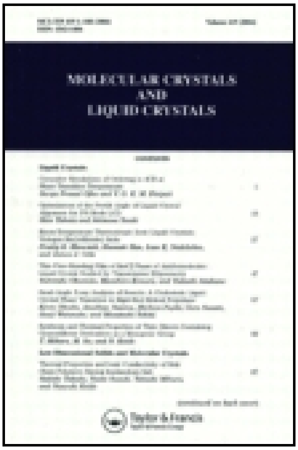

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METASTABLE STATES AND CDW CONDUCTIVITY IN $NbSe_3$

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A study of the response of niobium triselenide to pulsed currents shows that the field-induced motion of the charge-density waves (CDWs) leaves them in long-lived metastable states in which, presumably, some distortion is stabilised by pinning. Evidence of this is provided by a reduction in Ohmic conductivity after current flows non-linearly through a specimen originally in thermal equilibrium, and by a transient increase in the non-linear conductivity on subsequent reversals of the current. A gradual increase in the non-linear conductivity during pulses applied repeatedly in the same sense is found to arise from a thermally-induced change in the strength of the pinning. The possible origin of this change is discussed.

INTRODUCTION

It is now accepted that the remarkable electrical properties of niobium triselenide are the result of the charge-density waves (CDWs) in that material being so feebly pinned that quite weak applied electric fields may induce them to move, and so to carry current in the manner outlined long ago by Frohlich (1). Two independent CDWs occur in $NbSe_3$, and are present below onset temperatures $T_1 = 144K$ and $T_2 = 59K$ respectively, with the apparently incommensurate wave-vectors $\vec{q}_1 = (0, 0.243, 0)$ and $\vec{q}_2 = (\frac{1}{2}, 0.263, \frac{1}{2})$ (2). They will be referred to here as q_1 and q_2. Their field-induced motion, in the presence of pinning by impurities or other crystal defects, is thought to be responsible for a rapid increase in conductivity with the strength E of an applied steady field, commencing at a well-defined threshold value E_T; for the accompanying appearance across the specimen of excess noise, in whose spectrum discrete (and current-dependent) frequencies are prominent; and also for an increase with frequency of the Ohmic conductivity in weak alternating fields (3-6).

This paper is concerned with three further phenomena, observed using pulsed fields and reported briefly elsewhere, which also involve movement of the CDWs (7). They show that the CDWs do not move rigidly, but suffer distortion, into long-lived metastable states, as a result of their displacement from equilibrium. The phenomena, discussed under separate headings below, are a lasting decrease in the Ohmic conductivity following the temporary application of a field $E > E_T$; a phenomenon to be referred to as the 'overshoot', whereby a transient increase in the non-linear conductivity, to a value greater than that eventually established, follows application of a pulsed field in a direction opposite to that of the previous pulse; and a gradual rise of the non-linear conductivity towards its ultimate steady value, seen when the field is applied in the same sense as previous pulses.

A detailed investigation of these rather complicated phenomena is still in progress and will be reported fully on completion. The present publication, which is intended only as an interim report, summarises the new information already obtained.

EXPERIMENTAL TECHNIQUES

Six $NbSe_3$ specimens, with residual resistance ratios R(300K)/R(4.2K) ranging from 60 to almost 200, have been examined to date, mainly at temperatures T below T_2. All have shown qualitatively similar behaviour, but except where otherwise noted the results presented here will refer to a specimen having resistance ratio 190, for which the minimum values of E_T are about 60 mV cm^{-1} (near 120K), and 10 mV cm^{-1} (near 50K).

Specimens are measured in a four-terminal configuration with current flow parallel to the crystallographic b-axis. Contacts are of silver or gold paint, or of indium. Damage from thermal cycling is avoided by supporting specimens by their leads, of fine gold wire, radius 0.03 mm. An active bridge circuit, described in reference 7, is used to observe the development with time t of the quantity $U(t) = R_0 I - V$, where I(t) is the current through the specimen and V(t) the potential difference between its voltage terminals, and R_0 is the resistance V/I in the Ohmic (low-current) regime. Most of the experiments consist of applying pulsed or more complicated stepped waveforms of current I(t), and recording, either photographically from an oscilloscope or by using a sampling circuit to transfer its waveform to a chart recorder, the quantity U(t) which describes the non-linear (or perhaps a change in the linear) response of the specimen.

THE EFFECT OF NON-LINEAR CONDUCTION ON THE OHMIC RESISTANCE

When a current pulse, sufficient to cause non-linear conduction, is applied to a $NbSe_3$ specimen at a temperature $T < T_2$, which has previously cooled in zero applied field from above T_2, the Ohmic resistance $R_0(T)$, monitored using a suitably weak pulse, is found to increase by an amount $\delta R_0(T)$ which may be as much as 2% of R_0. At constant temperature this increase persists apparently indefinitely (and certainly for several minutes), but the original R_0 can be recovered by heating above T_2 and returning. No corresponding increase has been detected at temperatures between T_2 and T_1 after cooling from above T_1; if such an increase exists it does not exceed 0.02% of R_0.

Some values of δR_0, recorded at various T after applying fields $E \gg E_T$, appear in figure 1 as the ratios $f = \delta R_0(T)/R_0(T)$ and $g = \delta R_0(T)/R_0(300K)$. Measurements did not extend below 25K, where E_T became inconveniently large, and the phenomenon was not detected with $T \geqslant 55K$.

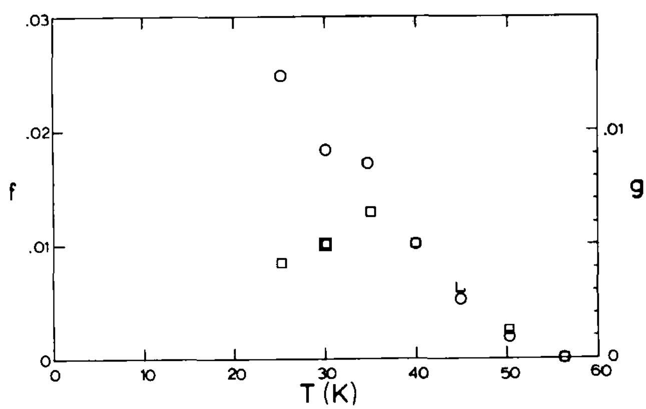

FIGURE 1 Increases δR_0 observed in the Ohmic resistance, following non-linear current flow. Circles denote values of $f = \delta R_0(T)/R_0(T)$, and squares values of $g = \delta R_0(T)/R_0(300K)$.

Although some modification of the Ohmic resistance might conceivably arise through motion of the CDW rearranging dislocations or other mobile defects of the crystal lattice, the observed δR_0 (which at 35K exceeds the residual resistance $R_0(4.2K)$) seems far too large to be accounted for in that way. It is concluded, therefore, that the change brought about by the current is in the CDW q_2 itself, which is modified from its equilibrium condition into a metastable (and presumably distorted) state. Such a conclusion is not inconsistent with the X-ray diffraction results (2), even though they provided no evidence of any current-induced change in $\vec{q}_2$, for local distortions of the CDW need not alter the averaged wave-vector thus measured. They might, however, reduce the Ohmic conductivity by scattering the 'normal' electrons, and also by changing their local abundance by modifying the Fermi surface. In the former case one might expect δR_0, and in the latter $\delta R_0/R_0$, to be related in a roughly quadratic fashion both to the amplitude of the CDW and to the amounts by which its wave-vector departs from uniformity.

The present data are not sufficient to distinguish between these possibilities. An experimental complication, perhaps responsible in figure 1 for the decrease of g below 35K, is that as the non-linear current rises δR_0 increases in sudden steps, as if different domains contribute when their appropriate threshold fields are surpassed.

THE 'OVERSHOOT' PHENOMENON

The essential features of the overshoot phenomenon are illustrated in figure 2. On applying a current pulse of sufficient amplitude to a specimen in which current previously flowed non-linearly in the opposite direction, U(t) rises at first beyond its eventual steady value, towards which it subsequently decays approximately in exponential fashion, with time-constant tending to decrease as I increases. The phenomenon is observed both below T_2, and also between T_2 and T_1 when only q_1 is present. It does not occur on applying a pulse in the same direction as that of the previous current.

It is evident that the metastable state established when current flows non-linearly in one direction is not the same as that appropriate to current flow in the opposite sense, and that the overshoot phenomenon is associated with the transition from one metastable state to the other. That the phenomenon occurs at temperatures above T_2 shows that, despite the absence of any detectable effect on R_0, metastable states can be established in q_1 as well as in q_2.

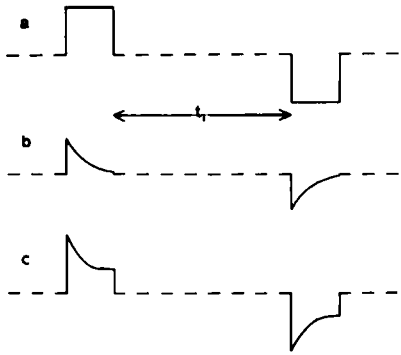

FIGURE 2 The 'overshoot' phenomenon. One period of the repetitive current waveform I(t) is shown at (a). The response U(t) is shown at (b) and (c) respectively for I less than, and I greater than, the threshold current I_{T1} for nonlinear d.c. conduction.

An account of the overshoot phenomena observed at 42K in a specimen having resistance ratio 60 has been given in reference 7. The transient in U(t) was found to be almost independent of the interval t_1 defined in figure 2, indicating that the lifetime of the metastable state was at least a few hours, and also showed an interesting threshold behaviour, whereby an increase in the pulse current in one sense tended to reduce the current subsequently required in the opposite direction to produce the phenomenon. It was suggested, therefore, that in its metastable state q_2 is deformed elastically between points where it is most strongly pinned, and is prevented from relaxing when the current is removed by the pinning present elsewhere. The transition between opposite metastable states leads to a transient increase in conductivity both as a result of the Frohlich current carried by the moving sections of the CDW, and perhaps also because the Ohmic conductivity increases as the CDW passes through its equilibrium configuration. When ascribed solely to Frohlich conduction, the observed transients were found to correspond to the passage through the specimen of charges Q which, taking the relevant carrier concentration as 2.4×10^{19} cm^{-3} (8), were equivalent to the mean displacement of the CDW by up to 0.28 μm. Recent electron micrographs (9), showing what appear to be moiré patterns between CDWs having wave-vectors different by a few percent, suggest that displacements of that order may be possible even though parts of the CDW remain fixed.

A similar picture emerges from the present experiments, on a specimen with weaker pinning. Between 40K and 55K the transients in U(t) exhibit much the same time-constants, typically 15 μs or less, as were reported previously; their amplitudes, when expressed in terms of displacement of the CDW, tend however to be smaller, perhaps because the pinning is less able to sustain distortion of the CDW. A slight relaxation of the metastable state, during the first 50 μs after current has been removed, has been detected as a decrease, as the interval t_1 between pulses is increased, of the amplitude of U when I is just above the threshold value for its occurrence. This relaxation has not proved sufficient to give rise to any clearly detectable Frohlich current. The transients in U(t) observed when $T_2 < T < T_1$ have longer time-constants (typically 50 μs) and correspond to values of Q about 3 times those for $T < T_2$.

THE ESTABLISHMENT OF NONLINEAR CONDUCTION FOR UNIDIRECTIONAL CURRENTS

The manner in which U(t) develops in response to a current pulse applied in the same sense as previous current flow is illustrated in figure 3. Although non-linear conduction first becomes possible when I exceeds the value I_{T1} which corresponds to E_T, the rise of U to its eventual d.c. value is not instantaneous, but approximately exponential.

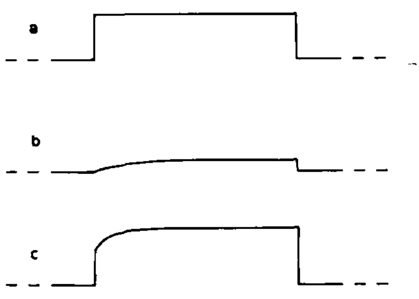

FIGURE 3 The response to unidirectional current pulses. One pulse of the applied current I(t) is shown at (a). The response U(t) appears at (b) for the case $I_{T1} < I < I_{T2}$, and at (c) for $I > I_{T2}$.

The rise becomes more rapid as I is increased, until a second threshold current I_{T2} is reached. With further increase of I, the initial rise of U becomes apparently instantaneous, though still followed by a gradual approach to the final value, at a rate now almost independent of I. The gradual increase in U is absent (or greatly reduced) in circumstances such that the overshoot phenomenon is present. The existence of the two thresholds, corresponding to I_{T1} and I_{T2}, probably accounts for certain discrepancies between values of E_T measured using d.c. and pulsed techniques (4, 10).

It is shown in reference 7 that the gradual increase in U does not arise from inertia of the CDW, since U appears to vanish immediately I is removed and, having once attained a steady value with $I > I_{T1}$, responds immediately to later changes in I provided that I_{T1} is always exceeded.

This behaviour has now been examined more thoroughly, by extending measurements to different temperatures and by using a variety of waveforms of I(t). Full details of the experiments will be published in due course. It is found that the dependence of U on the magnitude of I is consistent with the gradual rise being the result of a decrease in the threshold field for nonlinear conduction. This field, when $I > I_{T2}$ is applied, falls from the value corresponding to I_{T2} to the d.c. value E_T, which corresponds to I_{T1}. When I is temporarily removed, or reduced below I_{T1}, the threshold for immediate non-linear conduction when it is re-applied gradually recovers, the increase having approximately the same characteristic time as is observed in the development of U when $I > I_{T2}$. These changes in threshold field are seen only when the metastable state existing when no current is present is that established by I (or some other current in the same direction). The establishment of an opposite state causes the threshold for non-linear conduction of I to return approximately to E_T, and no gradual rise in U is then seen when I is re-applied.

In the present specimen the changes in threshold field were about 7 mV cm^{-1} ($\approx 0.1\ E_T$) in the case of q_1 at 120K, and 5 mV cm^{-1} ($\approx 0.5\ E_T$) for q_2 at 50K. The dependence on T is not very pronounced near these temperatures, but has yet to be studied in detail. It has been noted that the effect on U(t) of the decrease in threshold field is less obvious in more strongly pinned specimens, such as that discussed in reference 7, but this may be a consequence of the less rapid variation of conductivity with $E - E_T$.

A striking dependence on temperature, and also differences between specimens, has been found in the rate at which U(t) approaches its final value. As the approach departs markedly from a simple exponential, its characteristic time

τ is defined here as the time taken for $(1 - 1/e)$ of the gradual change in $U(t)$ to be completed. The dependence of this quantity on inverse temperature is shown in figure 4. The data for $T < T_2$ were obtained by observing the approach of U to its steady value with $I > I_{T2}$ and refer to the decrease of threshold field in the presence of I; some for $T > T_2$, denoted □, were obtained using short current pulses separated by intervals much less than τ, and in effect describe the recovery when $I = 0$.

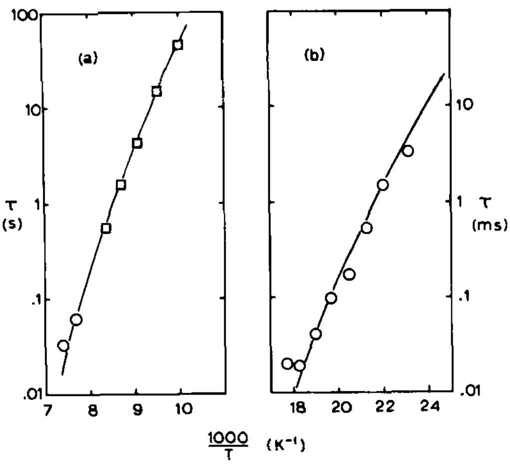

FIGURE 4 The variation with temperature T of the times τ characterising changes in threshold field. For explanation of symbols see text.

Both when only q_1 is present, and when q_2 provides the non-linear conduction, the variation of τ with T^{-1} is approximately linear. If attributed to thermal excitation to a fixed energy W, the data for q_1 and q_2 give respectively the values $W = 0.23$ eV and $W = 0.094$ eV. They are, however, consistent also with a temperature-dependent excitation energy $W = 2\Delta(T) = 2\alpha k_B T_c (1-T/T_c)^{\frac{1}{2}}$, where $2\Delta(T)$ is a mean-field approximation for the single-electron energy gap associated with the CDW and is expected to apply near its onset temperature T_c. The curves in figure 4 correspond to the value $\alpha = 7$ (for a Peierls instability in one dimension α takes the BCS value 3.06); whether their close agreement with the data for both CDWs is of any significance is not known.

CONCLUDING DISCUSSION

There seems to be no need to venture beyond simple models, in which an incommensurate CDW deforms elastically under the combined influence of the applied field and pinning by impurities, to account at least qualitatively for the occurrence of metastable CDW states, for the effect of their formation on the Ohmic conductivity, and for the main features of the overshoot phenomenon. It is far from clear, however, that such models can provide an adequate explanation of the changes in threshold field described above.

That motion of a CDW should reduce the effect of pinning is not, in itself, surprising. The present theory of the weak pinning of an incommensurate CDW (11) supposes that in equilibrium it distorts slightly, so as to take advantage of the reduction in potential energy offered by impurities, distributed randomly. If such a CDW is displaced from the position where it is in equilibrium (perhaps metastable), its distortion ceases to be appropriate for the new arrangement of impurities it encounters, and the pinning becomes less effective until readjustment has taken place. A recovery of threshold field following removal of current clearly might arise in this way.

It is more difficult to predict the corresponding behaviour of U(t) when I is present, for there is no satisfactory theory of the effect of pinning on a moving CDW. It is obvious, however, that a dependence of U solely on the distance moved by the CDW from its former equilibrium position cannot account for τ becoming practically independent of I when $I > I_{T2}$. Possibly τ might then refer to some change in the moving CDW after it has escaped from pinning, but the magnitude of τ seems to preclude even this: using the carrier density quoted earlier, the distance through which q_2 travels as U rises to its d.c. value is found, in some instances, to exceed the length of the specimen by an order of magnitude.

The alternative is to suppose that the changes to which τ refers do not occur in the moving CDW, but are associated rather with the centres responsible for the pinning. These changes evidently proceed at a rate determined thermally, towards steady states (and thus threshold fields) which appear to depend on the metastable condition of the CDW. It seems, therefore, that the distortion of the CDW in the vicinity of the pinning centres governs, to some extent, the effective strength they ultimately reach. The mechanism by which this happens, and the role of thermal excitation, remain matters for conjecture.

Of the various possibilities being considered, one of the more promising is that the CDWs in $NbSe_3$, rather than being truly incommensurate, in fact consist of commensurate domains separated by discommensurations (12) which are subject to pinning, and whose motion provides the Frohlich conduction. In a metastable state these discommensurations are distorted from their approximately regular arrangement in thermal equilibrium, and it seems not implausible that the changes in threshold field arise from the creation, near the pinning centres, of new surfaces of discommensuration in regions where the old ones have moved far apart. Whether or not that is the case seems more likely to be established by electron microscopy or X-ray diffraction than by electrical measurements alone.

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