

MOBILE IMPURITIES AND FROHLICH CONDUCTION IN NIOBIUM TRISELENIDE

J. C. Gill

H. H. Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, England.

ABSTRACT

A slow variation in the threshold field E_T for Frohlich conduction, which sometimes follows the onset or cessation of charge-density wave (CDW) motion in $NbSe_3$, is re-examined. The phenomenon can be induced by heating the specimen with indium, which apparently diffuses through the crystal with activation energy 0.30eV. The accumulation of the mobile impurity where its pinning effect is greatest accounts for a gradual rise in E_T after the CDW has come to rest, reversed after motion recommences. The form of E_T is consistent with diffusion in 1 dimension, over distances much greater than the CDW wavelength. This suggests that the impurities, which evidently couple strongly to the CDW only at widely-separated places, exert their pinning effect mainly at dislocations in the CDW.

INTRODUCTION

There is ample evidence that, although influenced also by the size and physical condition of the specimens, threshold fields E_T for Frohlich conduction in charge-density wave (CDW) materials depend on the abundance of chemical impurities. The impurities are usually assumed to occupy fixed substitutional sites, and to pin the CDW by enabling it to reduce the total energy by distorting elastically. Alternatives to this Fukuyama-Lee-Rice (FLR) model [1,2] have however been suggested. One mentioned by Lee and Rice [2], and now gaining experimental support [3], is that motion requires the glide of dislocations in the CDW, which impurities may pin. It has also been suspected [4] that some pinning impurities may be mobile, as in those layered materials where interstitial atoms diffuse thermally even at low temperature. However, though the effect of mobile impurities on the CDW amplitude has been described [5], clear evidence of their contribution to E_T has yet to be reported.

One characteristic of pinning by such impurities (when not sufficiently mobile to move with the CDW at detectable velocity) is expected to be a gradual increase in the effective E_T after the CDW stops moving. This will develop as impurities accumulate where their energy is lowest (and pinning effect greatest), and be reversed when motion recommences.

The slow variations in E_T noted in some early studies of $NbSe_3$ [6], unexplained then and not reliably reproduced since, now seem to have been of that kind. The changes, for the CDWs forming at 144K and 59K, were characterised by activation energies respectively 0.23eV and 0.094eV, apparently for thermal diffusion of two species of impurity, unidentified but perhaps acquired from the silver paint then used for terminals.

The discovery [7] that $NbSe_3$ specimens consistently exhibit the slow variation in E_T after being heated in contact with indium has led to the experimental re-examination of the phenomenon briefly described below.

PREPARATION OF SPECIMENS

In the present experiments the heat treatment consisted of maintaining the $NbSe_3$ specimen, of representative dimensions 3mm x 10 μ m x 2 μ m, and provided usually with four leads of indium wire (diameter 15 μ m, spacing 0.5 to 1mm) lightly pressed to its surface, at 120°C for about 15 minutes. The operation was performed in an atmosphere of helium, pressure \sim 10 torr.

Such treatment leads to no significant change in the Ohmic resistance above 30K, or in E_T for the CDW whose onset temperature T_c is 59K. However, E_T for the CDW with $T_c = 144K$ acquires a time-dependent component, with the features expected of pinning by mobile impurities, and greater in some

(received October 27, 1989)

cases than the original E_T ($\sim 0.2\text{Vcm}^{-1}$). Below 100K, the time-dependence becomes too slow to be readily apparent.

It has been confirmed that this effect does not result from heating in the absence of indium contacts, or from their prolonged presence at room temperature (even for two years). Accordingly, it is concluded that indium enters the heated specimen, and thereafter behaves as a mobile (presumably interstitial) impurity above 100K. The concentration and distribution of indium have yet to be measured; E_T provided no indication that the distribution along the specimen was uneven on a large scale.

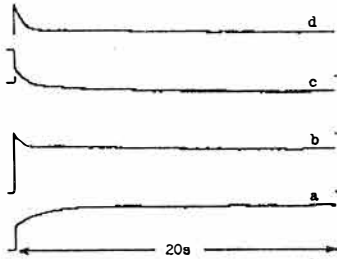


Figure 1. Slow changes in I_c recorded at 115K, following polarization by various I_P . For details see text.

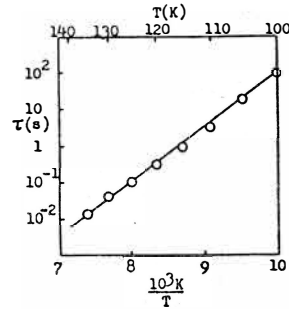


Figure 2. The variation of τ with temperature. The line corresponds to activation energy 0.30eV.

TIME-DEPENDENT THRESHOLD PHENOMENA

Instead of recording E_T directly, its variation with time t was observed by recording the Frohlich current I_c after applying a steady field E . If E is not too large, small changes in $I_c(t)$ correspond to changes of similar form (but opposite sign) in $E_T(t)$, which in effect displace the I_c - E curve. A steady "observing" current $I_0 \gg I_c$ provided the field E , and $I_c(t)$ was recorded using a bridge to subtract the Ohmic part of the total current.

The form of $I_c(t)$ depends on the condition of the CDW immediately before I_0 is applied. Four examples appear in figure 1.

In record a, the CDW has been at rest, after previous "polarization" by a current $I_P = +I_0$, long enough for the impurities to have reached equilibrium with it. When motion is resumed E_T decreases monotonically, from the equilibrium value E_{T0} to a steady-state value E_{TM} . The decrease is characterised by the time τ in which E_T falls from E_{T0} to $(E_{T0} + E_{TM})/2$. A similar time characterises the recovery towards E_{T0} after I_0 ceases.

Record b shows $I_c(t)$ after similar polarization by $I_P = -I_0$. A smaller E_{T0} now applies, in this case (though not always when I_P is opposite to I_0) less than E_{TM} , so that I_c is greater initially than in the steady state. Although superficially similar, this is not the well-known pulse-sign memory phenomenon. Here I_c decays over several seconds, whereas the pulse-sign memory transients (also observed, though not when the CDW had been at rest for much longer than τ) lasted typically 100 μ s.

In records c and d I_0 is applied immediately after polarization by a current I_P of greater magnitude. Evidently, as I_c falls as the new steady state is established, E_{TM} decreases as current through the specimen rises.

In each case the rate of approach to the steady-state is fiercely dependent on the temperature T . The dependence on T of the time τ defined above, shown for one specimen in figure 2, corresponds to an activation energy (presumably for the thermal diffusion of indium) of 0.30eV.

DISCUSSION

Qualitatively, these phenomena are easily explained in terms of mobile impurities, whether they pin in the FLR manner, or couple to dislocations in the CDW. In either case the tendency of the impurities to accumulate where their pinning effect is greatest (and energy least) when the CDW is stationary, and to disperse when motion recommences, will account for the gradual change of E_T between the values E_{T0} and E_{TM} . That E_{T0} is smaller for motion resumed in the opposite sense is not unexpected, as memory of the previous direction of motion, preserved as distortion of the stationary CDW, will be transferred to impurities reaching equilibrium with it.

A quantitative theory of the phenomena remains to be developed. However, some features are clearly not easy to explain in FLR terms, but present no obvious problem if the pinning is of dislocations. One such is the slow decrease of E_{TM} with increasing I_C . This apparent persistence, when $E \gg E_T$, of concentrations of impurities, like that of mode-locking and broadening in nmr spectra [8], suggests that the local phase of the CDW advances in steps of 2π . This might be expected if the motion is of dislocations, but requires extreme assumptions if the FLR model is to apply.

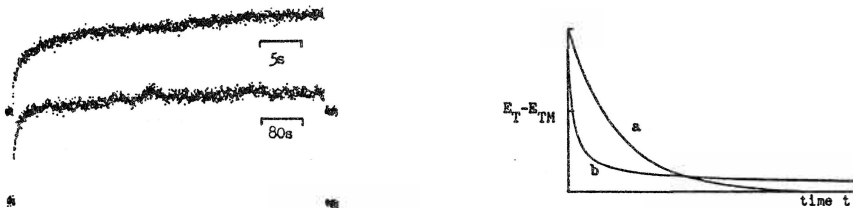


Figure 3. Comparison between $I_C(t)$ observed, and predicted forms of $E_T - E_{TM}$

Clearer evidence of the inadequacy of the FLR model is available in the form of $E_T(t)$. An example (of $I_C(t)$, as figure 1a but for a specimen with less I_n) is shown in figure 3. If the FLR model applies, changes in E_T involve diffusion of impurities over distances no greater than half the CDW wavelength. A near-exponential decay of $E_T - E_{TM}$ is then expected, as in curve a in figure 3 (based on four impurity sites per half-wavelength). If, on the other hand, the impurities must diffuse to widely-separated dislocations to produce pinning, one expects a form closer to curve b, which corresponds to unrestricted diffusion in one dimension.

As the approach of E_T to E_{TM} is roughly of that form, it is concluded that impurities produce their pinning at places many wavelengths apart. For large t , $E_T - E_{TM}$ varies roughly as $t^{-1/2}$, consistent with diffusion in one dimension. Assuming this to indicate that the impurities move parallel to the $NbSe_3$ chains (an alternative would be for the pinning to occur on planes), it seems reasonable to conclude that the widely-separated places where pinning occurs are indeed dislocations in the CDW.

REFERENCES

1. H. Fukuyama and P.A. Lee, *Phys. Rev.* B17 (1977) 535.
2. P.A. Lee and T.M. Rice, *Phys. Rev.* B19 (1979) 3970.
3. see the preceding paper; also A. Jánossy, G. Kriza and T. Csiba (this conference)
4. J. Dumas and C. Schlenker, in *Charge Density Waves in Solids* (eds. Gy. Hutiray and J. Sólyom), Springer-Verlag, Berlin (1985) p.389.
5. P. Lederer, G. Montambaux and J.P. Jamet, *Mol. Cryst. Liq. Cryst.* 121 (1985) 99.
6. J.C. Gill, *Mol. Cryst. Liq. Cryst.* 81 (1982) 73.
7. I am grateful to P.J. Yetman for noticing this effect.
8. J.R. Tucker, W.G. Lyons and G. Gammie, *Phys. Rev.* B38 (1988) 1148.