RICHARDSON-SCHOTTKY EFFECT IN SOLIDS

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The emission-limited J-V characteristic of a metal-vacuum interface is described by the Richardson-Schottky equation[1]:

$$J=\frac{4\pi e m(kT)^2}{h^3}\exp(-\varphi/kT)\exp(\beta E_0^{1/2}), \qquad (1)$$

where $\beta=(e/kT)(e/\pi\epsilon_0 K)^{1/2}$, ϵ_0 is the permittivity of free space, K is the dielectric constant, and E_0 is the field at the cathode-vacuum interface; the other symbols have their usual meaning.

This equation has also been used with some success to describe the emission-limited characteristic in solids. It is the object of this note, however, to show that if the electronic mean free path is very small, as is usual in insulators, the above equation is not strictly correct.

Figure 1(a) shows the energy diagram for an Ohmic contact in a metal-insulator-metal junction, and Fig. 1(b) illustrates the transitional stage of the Ohmic contact to a blocking contact. At fields beyond the transition field the current saturates if there is no means of reducing the barrier at the interface, resulting in the Richardson (saturation) current equation. The means for reducing the interfacial barrier height is provided by the interaction of the image force with the applied field, which results in a reduction, $\Delta\varphi$, of the barrier height given by [see Fig. 1(c)]

$$\Delta\varphi=\beta E_0^{1/2}kT. \qquad (2)$$

If the electronic mean free path in the insulator is very long, i.e., equal to the insulator thickness, then the J-V characteristic of the junction will be described by the Richardson-Schottky equation, Eq. (1) above, which is based on hot-electron injection across the interspace between the electrodes; that is, the electron energy is conserved across the interspace.

However, within the insulator the energy of the electron is not conserved, and at all points inside the insulator the current flow is described by the usual equation

$$J=en_x\mu E_x, \qquad (3)$$

where n_x is the charge density at x, E_x is the electric field at x, and μ is the electron mobility in the insulator.

Eq. (3) must also hold at the cathode-insulator interface, i.e., at $x=0$, thus

$$J=en_0\mu E_0, \qquad (4)$$

where

$$n_0=\int_{(\varphi_0-\Delta\varphi)}^{\infty}N(\epsilon)F(\epsilon)d\epsilon, \qquad (5)$$

where $F(\epsilon)$ is the Fermi-Dirac distribution function, and $N(\epsilon)$ is the density of states in

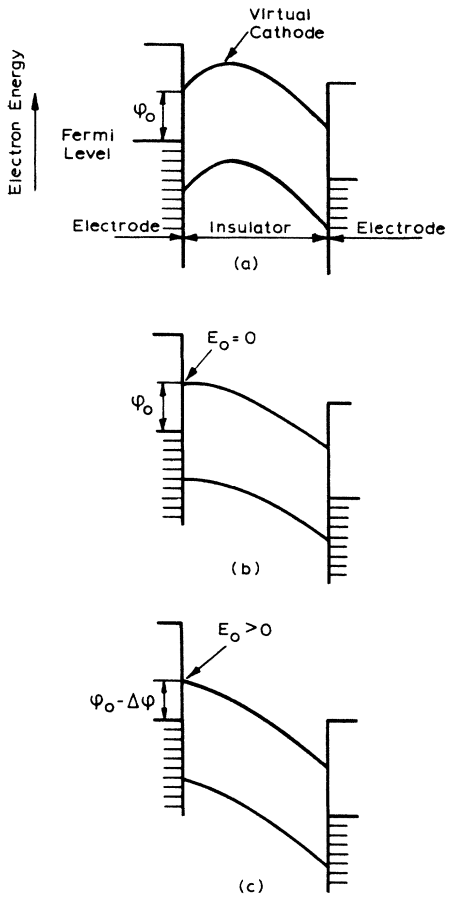

FIG. 1. Energy diagram of metal-insulator-metal junction showing (a) space-charge-limited condition; (b) transition from the space-charge-limited to the emission-limited condition; and (c) emission-limited condition.

the insulator which can be taken as

$$N(\epsilon) = 4\pi/(2m/h^2)^{3/2}[\epsilon-(\varphi_0-\Delta\varphi]^{1/2}.$$

Integrating (5) we get

$$n_0 = 2\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \exp(-\varphi/kT)\exp(\beta E_0^{1/2}). \quad (6)$$

Substituting (6) into (4) we arrive at

$$J = 2e\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \mu E_0 \exp(-\varphi/kT)\exp(\beta E_0^{1/2}). \quad (7)$$

Eq. (1) and (7) are incompatible, but differ only by the pre-exponential factor. The J-V characteristic will be determined by which of the two equations is the limiting case; and this is (5) as can be seen by evaluating the pre-exponential terms for $T = 300°K$ in each of the equations; thus

$$J = 1.08\times10^7 \exp(-\varphi/kT)\exp(\beta E_0^{1/2})\ \text{A/cm}^2, \quad (1)$$

$$J = 1.6\mu E_0 \exp(-\varphi/kT)\exp(\beta E_0^{1/2})\ \text{A/cm}^2. \quad (7)$$

Assuming $\mu = 10$, it will be seen that fields of 10^6 V/cm are required before (1) becomes the limiting mechanism.

At $E_0 = 0$, i.e., the transition field, J in (7) becomes zero. This does not mean, of course, that the current through the system is zero. This condition corresponds to the virtual cathode being at the cathode-insulator interface, the current being carried across the interface solely by the diffusion process. However, for fields slightly in excess of the transitional field the diffusion current becomes neglible compared to the field current.

It will be noted that there is no clear distinction in this case between the bulk-limited and electrode-limited processes, because each plays a part in the conduction process. The density of the free carriers at the interface is electrode limited [see Eq. (5)], while the mobility, which determines the velocity, is a bulk property.

[1]A. J. Dekker, Solid State Physics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1957), pp. 220-226.

PHONON-COUPLED PAIR SPECTRA OF K_2ReCl_6 IN SINGLE CRYSTALS OF K_2PtCl_6†

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The optical spectra of dilute single crystals of K_2PtCl_6 containing Re^{+4} show absorption peaks which may be assigned to ion pairs of Re^{+4} in addition to lines arising from the single ion. The diamagnetic cubic crystal, K_2PtCl_6, has an antifluorite, face-centered structure in which Re^{+4} readily substitutes for the platinum ion. In a cubic environment the rhenium ground-state configuration, t_{2g}^3, forms orbital states which transform like the $^4A_{2g}$, ^2E_g, $^2T_{1g}$, and $^2T_{2g}$ representations of the cubic group. Under spin-orbit interaction, further removal of degeneracy occurs to give states which transform like Γ_6, Γ_7, and Γ_8 of the double group, which are two-fold degenerate except for Γ_8 which is four-fold degenerate. The spectrum reported in this note arises from the free-ion transition from $^4A_{2g}$ (Γ_8) to $^2T_{2g}$ (Γ_7) and the associated pair transitions.

The group theory of the vibration spectrum of this crystal structure has been considered by Pollock.[1] He has shown that there are three odd modes of the chloride ions relative to the rhenium ion in addition to the reststrahlen modes of K^+ moving with respect to the $ReCl_6^=$ complex. The three modes of the complex transform like Γ_{4u}, Γ_{4u}, and Γ_{5u} and will be given the usual notation of ν_3, ν_4, and ν_6, respectively. Woodward and Ware[2] have shown that ν_3 is about 313 cm^{-1} and ν_4 is 172 cm^{-1} at room temperature. Recently it has been shown that ν_6 is 124 cm^{-1} at 4.2°K.[3]

At 4.2°K, a 5% Re in K_2PtCl_6 crystal shows four relatively intense narrow lines which are assigned to the electronic transition[4] $^4A_{2g}$ (Γ_8) $\rightarrow$ $^2T_{2g}$ (Γ_7) coupled with o-o, ν_6, ν_4, and ν_3 vibration modes. In addition, resolved fainter lines are observed near the o-o and ν_3 absorptions as shown in Figs. 1 and 2. An unresolved broadening near ν_4 is observed, but no additional lines are clearly evident near ν_6.

The faint lines near the o-o transition are