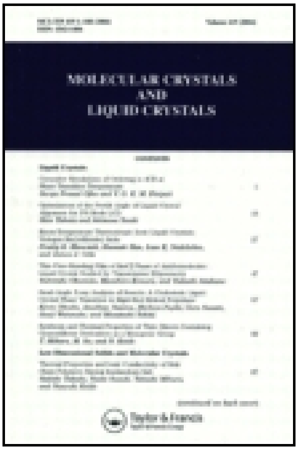

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Hot Electron Spectroscopy in Molecular Crystals

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Hot Electron Spectroscopy in Molecular Crystals[†]

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The well-known phenomena of electrons passing through a large potential gradient and tunnelling through a thin insulating layer across which a voltage is applied have been employed to obtain sufficiently energetic electrons for thermionic emission to be observed at room temperature.[1, 2, 3] The tunnelling effect has also been used to inject carriers into silicon[4] and n type CdS.[5] In this note we report some preliminary results of experiments utilizing these effects to inject electrons into molecular crystals. While at present these results are not yet precise, they indicate that this technique may be very useful for the investigation of the nature of the conducting states in insulating materials. We have used both a reversed biased silicon p–n junction and a metal–metal oxide–metal arrangement to obtain hot electrons (most of our results were obtained by the *former*). In this way we have obtained information on the position of what is presumably the lowest conductivity band. At present we have results only on anthracene, although other crystals are also being investigated.

In the p–n junction arrangement, the same diodes and holders

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were used to measure the emission current into the vacuum and into anthracene. After the vacuum results were obtained, an anthracene crystal was attached to the junction by placing an anthracene crystal upon a silicon diode, heating the silicon diode to a temperature just above the melting point of the crystal. A small amount of the interface was allowed to melt and the whole structure was then cooled slowly. A strong mechanical bond between the anthracene and the diode was formed. Visual examination of the interfacial region after this procedure showed no additional defects. The anthracene crystals used were cut from a crystal obtained from the Harshaw Company and were approximately 2 × 2 × 1 mm. Silver paint on the anthracene was used as the anode.

The tunnel diode arrangement was fabricated by evaporating a few hundred angstrom thick film of aluminum onto the crystal, oxidizing about 25 Å of it in air, and then evaporating a film of gold over the Al_2O_3 aluminum layers. Emission into the vacuum from the gold side or into anthracene from the aluminum side could be observed when the proper bias was applied.

The emission current from a reversed p–n junction obeys Richardson's equation.[2] Since the temperature of the electrons depends upon the electric field squared,[6] Richardson's equation may be written as:

$$i_v = A_v \beta^2 V_j^4 \exp\left[-\frac{e\phi}{\beta V_j^2}\right] \tag{1}$$

where β is a parameter relating the total voltage drop across the junction to the electron temperature; V_j is the total voltage drop across the junction (applied voltage plus band gap); and where ϕ is the work function of the silicon. For injection into the crystal, the injected current is:

$$i_c = A_c \beta^2 V_j^4 \exp\left[-\frac{e(\phi-\alpha)}{\beta V_j^2}\right] \tag{2}$$

where α is the electron affinity of the crystal (polarization energy + molecular electron affinity).

The results of emission into the vacuum and into anthracene for one of the p–n junctions tried is shown in Fig. 1. The current into the anthracene did not vary significantly with the voltage applied across the anthracene and no current was observed due to injection when the voltage across the anthracene crystal was reversed. Thus we were observing the saturation current and assuming A_c and A_v are of the same order of magnitude, the value of α may be obtained either from the slopes of the curves in Fig. 1 or from the ratio of the currents into vacuum and anthracene at a particular junction

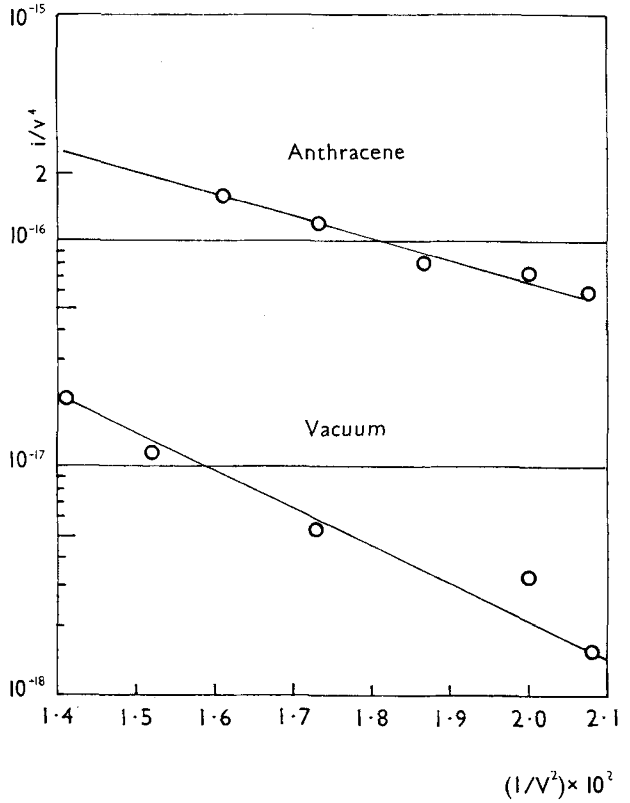

Figure 1. Semi-log plot of the emission current divided by the voltage to the fourth power *vs.* the $(\text{voltage})^{-2}$ from a p–n junction into the vacuum and into anthracene.

voltage. For the types of diodes used, Klein[2] determined the electron temperature at $1/V_j^2 = 1.82$ to be approximately 5900° K. From the ratio of the currents at $1/V_j^2 = 1.82$ a value for α of about 1.6 eV is obtained. The ratio of the slopes is equal to $\phi/(\phi-\alpha)$ which according to Fig. 1 $\phi/(\phi-\alpha) \approx 1.9$. Since ϕ is equal to 4.2 eV,[2] α is about 1.9 eV. The scatter of the results makes the uncertainty in the slope very great. (The errors however are in the direction of making α smaller rather than bigger.)

The threshold voltage for injection into anthracene from a tunnel diode was 2.8 V and the current increased from 10^{-12} to 10^{-10} A when the voltage was increased to 3.2 V. Since α is approximately the difference between the aluminum work function and the threshold voltage, $\alpha \approx 1.4$ eV. Considering the accuracy of our measurements at this time, which is still very poor, we consider this to be fair agreement and a value of $\alpha = 1.6$ eV does not seem unreasonable. A more accurate determination requires more precise data and these experiments are being performed.

In the analysis of these results, we have assumed that band bending at the surface and the presence of surface states do not significantly effect our results. Just how large an effect these might create is not known at present and is being studied.

One would hope that eventually these experiments could be performed sufficiently accurately so that data on density of states could be obtained. Harrison[7] in a very beautiful theoretical paper has indicated that density of states are not important except near a band edge. On the other hand, recently Esaki[8] has obtained some experimental data indicating that in tunnelling, the density of states is very important. While this is still an open question, it would seem that insulators and particularly organic crystals are excellent media to study because of the expected rapid variations in the density of states.

The work function of anthracene has been measured and is about 5.6 eV.[9, 10] The band gap is equal to the work function minus the electron affinity of the crystal. Therefore the band gap in anthracene is about 4 eV. This value is consistent with the recent results of Helfrich and Schneider[11] who observed fluorescence

(3.1 eV) due to recombination radiation and of Pope[12] who determined the band gap to be 3.7 eV in tetracene.

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REFERENCES

1. Bartelink, D. J., Moll, J. L., and Meyer, N. I., *Phys. Rev.* **130**, 972 (1963).
2. Klein, J., Emission of Hot Electrons from a p–n Silicon Junction, Thesis Doctor 3rd cycle, Ecole Normale Supérieure, University of Paris 1965.
3. Lebrun, J., *L'Onde Electrique* **43**, 1023 (1963).
4. Gray, P. V., *Phys. Rev. Letters* **9**, 302 (1962).
5. Jaklevic, R. C., Donald, D. K., Lambe, J., and Vassell, W. C., *Applied Phys. Letters* **2**, 7 (1963).
6. Wolff, P. A., *Phys. Rev.* **95**, 1415 (1954).
7. Harrison, W. A., *Phys. Rev.* **123**, 85 (1961).
8. Esaki, L. and Stiles, P. J., *Phys. Rev. Letters* **14**, 902 (1965).
9. Lyons, L. E. and Morris, G. C., *J. Chem. Soc.* 5192 (1960).
10. Pope, M., *J. Chem. Phys.* **37**, 1001 (1962).
11. Helfrich, W. and Schneider, W. G., *Phys. Rev. Letters* **14**, 229 (1965).
12. Pope, M., Burgos, J., and Ciachino, J., *J. Chem. Phys.* To be published.