity. However, if the trapped states happen to be the lowest energy states, then the conduction process may be treated essentially as a classical diffusion problem. We will see later how to do this.

Consider now the thermoelectric effects, namely the Seebeck coefficient α and Peltier coefficient π. (These two coefficients are related by the equation $\alpha = \pi/T$.)

We would like to set up a general method for calculating the Peltier coefficient. From the definition we know that this coefficient is simply the heat absorbed from an external reservoir when electrons are removed from the material in such a way so as to maintain the temperature constant. Let us now see how to calculate this heat. If we assume that the volume of the material is maintained constant when the electrons are removed, we may write the change in internal energy of our system

$$\mathrm{d}E = \left(\frac{\partial E}{\partial S}\right)_N \mathrm{d}S + \left(\frac{\partial E}{\partial N}\right)_S \mathrm{d}N \tag{5}$$

Using the standard thermodynamic relations we may write

$$\mathrm{d}E = T\,\mathrm{d}S + \mu \mathrm{d}N \tag{6}$$

where μ is the chemical potential of the electrons. If we further write

$$\mathrm{d}E = \bar{E}\mathrm{d}N \tag{7}$$

where $\bar{E}$ is the average energy of the electrons removed from the solid, we see finally that

$$\mathrm{d}Q = T\mathrm{d}S = (\bar{E} - \mu)\,\mathrm{d}N \tag{8}$$

Remembering that the Peltier coefficient is defined per unit charge rather than per particle we see immediately that

$$\pi = \frac{\bar{E} - \mu}{e} \tag{9}$$

where e is the electron charge.

What can we say in general about μ and $\bar{E}$? We know that μ, by definition, is the change in free energy on adding an additional electron. Now on adding an electron we get three contributions to the change in free energy.

(*i*) When an electron is added to the crystal, the energy is increased by $(E_0 - \Delta E_T)$ in the case of the trapped states. (In the case of the band states the increase in energy will depend on how full the band is when the additional electron is added. In the case of low concentrations, that is, a nearly empty band, the increase in energy will be essentially $E_0 - \Delta E_B/2$.)

(*ii*) There will be an entropy term, due to the entropy of mixing, given by $\boldsymbol{k}T \ln (c/c_0 - c)$, where c is the concentration of conduction electrons and c_0 is the concentration of states accessible to the electron.

(*iii*) Finally, there will be a contribution due to the magnetic structure. This latter we will simply term ΔG_M for the moment. (In the case of trapping we are going to neglect the entropy change arising from the distortion surrounding a trapped carrier. This is small under normal conditions[1].) Thus we may write in the case of trapping

$$\mu = E_0 - \Delta E_T + \Delta G_M + \boldsymbol{k}T \ln \frac{c}{c_0 - c}$$

In the band case $-\Delta E_T$ must be replaced by $-(\Delta E_B/2)$.

We now want to see how these concepts on the electrical properties can be applied to the transition metal compounds.

We may first examine the electrical properties in a material in which the lowest set of energy levels are those of the band. Before going into this, we might ask how bands arise in real crystals. Consider the classic example of germanium. Here each germanium is bound to four nearest neighbours by four covalent bonds. Each covalent bond consists, of course, of two electrons, one contributed by each germanium taking part in the bond. If we now take an electron from one of the bonds and remove it to another part of the crystal so that the interaction between the electron and the broken bond is zero, we see that we have created a free electron and a defective bond. This defective bond is commonly referred to as a hole. Now the electron which has been removed from the bond can have some kinetic energy. Thus a whole series of energy states are available to the electron starting from the energy required to break the covalent bond on up. This band of energy states formed from the electron so created is called the conduction band. The band formed by the electrons in the bonds is referred to as the valence band. Based on this picture, we might draw the energy level diagram for the electrons in pure germanium as shown in *Figure 2.*

Thus far we have discussed only the situation where electrons come from the valence band. However, there is another way to introduce free carriers into the conduction band. If, for example, we replace an atom of germanium by an atom of arsenic, we know that arsenic has one additional electron outside of closed shells than has germanium. Therefore, this electron is not needed in forming the necessary four bonds in the crystal. It is, therefore, not as tightly bound as are the electrons in the covalent bond. Schematically we may put in these levels as shown in *Figure 2.*

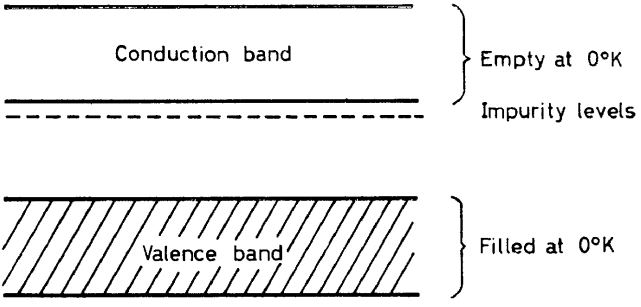

Figure 2

We have just discussed the width of the conduction band in terms of the kinetic energy possessed by the electron. Classically, therefore, there should be no limit to the width of such a conduction band. However, quantum mechanically one does indeed find only certain energy ranges of states are permissible. This comes about essentially from the wave nature of the electron, for when the electron has a wavelength equal to twice the lattice spacing it cannot be propagated through the lattice due to Bragg type reflection. We can understand the situation qualitatively if we consider an electron initially at rest to which we apply an electric field. The electron will be accelerated in the direction of the field and will increase in energy. However, we have already seen that an increase in energy means a decrease in the wavelength of the electron. As the wavelength decreases we begin to get partial reflection of the electron due to the periodically spaced planes of atoms. This can be thought of as a reduction of the net current in the direction of the field or, in turn, as a reduction of the net velocity of the electron. In other words, the acceleration of the electron is now opposite to that of the electric field. As we continue to accelerate the particle the wavelength gets shorter. We finally come to the point of total reflection, and we therefore have a standing wave in the crystal equivalent to zero velocity for the electron. Thus we have the unusual phenomenon that under the application of an electric field an electron increases in velocity to a certain maximum value and then decreases to zero. This phenomenon is commonly discussed in terms of effective mass. When the acceleration is opposite to that of the electric field, one describes this in terms of a negative electron effective mass. Normally one finds that in the lower half of the band the effective masses are positive, whereas in the upper half of the band, in the higher energy states, the effective masses are negative. These negative

effective masses will play a very important rôle in the electrical properties of the transition metal compounds.

We might consider briefly those properties of the crystal which help in determining the width of this band. We have already mentioned one factor, namely, the overlap of the electron wave functions on neighbouring atoms. In addition, the degree of order in the crystal is important. At absolute zero where atomic motions are at a minimum, the band width is at its maximum. As we go to higher temperatures, the atomic vibrations increase and the band width decreases because of this increased disorder. In most semiconductors where the bands are very wide this decrease is not observed. We will presently see why. Another form of disorder is that related to the magnetic properties of the crystal. At absolute zero where we might have a perfect ferromagnetic lattice, the band width is a maximum. As we approach the Curie point, the band width will decrease because of the spin disorder. It is thus possible that the proper description of the electrons might change from the band states to the trapped states on going through the Curie temperature.

We now ask how the energy levels of the band will be populated by the electrons. For the cases that we will consider, the density of conduction electrons will be small, and therefore we can use classical statistics. This means that the number of particles n_i in any energy level E_i will be proportional to the exponential

$$n_i \propto e^{-E_i/\mathbf{k}T} \tag{10}$$

The important thing to observe is that if the energy of a particular level is say 4 or 5 times $\mathbf{k}T$, that level only has a very small chance of being occupied. Thus we can conclude that only those levels within several $\mathbf{k}T$ of the bottom of the conduction band will be of interest to us.

TRANSPORT PROPERTIES IN A BROAD BAND

We are going to consider two cases now, one case where the conduction band width is very large compared to kT, and the other where the band width is of the order of $\mathbf{k}T$. Let us treat the broad band first. This is the common case. We briefly review the properties here so that an appropriate comparison may be easily made with the other cases. The conductivity is simply proportional to the number of carriers in the band times the mobility of the charge carrier, the mobility being defined as the velocity of a carrier under the application of unit electric field. We have already seen that the number of particles in the conduction band will be some exponential function of the temperature, and we also can say that, in general, the mobility μ of an electron will decrease with increasing temperature. We have seen, for example, that the increase in the atomic vibrational amplitudes with temperature will have this effect. Therefore, we might write the conductivity in the following form

$$\sigma = \mu(T)e^{-E/2\mathbf{k}T} \tag{11}$$

In the case of a pure material where the electrons in the conduction band can come only from the valence band, E is the energy separation between

the top of the valence band and the bottom of the conduction band, the so-called energy gap. If the carriers in the conduction band arise from the impurities, E is the energy separation of the impurity levels from the bottom of the conduction band. Clearly the temperature dependence of the mobility will be marked unless $E \gtrsim 2\mathbf{k}T$.

Let us now examine the behaviour of the Peltier coefficient in this limit of band width large compared to $\mathbf{k}T$. If we measure $\bar{E}$ from the bottom of the conduction band, that is, if $\bar{E}$ is the average *kinetic* energy of the electrons removed, we may approximate the Peltier coefficient

$$\pi = \frac{1}{e}\left[\bar{E} - \mathbf{k}T \ln \frac{c}{c_0 - c}\right] \tag{12}$$

We have neglected any magnetic contributions. These will be discussed later. Now in equation (12) $\bar{E}$ is the average kinetic energy of the electrons leaving the crystal. This is *not* necessarily the average kinetic energy of the electrons in the conduction band. For example, suppose the high energy electrons have very small mobility, that is, they have a very small velocity under the influence of an electric field. In this case most of the current would be carried by the low energy electrons and $\bar{E}$ would be correspondingly low. It turns out that for wide band semiconductors we can write

$$\bar{E} = A\mathbf{k}T \tag{13}$$

where the constant A is only a function of the scattering mechanism for the electrons. It is usually a number of the order of unity.

It remains to examine the second term in the expression for the Peltier coefficient. Using our previous ideas we can give a rather simple argument which leads to essentially the correct answer. The meaning of c is clear. This is simply the concentration of free electrons in the conduction band. Now c_0 is concentration of states accessible to the electrons. We can roughly approximate this quantity from the spatial volume associated with an electron. We have already seen that this is

$$\lambda^3 = \frac{h^3}{(2m^*\mathbf{k}T)^{3/2}} \tag{14}$$

c_0 is then roughly the reciprocal of this quantity divided by N, the total number of atoms. For concentrations c much less than c_0 we may neglect c in the denominator of the logarithmic term in equation (12). We can finally write

$$\pi = \frac{kT}{e}\left\{A - \ln \frac{ch^3}{(2m^*\mathbf{k}T)^{3/2}}\right\} \tag{15}$$

This is very close to the exact expression. The exact expression for the Seebeck coefficient $\alpha(=(\pi/T))$ is

$$\alpha = \frac{\mathbf{k}}{e}\left\{A - \ln \frac{ch^3}{2(2\pi m^*\mathbf{k}T)^{3/2}}\right\} \tag{16}$$

It should be remarked that the argument of the logarithm is always less than unity. Thus this term gives a positive contribution to the Seebeck coefficient. We see that the temperature dependence of the Seebeck coefficient comes about from the explicit dependence in the denominator of the logarithmic term or from the implicit dependence in c, the concentration of free carriers.

The fact that the Seebeck coefficient increases as $m^* T$ increases has a rather simple explanation. The logarithmic term is essentially the entropy of mixing. Increasing $m^* T$ increases the total number of states available to the electrons. This has the same effect as lowering the concentration. Both of these effects increase the entropy of mixing.

TRANSPORT PROPERTIES IN A NARROW BAND

Let us consider now what happens when the width of the conduction band becomes of the order of kT^2. We have previously said that energy levels in the upper half of the conduction band behave as if they had a negative mass, that is, electrons in these states are accelerated in the direction opposite to the electric field. In the normal wide band semiconductors one does not need to worry about these states of negative mass for they are many, many kT above the bottom of the band, and are therefore not occupied. However, with a band width of the order of kT, we recognize now that energy levels even at the top of the band will be partially populated. Thus we are going to have to ask what are the consequences of having electrons with both positive and negative effective masses.

Consider first the electrical conductivity. We make the assumption to start with that the band width is extremely small compared to kT. This means that all the energy levels in the band are equally populated. Thus we would expect to have as many electrons of positive mass as of negative mass. If we now apply an electric field to this solid, we easily see that the total current flow would be zero for there would be as many electrons flowing in the one direction as in the other. Thus we see that the conductivity goes to zero as the band width over kT goes to zero.

We can get an expression for this conductivity rather easily. As we have just seen, the dominant effect is the cancellation of carriers because of the two signs of effective masses. Therefore, we might say that the conductivity is roughly proportional to the difference between the number of carriers in the bottom half of the band and the number in the top half. We can easily estimate this ratio.

To do this we assume that the average energy of the states of positive mass is $\Delta E_B/4$ and the average energy of the state of negative mass is $(3/4)\Delta E_B$. This is shown in *Figure 3*. Then we may write that the ratio of the number

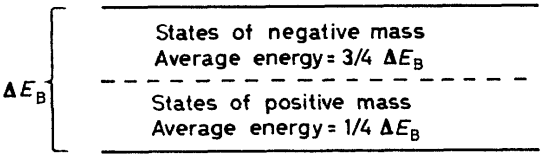

Figure 3

of electrons in the two groups of states is

$$\frac{N_+}{N_-} = \frac{e^{-\frac{\Delta E_B}{4kT}}}{e^{-\frac{3\Delta E_B}{4kT}}} = e^{\frac{\Delta E_B}{2kT}} \tag{17}$$

where N_+ refers to the number of electrons having a positive effective mass. Then, it follows that

$$\frac{N_+ - N_-}{N_+ + N_-} = \frac{e^{+\Delta E_B/2kT} - 1}{e^{+\Delta E_B/2kT} + 1} = \approx \frac{\Delta E_B}{4kT} \tag{18}$$

The latter equality follows, of course, when the exponent is small. Thus we see that σ behaves qualitatively as we expected.

Now let us examine the Peltier coefficient as the band width goes to zero. We can do this most simply from equation (12). Consider first the term $\bar{E}$. As we have seen, $\bar{E}$ is the average kinetic energy of the electrons contributing to the current. However, as the band width goes to zero, this average kinetic energy must obviously also go to zero. Thus $\bar{E}$ vanishes in the limit of very narrow band width. Looking now at the second term in the Peltier coefficient, we have seen that as the band width gets small, the effective mass increases. Thus the quantity in the denominator will increase. Now the total number of states available to the electron obviously cannot exceed the number of atoms in the crystal. Therefore, as the band width becomes narrower we quickly reach a point where the number of available electron states is equal to the number of atoms in the crystal. This means that c_0 becomes essentially unity. Thus we may write the Peltier coefficient for a narrow band material

$$\pi = -\frac{kT}{e} \ln \frac{c}{1-c} \tag{19}$$

Finally, it might be interesting to mention the result for the electronic component of the thermal conductivity. If we go through the calculation[2] we find that the thermal conductivity K is

$$K \approx \left(\frac{\Delta E_B}{kT}\right)^3 \tag{20}$$

It is easy to understand this result qualitatively. For in the limit of zero band width all the conduction electrons have the same energy independent of temperature. Therefore, remembering that thermal conductivity is measured at zero current, we see that no net energy or heat can be transferred. An interesting point here is that the Wiedemann-Franz ratio ($K/\sigma T$) goes to zero as the band width goes to zero.

These results involving the thermal conductivity have not yet been verified experimentally.

TRANSPORT PROPERTIES IN THE TRAPPED STATES

Having discussed the broad band and narrow band treatments of the transport properties, we may now consider the case where the charge carriers are trapped. First, let us discuss the particular kind of trap under consideration. When we put an electron, a charged particle, on a given atom in the crystal, this tends to distort the surroundings, both by virtue of the additional charge and by virtue of the fact that the size of the atom is changed. Now we postulate that this particle cannot move unless in some way the distortion can be carried along with it. From a quantum mechanical point of view, the charge carrier can only move if the site on which the particle rests and the site to which the particle is going are degenerate with one another, that is, if they possess the same atomic configurations. This is akin to the familiar concept of resonance between two degenerate states. This equivalence can occur in an infinite variety of ways. For example, one can completely remove the distortion from the site of the charged carrier itself, thus making the initial and final site equivalent. Or one can create an atomic distortion around the final site identical to that which exists at the initial site. And finally more generally, the distortion can be partially removed at the initial site and a corresponding distortion created at the final site. If we now consider that the forces involved in displacing the atoms are of an elastic nature, and if we consider that the force constant of the atoms surrounding the charge carrier is equal to k and the force constant around the final site is equal to k', we may easily write down the work[3] necessary to make the two sites equivalent. A schematic representation of the situation is given in *Figure 4*. The depth of the well on the left, ΔE_T, at

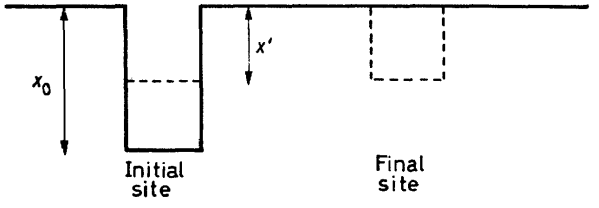

Figure 4

the site of the charge carrier, is equal to $1/2\, \boldsymbol{k} x_0^2$ where x_0 is the displacement of the nearest neighbouring atoms. If we now alter this displacement to a value x' and create an equal displacement x' at the final site, we must do an amount of work

$$\omega = \frac{1}{2}\boldsymbol{k}(x' - x_0)^2 + \frac{1}{2}\boldsymbol{k}'x'^2 \tag{21}$$

Now we postulate that the mechanism of motion will be that requiring the minimum value of this work. Thus if we minimize this work with respect to x' we find for the minimum value

$$\omega_{\min.} = \frac{1}{2}\boldsymbol{k}x_0^2 \frac{\gamma}{1+\gamma} = \Delta E_T \frac{\gamma}{1+\gamma} \tag{22}$$

where $\gamma = k'/k$. We see for example that if the force constants are equal the activation energy is equal to half the trapping energy. In practice one actually expects that the two force constants will be fairly close to the same value. In what follows we will simply assume this. This quantity $\omega_{\text{min.}}$ then represents the activation energy for the particle to jump to a neighbouring site. We now postulate[4] for the frequency of a jump

$$\nu = \nu_0 e^{-\omega_{\text{min.}}/kT} \tag{23}$$

The quantity ν_0 is normally found to be of the order of the optical mode frequencies of the crystal, that is approximately 10^{13}. The activation energy can range all the way from zero up to something of the order of 1 e.V. Using this expression for the jump frequency we can find the electrical conductivity. From the Einstein relation we have

$$\sigma = \frac{ne^2D}{kT} \tag{24}$$

where n is the number of carriers per unit volume and

$$D = \beta a^2 \nu \tag{25}$$

β is a structure dependent parameter, a is the lattice constant and ν is given by equation (23). Thus we may finally write the conductivity

$$\sigma = \frac{ne^2\beta a^2}{kT}\, \nu_0 e^{-\omega_{\text{min.}}/kT} \tag{26}$$

We see that the conductivity has two separate dependences on temperature. It should be pointed out that there is actually a third, for as we shall see, the magnetic properties give an additional temperature dependence.

Let us go on now to the Peltier coefficient for this type of compound. Again we must consider the same two terms as in previous cases. The first term $\bar{E}$ represents the average energy lost by the solid when a carrier leaves. What is this quantity in the trapping limit? When a particle leaves there is a decrease in energy of $(E_0 - \Delta E_T)$. There is an additional effect that comes in if the two force constants are not equal; however, as this term is normally small we will not discuss it further here. Thus

$$\bar{E} = E_0 - \Delta E_T$$

and therefore

$$\pi = \frac{1}{e}\{\bar{E} - \mu\} = \frac{-kT}{e} \ln \frac{c}{c_0 - c} \tag{27}$$

We see therefore that the activation energy for jumping does not enter.

We must reserve discussion of the Peltier coefficient for a moment in order to examine the significance of c and c_0 in compounds where trapping occurs. In order to see the problem clearly, let us examine the situation in a real compound. We will choose $Li_{1-x}Ni_{1-x}O$. We assume that for each lithium atom

added to a crystal one of the nickel ions will be converted from divalent nickel to trivalent nickel. This implicitly assumes that the lithium has a valence of plus one and the oxygen remains minus two. At very dilute concentrations and at very low temperatures, it is clear that the trivalent nickel will be on sites nearest neighbours to a lithium atom. This arises because the lithium is effectively a minus charge in the divalent lattice whereas the nickel plus three represents a positive charge in this lattice. Thus there will be a binding between the impurity or the lithium ion and the hole on the nickel plus three. As the temperature is increased we will expect some of the holes to be torn free of the lithium sites. By free we mean that the hole has been removed sufficiently far from the lithium so that there is no longer any interaction between it and the lithium. In practice this probably means that the hole has been removed to a distance several lattice constants away. A hole once free is now able to wander at random throughout the lattice provided, of course, that the appropriate activation energy for a jump is supplied each time. Under these conditions of very dilute concentrations the meanings of c and c_0 are the normal ones, namely, c is the number of carriers which has been freed from the impurity sites, and c_0 is the number of sites in the crystal available to these charge carriers. To get c_0 we must remember that the impurity sites are not available to the charge carrier nor are those sites immediately surrounding the impurity. However, at dilute concentrations c_0 is effectively unity. When we go to higher concentrations we immediately run into a problem. For the sake of discussion, let us go to a very high concentration, say 20 per cent lithium. At this concentration 95 per cent of the nickel atoms in the crystal have at least one nearest neighbour of lithium. Therefore, it no longer makes any sense to talk about the freeing of carriers from an impurity site. So it is clear that this concept needs to be modified. Consider a more moderate concentration of say 3 per cent. It is easily shown that 35 per cent of the nickel ions in the crystal have one nearest neighbour of Li. Furthermore, 10 per cent of the nickel ions have two nearest neighbours of Li. Now if 35 per cent of the lattice sites possess one lithium nearest neighbour, it is not difficult to believe that at this concentration it is possible for an electron to travel throughout the lattice, always travelling on sites possessing a single lithium neighbour. We need to make one further assumption. We assume that the electrons will always try to have the maximum possible number of nearest neighbours of lithium. This simply allows the electron to achieve its minimum electrostatic energy. This leads us to the following picture of the conduction process at high concentration. For concreteness we will discuss the 3 per cent concentration. At absolute zero all of the charge carriers will be on sites possessing two or more lithium neighbours. Now we have already seen that the sites possessing one nearest neighbour form continuous paths. However, it is easily shown that those sites possessing two nearest neighbours do not have this property. Thus this set of states cannot carry a current. However, as the temperature increases, some of the electrons will be excited to higher energy states, namely, to the nickel ions possessing one nearest neighbour. These electrons can carry a current. As the temperature increases further some electrons will be excited to even higher levels, namely to that set of levels possessing no nearest neighbours of Li. Thus we have essentially two parallel paths of

conduction. With this information as background, we may now re-examine the Seebeck coefficient. In the interest of simplicity we give an argument, which although not completely correct, does give one a proper feeling for the situation and leads to the correct result. As the temperature is increased, we have seen that the concentration of free carriers will increase. This tends to decrease the Seebeck coefficient. However, as the temperature is further increased, the electrons have available to them not only the sites possessing one lithium nearest neighbour, but also the sites possessing no lithium neighbours. Therefore, we see that as the temperature increases, c_0 increases causing α to increase. Finally, at very high temperatures c_0 should be simply equal to $1 - c$, and the Seebeck coefficient becomes independent of temperature.

Finally, let us consider those factors which tend to influence the activation energy for a jump. We have seen that the activation energy is essentially proportional to the square of the displacement of neighbouring atoms surrounding a trapped carrier. Thus we are reduced to finding those factors which influence the displacement of the neighbouring atoms when the valence of the metal ion is changed. From *Figure 5* we see two possible

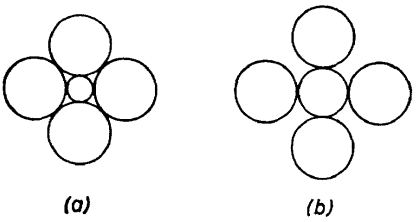

Figure 5

situations. In the first case we see that the anions are just at the point of touching. Thus if we substitute a much smaller atom in the metal site, the surrounding lattice really cannot distort very much. As a result we expect a small activation energy for jumping. On the other hand, in the second case shown in the figure the distortion is not inhibited by such considerations. Therefore we may conclude that the activation energy will be large for materials in which the radius of the cation to the radius of the anion is large. Thus we would predict that the activation energy for MnO, CoO, NiO should decrease in that order. In addition, we would make the same prediction as one goes from MnS to MnSe. Both of these predictions are borne out by experiment.

INFLUENCE OF MAGNETIC PROPERTIES

Up to this point the magnetic properties of the material have not been discussed. We now wish to examine their possible effect. In discussing the jump frequency of an electron from one site to another, we assumed that the particle would jump when the atomic configurations surrounding the initial and final site were equivalent. However, this is not quite so. For Anderson[5] has shown that the transition probability for an electron to jump between neighbouring ions is strongly dependent on the relative orientation of the

net spin of the atom. In fact, in the limit of large spin, he shows that the transition probability is proportional to the cosine of half the angle between the spins. Thus, in this limit, the transition probability between antiparallel ions is zero and between parallel ions is unity, and we can easily see qualitatively the behaviour of the conductivity. At absolute zero, if we have a perfect antiferromagnetic state, the conductivity will be zero. As we increase in temperature we have two effects which simultaneously tend to increase the conductivity. First, due to the demagnetization with temperature more and more atoms are found having parallel spins. This means that more jumps are possible. In addition, due to the increase in temperature more carriers will possess the necessary activation energy for a jump. Thus we may expect the temperature dependence below the Curie point to be faster than the simple exponential due to the hopping. However, above the Curie temperature where the spins are randomly oriented, we expect no further magnetic contribution. Therefore, the effective activation energy should appear to be less. This is in fact what one does find experimentally.

While we are on the point of the activation energy for conduction, it is worthwhile to ask how this activation energy changes on going through the Curie temperature. We have seen that the activation energy for conduction is related to the elastic constants of the crystal. We also know experimentally that the elastic constants in a magnetic material do not suffer discontinuous charges on going through the Curie temperature. (Although it is true that there is an effect in the vicinity of the Curie temperature this is due to the movement of domain walls and is not a bulk property.) In view of this, we do not expect that the activation energy for conduction should change at the Curie temperature. It should be pointed out, however, that there are some data which appear to contradict this statement. Several workers[6, 7] have found discontinuities in the conductivity curve for nickel oxide in the vicinity of the Curie temperature. However, on examining this situation carefully, we conclude that this effect is probably not related to the Curie temperature. For one thing, one finds that the temperature at which this break occurs varies by over 100° from sample to sample. One can certainly not expect that the Curie temperature will vary so strongly. Furthermore, one finds that this effect disappears upon the addition of a small quantity of Li, whereas the magnetic properties are essentially unchanged. Thus one must attribute this discontinuity to some impurity or more likely to some property of the nickel vacancies which are normally found in this lattice.

Finally, let us discuss the effect that the magnetic properties might have on the Seebeck coefficient. In this case the possibility that a given atom can be in a number of different spin states gives an additional contribution to the chemical potential. It is not easy to get the general form of this expression; however, the two limits are simple. At $T = 0$, all moments are rigidly fixed so that the addition of an electron does not alter the magnetic contribution to the entropy. On the other hand, above the Curie temperature where the moments are random, it is easy to show that the change in entropy on adding a carrier is

$$\Delta S_M = k \ln \frac{2s_2 + 1}{2s_1 + 1}$$

where s_1 and s_2 are the spins of the two types of atoms involved. For NiO, where $s_2 = 3/2$ and $s_1 = 1$, we get a contribution to the Seebeck coefficient of the order of $25\mu v/°C$. Thus we can say that this contribution is zero at $T = 0$ rising to a constant value of $25\mu v/°C$ at and above the Curie temperature. Such a contribution is normally negligible.

CONCLUSION

These simple ideas are capable of giving us a rather good picture of the transport properties of transition metal semiconductors. In the trapping region the situation has already been sufficiently studied experimentally so that we may have some confidence in the results. In the narrow band region much experimental work remains to be done in order to have a clear picture.

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