Pinning, Memory and Motion of Charge-Density Waves in $NbSe_3$ and o-TaS_3.

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Abstract

Experimental studies of electrical memory phenomena in the charge-density wave (CDW) conductors $NbSe_3$ and orthorhombic (o-) TaS_3 are described, in an account devoted partly to review and partly to the presentation of new results.

Four classes of memory phenomenon are listed: I, hysteresis effects in the weak-field resistance; II, the 'pulse-memory' or 'overshoot' phenomenon, where a transient increase in conductivity occurs when current is first applied in a direction opposite to that in which it last flowed; III, phase-memory in the periodic response to steady fields; and IV, a miscellaneous group of transient phenomena, arising from current-induced changes in the threshold field for nonlinear conduction.

A study of electrical hysteresis in o-TaS_3 leads to the tentative conclusion that a change in threshold behaviour near 140K is the result of an increase in the resistance of the CDW to deformation, rather than to the onset of commensurability, which it is suggested only occurs at or below 55K. The occurrence of the pulse-memory phenomenon III has made it possible to show that, at least near the threshold for CDW motion, the periodic response arises from a modulation of the single-electron conductivity, presumably local in nature, and not from modulation of the Frohlich current.

Experiments on short sections of $NbSe_3$, in which the CDW is expected to behave as a single domain, provide evidence that the transients in the pulse-memory phenomenon II then correspond to Frohlich currents generated as the CDW makes transitions between metastable distorted states. A current associated with a partial relaxation of the distortion, observed after removal of the applied field, provides what is believed to be a direct demonstration of Frohlich conduction. In larger crystals the metastable distortion is concentrated near the current terminals, apparently because of the presence of intermediate domains at whose boundaries the CDW loses coherence. Transients of type IV, clearly not due to Frohlich currents generated as the distortion changes, are then also observed.

1. Introduction.

Niobium triselenide ($NbSe_3$) and the orthorhombic form of tantalum trisulphide (o-TaS_3) are the best known of a growing number of materials in which electrical conduction is thought to occur, essentially as proposed by Frohlich [1], through the motion of incommensurate charge-density waves (CDWs). The recognition of such conduction is based on three principal pieces of experimental evidence. In an applied steady field $\underline{E}$, the conductivity $\sigma(E)$ shows little or no variation until E exceeds a threshold value E_T at which continuous motion of the CDW apparently commences, and increases thereafter towards a high-field limit [2-5]. More remarkably, when $E > E_T$ the current contains near-periodic components whose frequency is approximately proportional to the current density contributed by the increase in $\sigma(E)$, and appears to be the rate at which the CDW is translated through wavelengths or, possibly, half-wavelengths [2,6,7]. Last, the linear response to alternating fields, of amplitude much less than E_T, is consistent with a heavily-damped driven oscillation of the CDW: as the frequency ν increases from zero, the conductivity $\sigma(\nu)$ at first rises rapidly, but then becomes practically constant from, typically, a few hundred MHz up to the highest frequencies (> 10 GHz) of measurement [8,9].

While these observations, and related experiments in which alternating and steady fields are combined [10,11], have established beyond reasonable doubt that Frohlich conduction is being observed, attempts to account in terms of a single model for the forms of $\sigma(E)$ and $\sigma(\nu)$, and for the periodic variation of the current, have been only partly successful. The models proposed have been in most cases phenomenological, regarding the CDW as moving classically in a 'pinning' potential responsible for the finite value of E_T. Difficulty arises, in particular, in accounting for the observed form of $\sigma(E)$ near threshold, and in reconciling it with periodic response to steady fields. Unless it is not truly a bulk property of the CDW (mechanisms have been proposed which would operate in finite domains [12,13] or at contacts [14, also 29]), the periodic behaviour appears to require that the CDW behaves as a rigid entity. The absence of any singularity in the derivative of $\sigma(E)$ at threshold seems inexplicable, however, unless motion of the CDW either is accompanied by its elastic distortion [15,16], or occurs in a multitude of independent domains to give, in effect, a continuous distribution of E_T [17]. The latter possibility may however be discounted as a general explanation, for there is ample evidence that the CDWs in both $NbSe_3$ and o-TaS_3 are capable of coherent motion over lengths ($\sim$0.1 mm) comparable with those of many specimens [18,19].

Whether the relevance of the various theoretical proposals will be tested decisively by future experimental studies only of the features already mentioned is open to doubt. Fortunately $NbSe_3$ and o-TaS_3 exhibit also a variety of electrical memory phenomena, involving long-lived metastable states of the CDWs whose existence is evidence of current-induced distortion. The study of these phenomena is still in its early stages, but promises to yield quite detailed information about the static and dynamic properties of CDWs, about their pinning, and also about the possible role of single-electron (i.e. non-Frohlich) conduction in CDW transport phenomena.

Some recent work in Bristol on these memory effects is described below, in an account devoted partly to review (§3) and partly to the presentation of new experimental results (§4). Since there is already some danger of confusion between superficially similar phenomena, four more-or-less distinct types of memory effect are first listed, in §2. Experiments on o-TaS_3 and $NbSe_3$ are then described, respectively in §3 and §4, with a few closing remarks added in §5. The discussion is not intended as a comprehensive survey of CDW memory phenomena, but has the more limited objective of demonstrating their use in the study of CDW properties in those two materials.

2. Electrical memory phenomena.

The electrical memory phenomena, in which conduction depends in a non-trivial way on previous electrical treatment, which have been reported in CDW conductors appear to be of four main types. They are I, electrical hysteresis affecting the resistance observable in weak fields; II, the so-called pulse-memory or overshoot phenomenon; III, phase-memory in the periodic response to steady fields; and IV, a miscellaneous group of phenomena, some of which may already contribute to II, which appear to arise from current-induced changes in the strength of pinning.

Hysteresis in the variation of conductivity with temperature is not uncommon in CDW materials, where thermally-induced changes in equilibrium wavevector are resisted by pinning. The memory phenomena I are the analogous electrically-induced effects, where some rearrangement of the CDW by an applied field (not necessarily requiring $E > E_T$) leads to a change in the single-electron conductivity [20-22]. Hysteresis in the Frohlich conduction, reported in $NbSe_3$ [23], evidently involves changes in E_T and is classified under IV.

The essential feature of the pulse-memory phenomenon [20,24] is that the nonlinear response to a pulsed field depends on the direction of the pulse immediately preceding. In its simplest form, to be illustrated in figure 6, the response to the second pulse is unremarkable (often corresponding immediately to the d.c. conductivity $\sigma(E)$) when the two pulses are in the same direction. After a preceding pulse in the opposite sense, however, the current rises initially to a greater value than that appropriate to $\sigma(E)$, towards which it subsequently decays. The origin of this transient increase in current is the main topic of §4.

The phase-memory phenomenon III was first noted [24] in the response of $NbSe_3$ to repetitive current pulses, to which the quasi-periodic component would synchronise only when an integral number of cycles was completed within the pulse. Evidently when a steady current is interrupted, memory of the phase of the periodic variation is retained, so that it continues from the same point in the cycle when current resumes. A study of the phenomenon in o-TaS_3 is described in §3.

The remaining memory effects IV, which are probably of diverse origins, arise when the effective value of E_T is influenced by previous electrical treatment. Assigned to this class, in addition to the dynamic hysteresis effect [23], are a slow growth of nonlinear conductivity occasionally seen in $NbSe_3$ [24], and also certain contributions to the transient conductivity which complicate the pulse-memory phenomena described in §4.

3. Experiments on o-TaS_3.

(a). Electrical hysteresis and the approach to commensurability.

It is now known from diffraction measurements [26] that the CDW which forms in o-TaS_3 at 215K is at first incommensurate, though as the temperature is reduced the departure of its wavevector q from the commensurate value $q_0 = \frac{1}{2}a^* + \frac{1}{8}b^* + \frac{1}{4}c^*$ decreases and has not been observed below 140K. This is strongly suggestive of the presence of discommensurations (DCs), whose readiness to remain in non-equilibrium arrangements is a likely source of hysteresis effects. It is, therefore, not surprising that the weak-field conductivity of o-TaS_3 shows hysteresis of thermal and, as is now described, electrical origin. As details are available in the literature [21], only the main features will be mentioned here. These are apparent in figures 1 and 2, which show respectively the forms of thermal and electrical hysteresis observed in 4-terminal measurements of resistance, with current I along the TaS_3 chains (i.e. parallel to the c- axis), and voltage V measured between the inner pair of terminals.

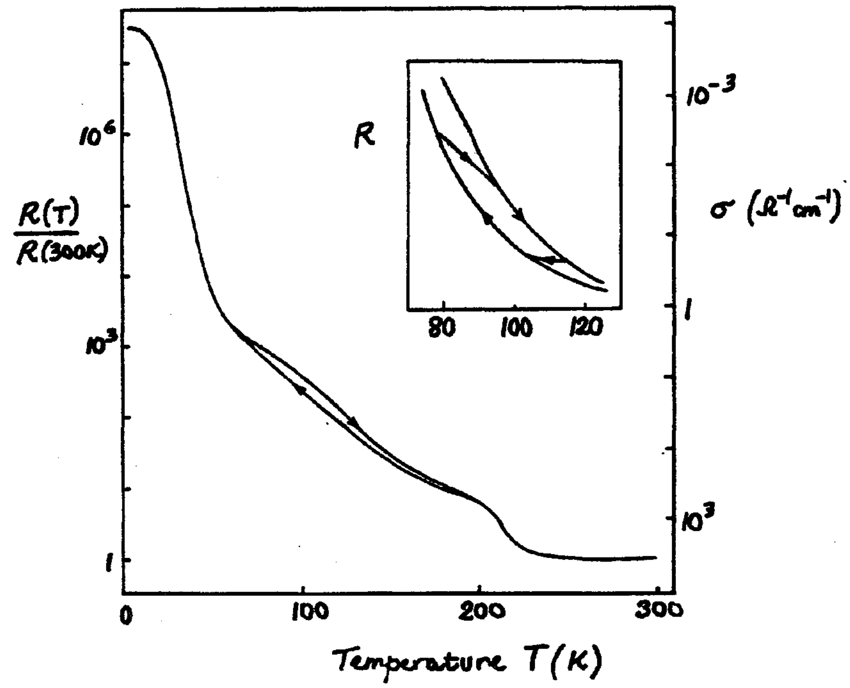


Figure 1. Thermally-induced hysteresis in the weak-field resistance R of o-TaS_3 A minor hysteresis loop is shown inset, with a linear scale of R.

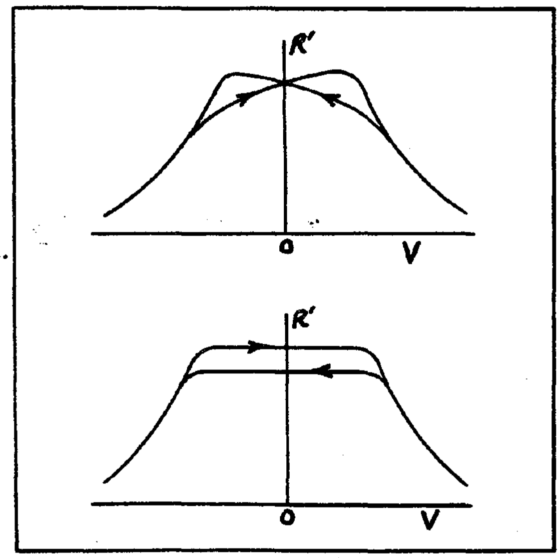


Figure 2. Electrically-induced hysteresis in the differential resistance R′ of o-TaS_3 specimens observed (a), between 205K and 140K, and (b), between 140K and 55K.

The thermal hysteresis is detectable in the weak-field resistance between 205K and about 55K. Clearly the CDW can be fully commensurate, if at all, only below the lower of those temperatures. The hysteresis is not apparent in the differential resistance $R' = dV/dI$ measured with $E > E_T$, evidently because the continuous motion of the CDW prevents the pinning from inhibiting the variation of $\underline{q}$ with temperature. The approach to 55K is accompanied by a rapid increase in the threshold field E_T, shown for one specimen in figure 3.

While one possible explanation of the increase in E_T is that it marks the onset of commensurability, it has also been suggested [26] that the CDW becomes commensurate at 140K, where in the diffraction experiments $\underline{q}$ became indistinguishable from $\underline{q}_0$. That some change takes place in the CDW at that temperature is apparent both in the variation of E_T, and in the ratio between the current density carried by the CDW and the frequency of the periodic response, which indicates an increase in the number of electrons participating in the motion. The occurrence of thermal hysteresis down to 55K is not necessarily in conflict with this suggestion, which requires commensurability only along the chain direction. However, a mere increase in the resistance of the CDW to deformation, arising from the change in electron density and unconnected with any onset of commensurability, seems sufficient to account for the behaviour of E_T, and especially for its rapid decrease, immediately below 140K.

The electrical hysteresis phenomena shown in figure 2 seem to be evidence of such an increase in rigidity. The diagrams show, schematically, the variation of differential resistance R' with voltage V, measured between silver-paint contacts. Between 205K (where it first appears) and 140K the hysteresis takes the form (a), the changes in R', as E varies between $+E_T$ and $-E_T$, being typically a few percent. An enhancement of the conductivity follows motion of the CDW, and is due presumably to some distortion which relaxes as E is reduced below E_T, causing R' to be field-dependent even as E passes through zero. Whether the relaxation involves changes in the total number of DCs, or merely in their distribution, is not at present known.

Below about 140K the hysteresis of form (a) is replaced by that of form (b), which persists down to 55K. The resistance now changes only slightly as E varies between $+E_T$ and $-E_T$, but may now depend on the direction in which current previously flowed nonlinearly with $E > E_T$. A difference between the pinning properties of the two inner (voltage) terminals is believed to be the source of this dependence. It is known from experiments on $NbSe_3$ [18] that silver-paint contacts may introduce sufficient pinning to prevent a CDW from

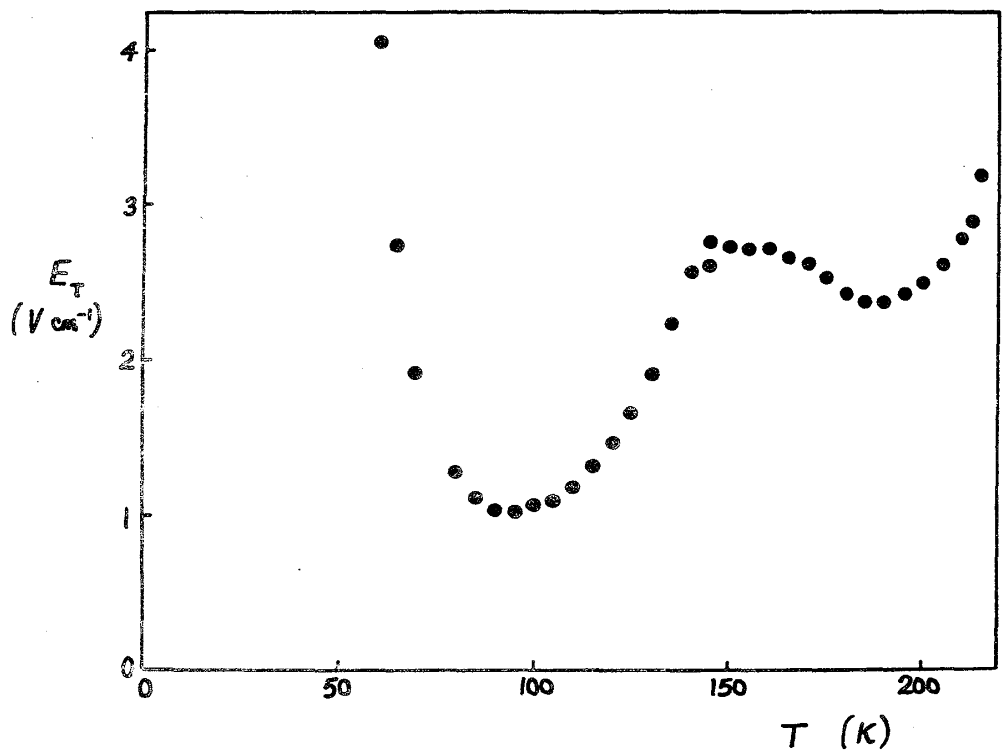


Figure 3. The threshold field E_T for continuous motion of the CDW, measured in one specimen of o-TaS_3. Others showed qualitatively similar behaviour, though the minimum threshold field was in some as low as 0.3 V cm^{-1}.

moving past, even when the contacts are used only as voltage terminals. Unless it is already separated into independent domains between which no correlation in phase exists, continuous motion of the CDW in the region between such contacts is accomplished by its 'breaking' in their vicinity. The electrical hysteresis observed in o-TaS_3 above 140K possibly arises from deformation of the CDW between strongly-pinning contacts of this kind. Below 140K, however, the asymmetrical behaviour of R' with respect to the previous direction of current flow indicates that the inner terminals have become inequivalent. Presumably the CDW then resists breaking sufficiently to be able to move past at least one of the terminals, so that if they differ in the resistance offered to the motion the resulting distortion of the CDW depends on its direction of motion and leads to the observed asymmetry. The improved resistance to breaking below 140K would be expected to accompany an increase in rigidity of the CDW, of which the reduced dependence of R' on field when $E < E_T$ is perhaps evidence.

(b). Phase-memory and the origin of the periodic response.

As mentioned in §1, it is not known how the periodic response of CDW conductors to steady fields is generated. It seems reasonable to identify its frequency ν with the so-called 'washboard' frequency v/λ, where v is the velocity and λ the wavelength of the CDW, or perhaps with some low multiple thereof, at least in cases where DCs are not present. Numerous models [12-14,17,27,28] have been proposed to account for the appearance of current components of this frequency, based usually on the premise that the periodic response represents a modulation of the Frohlich current. It is, of course, quite possible that several different mechanisms operate in real crystals. In the experiments now to be described, use is made of the phase-memory effect III to show that, in o-TaS_3 under certain conditions, the principal source of the periodic response is the modulation, as the CDW moves, not of the Frohlich current but of the single-electron conductivity.

In some specimens of o-TaS_3 the periodic response is easily seen at frequencies ν as low as 1 Hz. Figure 4 shows (symbols o) the relation between ν and the specimen current I for one sample at 77K. Some observed waveforms are also shown; as in most experiments, the response of the voltage V to a steady current I was in fact measured. The symbols • represent estimates of the nonlinear component I_{nl} of the current, defined as $I - V/R_n$ where R_n is the resistance when the CDW is at rest, measured with current slightly below the threshold value I_T at which the periodic response appears. The values of

Figure 4. The dependence on specimen current I of the fundamental frequency ν of the periodic response (o), and of the nonlinear part I_{nl} of the current (•), observed in o-TaS_3. Examples of the observed waveform are shown inset.

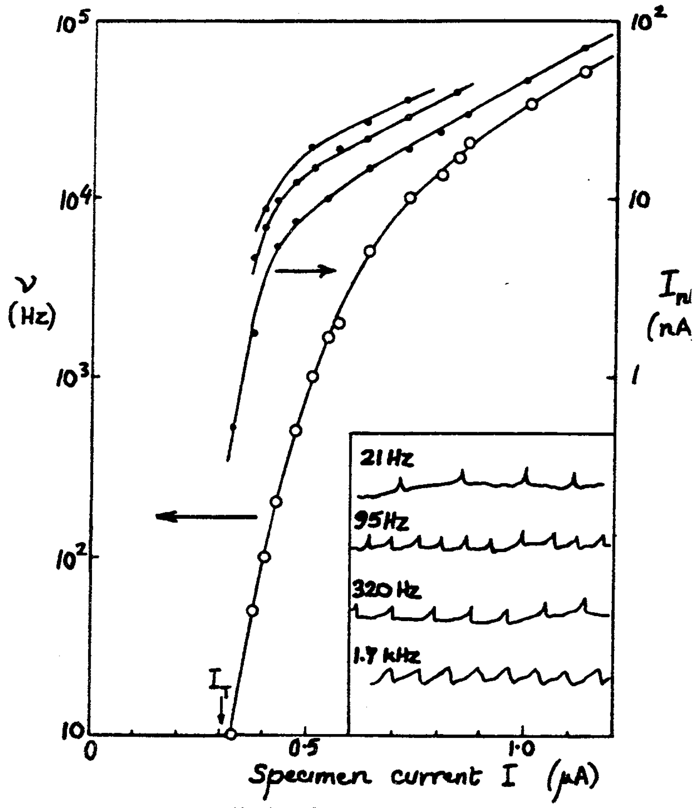
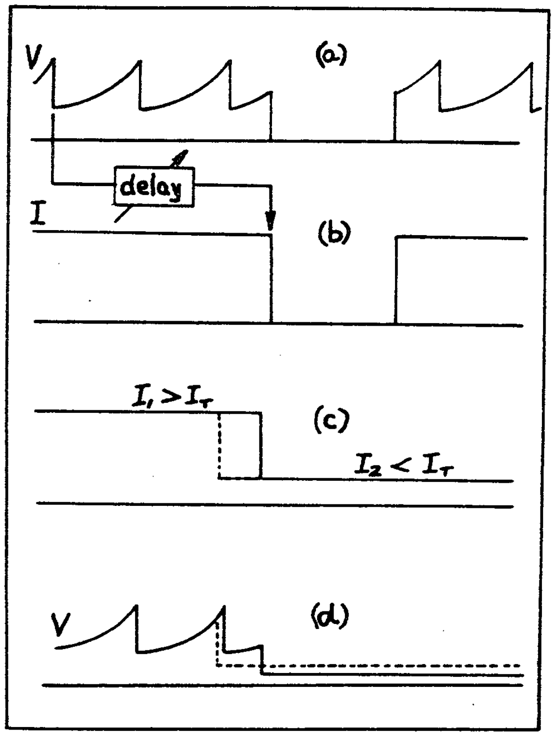


Figure 5. Waveforms (a) and (b) show the method used to observe the phase-memory phenomenon. The periodic variation of V continues when I is re-applied.
Waveform (d) shows the effect of reducing I (waveform (c)) at different stages in the cycle of V.



I_{nl} are not entirely consistent with one another, and over-estimate the Frohlich current I_c, because of the enhancement of single-electron conduction by the (not wholly reproducible) distortion of the CDW in the applied field. However, as ν increases towards 100 kHz, the measured values of I_{nl}/ν converge and become equivalent to a ratio $J_c/\nu \simeq 30$ A $cm^{-2}MHz^{-1}$ between current density and frequency. That this is much the same as has been observed at higher frequencies [26], where J_c could be identified with the Frohlich current density, justifies the assumption that, despite the difficulty in measuring I_c, the low values of ν observed here do indeed correspond to the washboard frequency.

The amplitude of the periodic variation of V, however, is much greater than could possibly arise from a modulation of Frohlich current alone. The required modulation of J_c is estimated, from the known resistance and dimensions of the crystal, to have amplitude approximately 0.06 A cm^{-2}. This, combined with the value of J_c/ν already found, implies that the displacement of the CDW during one cycle of the periodic variation of V is, when ν = 1 Hz, of the order of 2000 wavelengths. One must conclude, therefore, that the periodic response of o-TaS_3, at least when ν is as low as observed here, does not correspond to the modulation of Frohlich current but, presumably, must represent variations in the single-electron conduction.

This conclusion has been tested experimentally by making use of the phase-memory phenomenon III. Because of its large amplitude (typically 1 mV), the periodic waveform could be arranged to trigger the timebase of an oscilloscope so as to provide a repetitive display of V (or, in practice, of RI - V, with $R \simeq R_n$ a fixed balancing resistor). Also triggered was a delayed temporary reduction of the current I, from a value $I_1 > I_T$ to a value $I_2 < I_T$ at which motion of the CDW would cease and the cycle of V therefore be interrupted. This allowed the phase-memory phenomenon to be demonstrated directly. It was confirmed that when I was reduced to I_2 at any chosen stage in the cycle of V, memory of the point reached was retained, so that V continued from that point when I_1 was restored. This is shown in the upper part of figure 5.

By observing V while $I = I_2$ it was possible to detect this retention of phase information in the single-electron conductivity. The effect is illustrated in the lower part of figure 5: the resistance seen when $I = I_2$, and the CDW is at rest, depends on the point reached in the cycle of V when I_1 is interrupted. Preliminary measurements indicate that as the time t of the interruption is varied, the changes in resistance observed with $I = I_2$ correspond to those in $V(t)/I_1$. This establishes that in the conditions of the present experiments, though not necessarily generally, the periodic response of o-TaS_3 is due principally to the modulation of single-electron conductivity.

Precisely how the motion of the CDW leads to such modulation, and to phase-memory, has still to be established. It is, however, obvious that the modulation must arise locally. One possibility, suggested by the evident dependence of conductivity on the number and distribution of DCs, is that the periodicity is associated with their creation and destruction at places where the CDW is required to break, such as current terminals, voltage terminals if these introduce sufficient pinning, and major crystal defects. The basic frequency arising from such processes is $\nu = v/\lambda$, corresponding in o-TaS_3 (where $\underline{q}_{0c^*} = \frac{1}{4}c^*$) to the creation or destruction of DCs in groups of four. Since it is produced by a mechanism of relaxation oscillation, the resulting waveform is unlikely to be sinusoidal and could well take the form of those which appear in figure 4. More complicated waveforms, possibly with apparent frequency some multiple of v/λ , could result if two or more contributions were superposed.

A more complete account of these experiments, including the observation of a further periodic response which may represent the passage of individual DCs past obstacles, is shortly to be published [29].

4. Experiments on $NbSe_3$

The pulse-memory phenomenon II is closely related to the electrical hysteresis effects I. As with the form of I shown in figure 2(b), it seems clear that information on the direction of a current pulse is recorded as a metastable distortion of the CDW; although perhaps undetectable in the weak-field conductivity, the information is now recoverable as a transient non-linear response when a pulse is applied in the opposite sense. The most obvious explanation of this transient increase in conduction is that it is generated by the Frohlich mechanism, as the CDW moves in making a transition from one metastable state to another.

As first observed in $NbSe_3$ [20], the main features of the phenomenon were consistent qualitatively with that explanation. Moreover, the magnitude of the effect (corresponding to the passage of charges of the order of 10^{-9}C along a crystal of cross-sectional area 10^{-5} cm^2), which at the time seemed to require implausibly large distortions of the CDW, no longer presents a problem, in view of later revisions both in the number of electrons conveyed by the CDW, and in the distances over which it may retain coherence. Taking these respectively as 10^{21} cm^{-3} [27] and 0.1 mm [18], the charge transfer can be accounted for by changes in wavevector of the order of 1 part in 10^3.

There is, however, a possibility that the effects of a Frohlich current, associated with transitions between metastable states, may be simulated by changes in E_T of the kind assigned to class IV in §2. The doubt which this casts on the above explanation of the pulse-memory effect is reinforced by the recent experiments of Fleming and Schneemeyer on $K_{0.3}MoO_3$ [30]. In that material the pulse-memory phenomenon superficially resembles that in $NbSe_3$, but the much slower relaxation, and its dependence on pulse duration (which presumably arises from a wide distribution of relaxation times), lead the authors to suggest an origin in the gradual rearrangement of the CDW between domains with different pinning. Such a possibility has already received brief discussion [25] in connection with $NbSe_3$, where in some specimens there is a tendency, apparently unrelated to the pulse-memory phenomenon II, for E_T gradually to decrease when current flows nonlinearly in one direction, and to recover once the CDW stops moving.

It is of interest, therefore, to seek more positive evidence that the transition between metastable states makes a significant Frohlich contribution to the pulse-memory effect. The first results of some experiments on $NbSe_3$, undertaken with that aim, are presented below.

To provide a basis for discussion, a simple model of the metastable distortion, shown in figure 6, will be introduced. The CDW is assumed to be pinned strongly at the planes x = 0 and x = L, and between them to distort elastically under the influence of an applied field $\underline{E}$ parallel to x. Motion is opposed by uniformly-distributed weak pinning, up to an extent equivalent to a field of magnitude E_0. With $|E_x|$ below the threshold E_T for continuous motion, the eventual steady displacement y(x) of the CDW from its equilibrium position is given, in the linear approximation, by

$$\gamma y'' = -\rho \mathcal{E} \tag{1}$$

where γ is the elastic modulus of the CDW, ρ the charge density with which it is associated, and y(0) = y(L) = 0. The effective field $\mathcal{E}$ differs from E_x through the frictional effect of the weak pinning. An upper limit to $|\mathcal{E}|$ is assumed to be set by the breaking of the CDW at the points x = 0 and x = L, when $|y'(0,L)|$, which corresponds to the deviation of the CDW wavevector from equilibrium, reaches a critical value C. The threshold E_T is then given by

$$E_T = E_0 + 2\gamma C/\rho L . \tag{2}$$

The relation between $\mathcal{E}$ and E_x is shown in figure 6; the weak pinning, responsible for the hysteresis, is insufficient to prevent some relaxation of the distortion, after a field $E > 2E_0$ is removed, when $E_T > 2E_0$.
The displacement $y(x)$ (referred when $E > E_T$ to the equilibrium position which would apply if the CDW were at rest) is

$$y \quad = \quad (\rho/2\gamma)\,\mathcal{E}\,x(L - x), \tag{3}$$

so that in a transition between states corresponding to effective fields $\mathcal{E}_1$ and $\mathcal{E}_2$ the Frohlich current generated conveys past a given point x a total charge which is proportional to $(\rho^2/2\gamma)(\mathcal{E}_1 - \mathcal{E}_2).\ x(L - x)$.

In most experiments it is the current I, rather than the field, which is controlled, and the transition appears as a transient change in the measured voltage V, as the single-electron current compensates for the Frohlich component. Denoting by $v(t)$ the transient voltage appearing between points x_1 and x_2, the integral of v with respect to time t, taken over the transient, will be proportional to the quantity

$$S \quad = \quad (\rho^2/2\gamma)\ |\mathcal{E}_1 - \mathcal{E}_2|\ \int_{x_1}^{x_2} x(L - x).dx \quad . \tag{4}$$

For given L, the greatest possible value for S is $\frac{1}{3}\rho CL^2$, corresponding to the reversal of a field $E > E_T$ with V measured between points $x = 0$, L. The Frohlich current acts in this case to reduce V, and the sense of v is opposite to that of I. Because it could hardly arise from a mechanism of type IV, however, the observation of the transient associated with the relaxation of the CDW when $I = 0$, possible when $E_T > 2E_0$, would provide less ambiguous evidence of the Frohlich current generated by changing distortions of the CDW. This voltage, expected following removal of a field $E > 2E_0$, drives a single-electron current which, as it exactly balances the Frohlich conduction, has the same direction as the current due to E.

As it is the situation in which a model of this kind seems most likely to be valid, the pulse-memory phenomenon has been studied in a short length of crystal (to reduce the possibility of multiple domains) using, instead of the normal 4-terminal arrangement (N), a transposed version (T) in which the functions of the two pairs of terminals are interchanged. The two terminal configurations, together with dimensions of the specimen used, appear in figure 7. In the T configuration, the use of the closely-spaced inner terminals for current ensures that the CDW breaks in their vicinity [18] and provides, in effect, the strong pinning assumed in the model. The practical

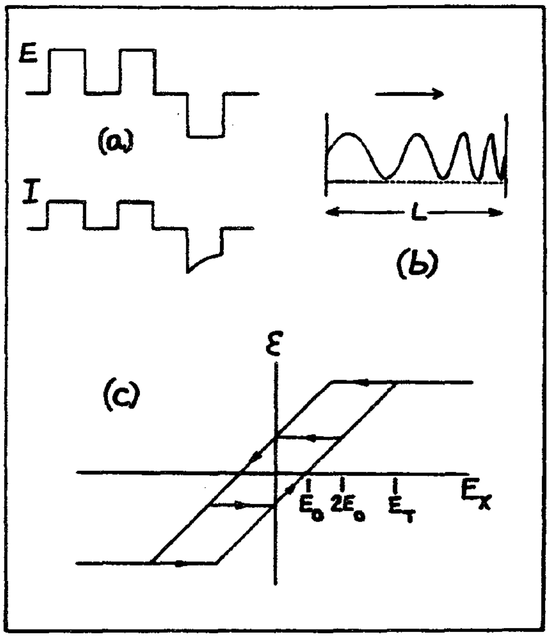


Figure 6. Illustrating at (a), the simple form of pulse-memory phenomenon in the response of current I to a pulsed field E; at (b), the elementary model introduced in the text; and at (c), the assumed relation between the effective field $\mathcal{E}$ and the applied E_x.

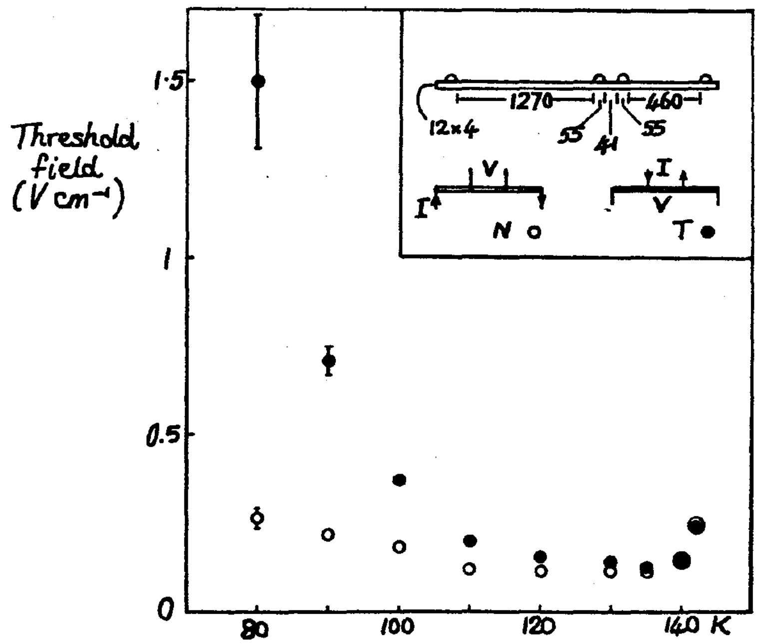


Figure 7. Apparent threshold fields measured in a $NbSe_3$ specimen using the normal (N; denoted o) and transposed (T; denoted •) 4-terminal configurations. These arrangements, and the dimensions of the specimen (in μm) are shown inset.

system departs, however, from the ideal geometry of figure 6 in that the thickness of the specimen (4 μm) and the area covered by the contacts (of indium wire, lightly pressed to the surface) were not negligible. It is anticipated that this may lead to current-dependence, and if the CDW loses lateral coherence to a spread of values, in the length L. Resistances measured in the linear regime showed that much of the current in the N configuration was diverted by the inner contacts, so that L need be little greater than their separation (41 μm).

Measurement has been confined to temperatures between 59K and 144K, where only the higher-temperature CDW, which retains coherence over lengths ~0.1 mm, is present. The breaking of the CDW at the inner contacts in the T configuration is evident from figure 7: the measured threshold fields exceed those for the N configuration, even at temperatures approaching 140K. With silver-paint contacts the difference develops, typically, only below 110K; clearly indium contacts, despite their diversion of current, introduce less pinning and allow the CDW to move more easily.

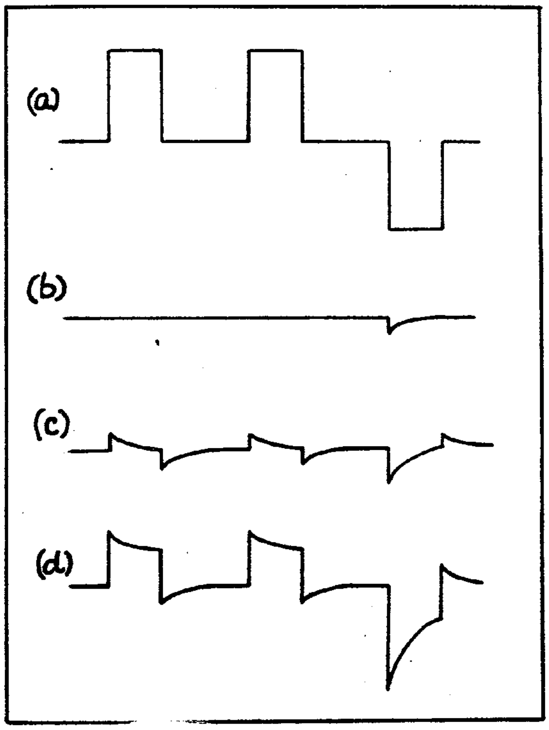
In terms of the model, the threshold field for the T configuration may be identified with E_T (the corresponding current is denoted I_T), and that for the N configuration, where the effective length of the crystal is much greater, approximates to E_0 (corresponding current I_0). For the present specimen E_T exceeds $2E_0$, and a possibility of relaxation when $I = 0$ therefore arises, below about 105K.

The relaxation is believed to have been detected in experiments performed below that temperature, mainly at 90K. Figure 8 illustrates the phenomena observed. Waveform (a) represents a pulsed current, applied in the T configuration. The positive- and negative-going pulses usually were of equal amplitude I_p, duration 100 μs, and were separated by up to 10 ms; no change in the memory effects was noticed, however, when the separation was increased to 1 s. At 90K the threshold currents I_T and I_0 were found to be 1.7 ± 0.2 mA, and 0.50 ± 0.05 mA, respectively. The waveforms (b) to (d) show, for various I_p, the behaviour of the observed quantity RI - V which, with R chosen to balance the weak-field resistance of the specimen, is proportional to the nonlinear contribution to the current. Not included is the effect of Joule heating, which increased the resistance of the specimen during the pulses, causing $|RI - V|$ to rise with characteristic time about 50 μs at a rate proportional to I_p^3. Corrections for this effect, which was already noticeable with $I_p \sim I_T$, were derived from the data for higher values of I_p.

As I_p increased from zero, pulse-memory phenomena first appeared in the simple form already illustrated in figure 6, as in waveform (b): a transient increase in $|RI - V|$ occurs when a pulse is applied in the opposite direction from that of the pulse immediately preceding. This 'reversal' transient approximated to a decaying exponential with time-constant 15 μs, except that the later stages were somewhat less rapid. In contrast to the behaviour described in [20], the time-constant showed no pronounced dependence on I_p. Neither was there any sign of a wide distribution of characteristic times, of the kind seen in $K_{0.3}MoO_3$: the slower components of the decay became only slightly more prominent as the pulse lengths were increased from 20 to 500 μs. The dependence on I_p of the amplitude of the reversal transient is shown in figure 9 (symbol o): the threshold current for its appearance is not significantly different from the value I_0 predicted by the model. With increase of I_p beyond this threshold, the response eventually assumed the form (c), to be replaced by (d) when I_p exceeded I_T. In these waveforms new transients follow each pulse, and appear at the start of pulses having the same direction as the previous pulse. The transients which follow the pulses are in the expected sense for relaxation of the CDW distortion when I = 0, and are provisionally attributed to that source. The other new transients are assumed to correspond to the re-establishment of the distortion, after it has partly relaxed, by current re-applied in the same direction. These 'relaxation' and 're-establishment' transients also were approximately exponential decays with time-constant 15 μs. Their amplitudes are shown as a function of I_p, by the symbols □ and • respectively, in figure 9. The values of I_p at which they first appear are difficult to locate precisely, but are clearly both close to 1 mA, which would correspond to the threshold $2I_0$ predicted by the model.

Although the model successfully predicts the onset of the three transients, their variation with I_p shows it to be oversimplified, though whether its inadequacy is simply the result of the non-ideal geometry has still to be investigated. According to the model, the quantity S (or, since all decay in a similar manner, the amplitude) for each transient should increase linearly with I_p between the appropriate threshold and I_T, and there reach a limiting value. In figure 9 the initial increase tends to be rather faster than linear, and a limiting value is approached only when I_p is substantially greater than I_T. For the reversal and re-establishment transients signs of approaching saturation are apparent for $I_p \simeq 2.5\, I_T$, heating effects having prevented accurate measurement for higher currents. The relaxation transient, observed with I = 0, was measurable for much greater I_p and reached saturation when $I_p \simeq 3I_T$. An assumption that the three transients approach saturation in the same way allows the maximum charge which in effect is driven through the specimen in each transition to be estimated, if only roughly. The values obtained for the relaxation, re-establishment and reversal transients were

Figure 8. Pulse-memory phenomena observed using the T configuration. An applied current waveform is shown at (a). The behaviour of RI - V, as the amplitude I_p of the pulses is increased, is shown in (b), (c) and (d). The reversal transient alone appears in (b). In (c) the relaxation and re-establishment transients are also present, and in (d) continuous nonlinear conduction appears.



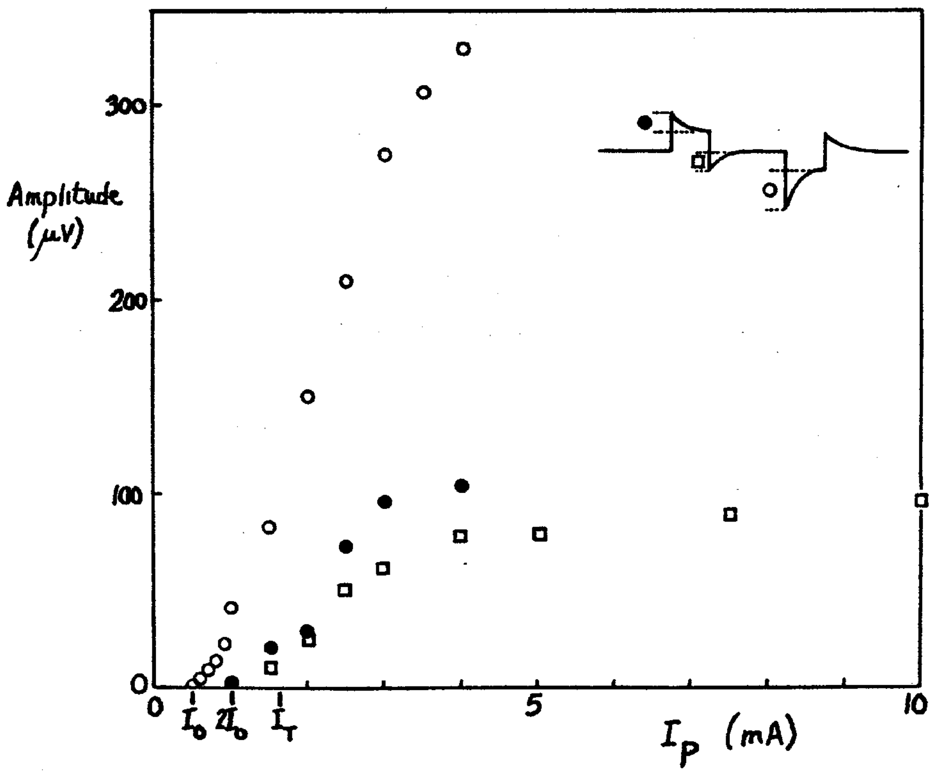


Figure 9. The dependence of the amplitudes of the reversal (o), relaxation (□) and re-establishment (●) transients on the amplitude I_p of the current pulses. The threshold currents predicted by the simple model are also indicated.

respectively 0.7, 0.8 and 2.6 nC. Of these the first two, which according to the model should be equal, do not differ significantly. It is interesting (but possibly fortuitous) that the last is greater than these by a factor 3.5, whereas the predicted ratio is $(2I_T - 2I_0)/(I_T - 2I_0) = 3.4$.

It is difficult to see how the phenomena just described, and especially the non-zero voltage observed when I = 0, could arise other than as a result of Frohlich conduction. A purely capacitative origin is clearly out of the question, if the magnitude of the charge transferred is as estimated. Since the estimate is based on the assumption that the specimen always retains its normal single-electron conductivity, it was confirmed that this was the case by observing the relaxation transient in the presence of a small applied current, whose contribution to V was entirely as expected. So also was the ability of the transient voltage to drive a current through an external circuit connecting the voltage terminals. The possibility of the transient arising thermoelectrically may be discounted on the grounds that the voltage is measured between points on the specimen remote from any source of heating, reverses in sign with reversal of the current pulse which it follows, and becomes independent of I_p when I_p is large. An electrochemical origin is, perhaps, less easily dismissed. Ionic conduction is known to occur in transition-metal chalcogenides, and could lead to polarisation effects which might resemble the phenomena described here. Whether such conduction is possible in $NbSe_3$ at 90K is not known. Departures from stoichiometry are small enough to have escaped detection, and although intercalation by chemical impurities is a possibility their concentration would have to be very large (10^{19} cm^{-3}) to account for the size of the transients observed, and would surely be detectable as an increase in the threshold E_0 above that observed in other specimens. Moreover, it is not clear that, even if electrochemical polarisation were to occur at the current terminals, it would generate the voltage observed: as no current flows in the neighbourhood of the voltage terminals in the T configuration, some redistribution of polarisation under the current contacts would be required. Compelling evidence against an electrochemical origin seems, however, to be provided by experiment: the relaxation transient was not seen above 100K, or at 90K when either the N configuration, or a 2-terminal configuration measuring one of the longer sections (0.5 or 1.3 mm) of the crystal, was used. Whether an electrochemical origin for the voltages observed in the absence of current in $K_{0.3}MoO_3$ may be similarly dismissed is not, at present, known.

It is therefore concluded that the pulse-memory effects seen in the present experiments were indeed the result of Frohlich currents generated in transitions of the CDW between metastable states. The success of the model in accounting for the threshold behaviour, though demonstrating the eleastic properties of the CDW, does not establish unambiguously the form of its metastable distortion. The assumption that it occurs throughout a region bounded by planes of strong pinning may be tested, however, by measurement using the N configuration. Suppose that the observed length L now lies between pinning planes a distance Λ apart, possibly but not necessarily coincident with the new current terminals. An elementary extension of the argument which led to expression 4 then predicts that the largest value of S (observed as a reversal transient, or perhaps as a combination of relaxation and reversal transients) will be greater than when the same length L is measured using the T configuration by a factor which ranges from $3-2L/\Lambda$, when L adjoins a pinning plane, to $3\Lambda/2L-L/2\Lambda$, when L lies centrally between two such planes.

This expectation that the transients will be more pronounced in the N than in the T configuration was not fulfilled experimentally. In the N configuration the pulse-memory transients were barely detectable, being equivalent to a charge transfer of the order of 0.1 nC, whereas in the T configuration the relaxation and reversal transients totalled 3.3 nC. A larger reversal transient was however seen by using the outer contacts in 2-terminal measurements of the response of the 1.9 mm length of crystal between them; this transient had characteristic time about 20 μs, and amplitude only about three times that seen using the T configuration. The model, if the appropriate value of L is taken as 1.9 mm, predicts a transient larger by a factor $(1.9/0.041)^2$, or approximately 2000.

The reason for this apparently catastrophic failure of an initially promising model is presumed to lie in its assumption regarding the distribution of distortion. The near-absence of pulse-memory transients in the N configuration, and the small effect of increasing L almost by a factor 50, suggest that the current contacts play a crucial role. The present results become explicable if one assumes that the coherent motion of the CDW occurs within domains whose lengths are not much greater than the separation (41 μm) of the inner contacts, and at whose boundaries the CDW is not pinned strongly but, perhaps, vanishes in amplitude. Metastable distortions then occur only in those domains which lie partly under one or both of the current contacts. The result is that in transitions between distorted states, the Frohlich currents generated flow only in the affected domains and are, consequently, limited to regions adjacent to the current contacts.

Finally, it is mentioned that in those cases where the current contacts were separated by much more than 41 μm, the response during the current pulses included large transient components whose decay was much slower (characteristic time 200 μs or more) than that of the pulse-memory transients discussed above. These slow components have yet to be investigated in detail. They bear some resemblance to those reported in $K_{0.3}MoO_3$, in that there is a noticeable dependence on pulse length, and pulse-memory effects are seen when the interval between pulses is reduced so as to be comparable with the decay time of the transients themselves. This decay time decreases as I_p increases, whereas the amplitude of the transients remains roughly constant once I_p exceeds the threshold current for continuous motion of the CDW. Since S thus decreases with increase in I_p , the transients cannot correspond to Frohlich currents generated in transitions between metastable states. They appear to arise from changes in threshold field, of the kind classified in §2 under IV. The origin of these changes is unknown. Areas in which it might profitably be sought include coupling between domains [25,30], pinning by mobile interstitial impurities [31], and perhaps adjustment of the boundary of the moving CDW at the current contacts [20].

5. Closing remarks.

The picture of CDW transport that emerges from this study of electrical memory phenomena contains some features not yet incorporated in theoretical models.

The mere occurrence of memory effects suggests that motion of a CDW results in its becoming in some way distorted, and this possibility is already included in some current theories. The experiments of §4 show that the higher temperature CDW in $NbSe_3$ distorts, in effect, as though it were an elastic medium. Direct confirmation that motion of the CDW is associated with a flow of current, as Frohlich predicted long ago, is also provided.
The simple picture, of an elastically deformable CDW restrained by uniformly-distributed pinning, is however complicated by the suspected presence of domains across whose boundaries the moving CDW apparently loses coherence without suffering excessive pinning. The induced destruction of coherence at closely-spaced current terminals, on the other hand, requires the application of a substantial 'breaking' force, represented by an increase in threshold field.

Distortion of the CDW in o-TaS_3 is found in §3 to modify the single-electron conduction to such an extent as to dominate the nonlinear behaviour near the threshold for Frohlich conduction. In those circumstances, at least, the periodic response to a steady field has been shown to arise from a local modification of the single-electron conductivity, rather than from any modulation of the Frohlich current.

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