Dislocations and the motion of weakly pinned charge-density waves: Experiments on niobium triselenide containing mobile indium impurities

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The threshold field E_T for conduction by the charge-density wave (CDW) which forms in $NbSe_3$ at 144 K has been studied in specimens containing about 1% of intercalated In. The In increases E_T by an amount δE_T, which is greatest when the CDW is at rest, and can be reduced almost to zero by its continuous motion. The time taken for δE_T to adjust to a change in the state of the CDW (of the order of 1s at 115 K) varies as $\exp(\theta/T)$, where T is the temperature and $\theta \approx 3200$ K. In a specimen which exhibits ''mode locking'' between an applied alternating field and the frequency ν of the quasiperiodic component of the current I_C carried by the CDW, the development of δE_T is accompanied by a decrease in the ratio I_C/ν. The pinning giving rise to δE_T is attributed to the minimization of free energy through the thermally activated diffusion of In in a potential exerted by the CDW. The greatest δE_T develops in the steady potential exerted by the CDW at rest; when the CDW is in motion the potential varies periodically at a rate fast compared with the diffusion, and δE_T, which responds to its mean value, is reduced accordingly. Various couplings between the In and CDW which might provide the potential are examined, and it is concluded that the only coupling consistent with the observed time dependence of δE_T is that between the In and the strain field of dislocations in the CDW. To account for the behavior of δE_T, it is necessary to assume that the dislocations are on the boundaries of localized regions of the CDW which remain pinned when the rest is in motion. The behavior of I_C/ν shows that such immobile regions expand as δE_T develops, and thus confirms their existence in a CDW which otherwise moves coherently. The coexistence of stationary and moving regions clearly conflicts with the model of Fukuyama, Lee, and Rice (FLR), which treats the CDW as an elastic medium, and is widely accepted as applying to $NbSe_3$ except when macroscopic crystal defects are present. The evidence of stationary regions in every specimen examined, even when perfect enough to exhibit complete mode locking, suggests that they are intrinsic to the depinning of a weakly pinned CDW from randomly distributed impurities. A modification of the FLR model is proposed, in which immobile regions appear as a result of the thermal nucleation of dislocation loops where large stresses arise from the nonuniformity of the pinning. [S0163-1829(96)03224-9]

I. INTRODUCTION

Cooperative electronic conduction of the kind proposed by Fröhlich,[1] in which current is conveyed through the motion of a charge-density wave (CDW), has now been identified in about a dozen quasi-low-dimensional metals.[2] The CDW's, which develop below a critical temperature T_P as a result of a Peierls instability, appear as a spatial modulation of conduction electron density $\rho(\mathbf{r})$, which approximates to the form $\rho_0+\rho_1\cos[\mathbf{Q}\cdot\mathbf{r}+\phi(\mathbf{r})]$, with Q incommensurate with the underlying crystal lattice. Although in a perfect crystal their energy would be translationally invariant, allowing perfect conductivity, CDW's are in practice ''pinned'' by crystal imperfections, so that the cooperative current I_C is induced by a steady field $\mathbf{E}$ only if E exceeds a threshold value E_T.

Numerous studies of CDW transport during the last 15 years have shown that the pinning in most crystals is provided by chemical impurities, present substitutionally in the lattice. In the conventional model of such pinning, introduced by Fukuyama, Lee, and Rice (FLR),[3] randomly distributed impurities couple to the electron density modulation $\rho_1\cos[\mathbf{Q}\cdot\mathbf{r}+\phi(\mathbf{r})]$ in the CDW, which becomes pinned by deforming elastically, adjusting the phase ϕ at the impurity sites so that the total energy is minimized. Distinction is made between ''weak'' pinning, where the phase correlation lengths L_ϕ remain large in comparison with the distance between neighboring impurities, and ''strong'' pinning, where the elastic modulus of the CDW is small enough for the coupling energy at individual impurity sites to be minimized.

Many features of the threshold behavior are consistent with weak pinning of this kind. In the case of $NbSe_3$, Thorne and co-workers[4,5] have demonstrated the pinning of the CDW by substitutional impurities, with L_ϕ much larger than the impurity separation, and have shown that the FLR model of weak pinning accounts for the variation of E_T both with impurity concentration, and with crystal thickness when smaller than the corresponding L_ϕ.

However, it is doubtful whether the FLR requirement that the CDW behaves elastically is met in practice. In an infinite crystal and in the weak-pinning limit, the random nature of the pinning leads to variations in local threshold field which cause the maximum stress on an elastic CDW to diverge as E approaches E_T.[6,7] Inelastic processes of phase-slip are then inevitable and, except in one-dimensional situations, lead to the generation of dislocations in the CDW, such as have been discussed by Feinberg and Friedel.[8]

That phase-slip of some kind occurs in the bulk of moving

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CDW's, rather than merely at current terminals, is evident from the behavior of the quasiperiodic component of the current I_C (the ''narrow-band noise,'' or NBN), and its accompaniment by low-frequency ''broadband noise'' (BBN). It has been shown by Middleton[9] that if the moving CDW were truly elastic, it would reach a unique steady state, dependent on the driving field E, with $\partial\phi/\partial t$ (and therefore the CDW current density J_C) everywhere varying periodically with the same frequency. In practice, the NBN in most specimens contains several components, but this symptom of spatial nonuniformity in I_C is associated with macroscopic imperfections in the crystal rather than with any fundamental failure of the FLR model. However, even in the best specimens, where the NBN has a single component, the variation of I_C is never exactly periodic in time, and it has recently been found[10] that in $NbSe_3$ the frequency ν of the NBN then varies in close correlation with the BBN. As the power spectral density of the BBN varies approximately inversely as frequency, this shows that variations of indefinite duration occur in the configuration of the moving CDW with respect to the pinning, and may be taken as evidence that it contains topological defects, namely, dislocations.

The experiments described in this paper are thought to provide more direct evidence of dislocations in the bulk of the CDW in $NbSe_3$, and to show that they are associated with regions which remain pinned even when the rest of the CDW is moving coherently. As it is unlikely that the pinned regions in all specimens are based on macroscopic defects, it is suggested that their presence is intrinsic to the depinning of weakly pinned CDW's from randomly distributed impurities, and is a result of the inadequacy of the FLR model.

The measurements were made on $NbSe_3$ specimens containing small amounts, of the order of 1%, of intercalated indium. Studies were confined to the CDW having $T_P=144$ K. As in other quasi-low-dimensional structures, notably the layered chalcogenides,[11] the In remains mobile at quite low temperatures. The effect of this on CDW conduction in $NbSe_3$ was discovered by Yetman,[12] and a preliminary account has already appeared;[13] a gradual increase in E_T after CDW conduction ceases, reversed when it recommences, is thought to result from the redistribution of In impurities by thermal diffusion, so that they develop their greatest pinning effect when the CDW is at rest, and disperse once motion is resumed. Similar behavior noted in some early studies of $NbSe_3$ (Ref. 14) probably arose in the same way, from mobile impurities not yet identified. Changes in E_T have also been reported in $NbSe_3$ containing hydrogen, and may be evidence of its mobility below 60 K,[15] and mobile impurities have been suspected as a cause of hysteresis in $K_{0.3}MoO_3$.[16]

The aim here will be to establish how the mobile impurities contribute to E_T, and from their effects to obtain information about the pinning and motion of the CDW. The following arrangement is adopted.

The experimental phenomena are introduced in Sec. II, and the case presented for the changes in E_T being the result of the redistribution of In through thermally activated diffusion. In one specimen, where ν could be measured by synchronizing to an applied alternating field, it was observed that a reduction of I_C/ν accompanied the increase in E_T. In Sec. III the origin of the coupling between the In and the CDW is considered. Coupling to the modulation of charge density (which would lead to a ''defect density wave''[17]) proves inconsistent with the experimental evidence. It is concluded that the coupling is to elastic strain in the CDW, by a mechanism of which the theory is outlined. The effects of coupling to the various strains present in the CDW are examined in Sec. IV. The observations are quite inconsistent with the coupling being to the strains associated with FLR pinning, with the obstructing effects of terminals or other obstacles to motion, or with discommensurations. They are, however, explicable if the coupling is to the strain fields of dislocations. The arrangement of dislocations which might account for the threshold behavior is considered in Sec. V. A necessary assumption is that the dislocations occur on the boundaries between the moving CDW, and localized regions which remain stationary. The decrease in I_C/ν as the pinning develops is evidence of an expansion of such regions, and thus of their existence. Changes in the size of stationary regions also account for certain features of the behavior of E_T, especially in specimens where the effect of In is greatest. The implications for the FLR model are discussed briefly in Sec. VI. The present experiments add to the growing body of evidence that a CDW weakly pinned by randomly distributed impurities does not depin as a whole.

II. EXPERIMENT

A. Specimens

Measurements of the effect of intercalated In on the bulk CDW conduction in $NbSe_3$ have been made on 15 specimens, listed in Table I in order of the parameter Γ (which measures the effect of In) to be introduced in Sec. II. Terminals (four or more) were of In wire, diameter usually 10–30 μm, pressed to the surface of the ribbonlike crystals. The lengths l refer to the separation of the inner terminals, which were the voltage terminals except where otherwise stated. The voltage V_{ps}($\sim$1 mV at 115 K) absorbed in maintaining phase-slip at the outer (current) terminals[18] accounted for only a few percent of the threshold field. Cross-sectional areas A were estimated from the resistance R at 300 K, taking the resistivity as 185 $\mu\Omega$ cm;[4] thicknesses d were found from A and the measured width. Crystals were from three growth batches (I–III), from which specimens having d greater than a few μm had resistance ratio $r_R=R(300\text{ K})/R(4.2\text{ K})$ roughly 70 (I) or 270 (II, III).

B. Treatment with In

Indium was incorporated in the specimens by heating to 120 °C in an atmosphere of helium (pressure $\sim$10 torr), for between 10 and 60 min. The In enters from the terminals, and is presumed to intercalate between the $NbSe_3$ chains.

The amount of In thus introduced has been measured in one specimen, using an electron beam microprobe analyzer to estimate the relative abundances of In and Nb from their L_α x-ray emissions. The presence of In was just detectable throughout the region between terminals 2 mm apart, with ratio In:Nb about 1%. The distribution within the cross section could not be measured, but the In is not likely to be confined to the crystal surface, which was not visibly changed by its presence. This specimen was not measured electrically, but there is no reason to expect it to differ from those that were.

TABLE I. Details of $NbSe_3$ specimens measured. Length l is measured between voltage terminals; A denotes the cross-sectional area, and d the thickness of the ribbonlike crystal. E_{T0} is the threshold field before intercalation of In. The quantities Γ and s are defined in Secs. II E and II G, respectively. Specimens 13 and 15, respectively, are specimens 6 and 9 after further intercalation of In.

Specimen no.	Batch	l (mm)	A (μm^2)	d (μm)	E_{T0} (115 K) (mV cm^{-1})	Γ (115 K)	s
1	II	2.7	125	1.7	65	0.04	4.0
2	I	1.3	25	2.2	150	0.05	4.2
3	III	2.0	45	3.5	72	0.07	4.0
4	II	2.3	26	2.3	84	0.09	4.0
5	II	1.1	1.3	0.33	270	0.11	3.2
6	II	1.3	630	7.6	41	0.11	2.4
7	II	1.7	60	2.1	98	0.12	2.9
8	I	0.58	18	1.15	280	0.13	1.4
9	I	0.43	17	0.94	310	0.20	1.7
10	II	1.7	0.7	0.25	400	0.26	1.5
11	I	0.7	22	2	190	0.27	1.5
12	II	0.9	5.8	1.4	114	0.52	0.6
13	II	1.3	630	7.6	41	0.60	0.6
14	III	1.9	40	3.3	70	0.81	0.8
15	I	0.43	17	0.94	310	1.37	0.5

The changes in threshold behavior which result from the heat treatment are described below. As the changes are not observed if the heating is done before the In terminals are attached, and affect the bulk properties homogeneously, they are attributed to a uniform distribution of In throughout the specimen.

C. Methods of measurement

The threshold behavior of the CDW which forms at 144 K has been studied, between that temperature and 59 K (where a second CDW appears), essentially by measuring the voltage V developed in response to a current I. The current I_C carried by the CDW was taken to be $I-I_S$, where $I_S=V/R$ is attributed to electrons not in the CDW, and R is the Ohmic value of V/I when $E<E_T$. Signals representing I_C, derived from an active bridge circuit, were recorded as a function either of time t or of I. Various pulsed waveforms of I [(a)–(c) in Fig. 1] were used, with repetition period t_r short compared with the relaxation associated below with the diffusion of In. Digital sampling techniques were used to record I_C when I was an ''observing'' current I_O, applied as pulses of duration $t_p \ll t_r$ (t_p was typically 1–3 ms, t_r 20 ms to 1.28 s). Elsewhere in the cycle, I was for a time zero, to allow ''lock-in'' detection of I_C, and might at other times assume a value I_P (the ''preparing'' current), of either sign relative to I_O, as in waveforms (b) and (c). An adaptation of these techniques to allow the influence of the In on the NBN frequency ν to be studied is described in Sec. II H.

D. Effects of indium intercalation on the Ohmic resistance

The intercalation of In has a small effect on the linear electrical conduction, noticeable only in the specimens containing the largest concentrations, of which one has been studied in detail. In this specimen (No. 14), on the addition of In, an increase in the Ohmic resistance R was detected both at low temperatures, where the ratio $r_R=R(300\ \mathrm{K})/R(4.2\ \mathrm{K})$ was reduced from 270 to 220, and also near 144 K, where the anomaly associated with CDW formation was displaced to higher temperature by about 1.3 K, without broadening the transition. For the other CDW no change in T_P ($\approx$59 K) was detected, and any is unlikely to have exceeded 0.5 K.

E. Threshold behavior in the steady state

As the In diffuses negligibly during the repetition period t_r, the continued application of any of the waveforms of I in Fig. 1 establishes a steady-state distribution. The threshold behavior in the states established by the various waveforms is considered here.

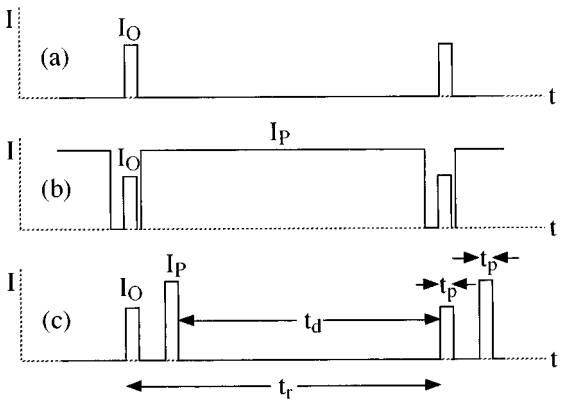

FIG. 1. Repetitive waveforms of current I used in experiments. The current I_C carried by the CDW is recorded while applying the ''observing'' current I_O as pulses of duration t_p, and repetition interval t_r. In waveform (a), I_O is applied alone. In (b) a ''preparing'' current I_P, of either sign relative to I_O, is present almost continuously. In (c), I_P is applied as pulses, preceding the next pulse of I_O by an adjustable interval t_d.

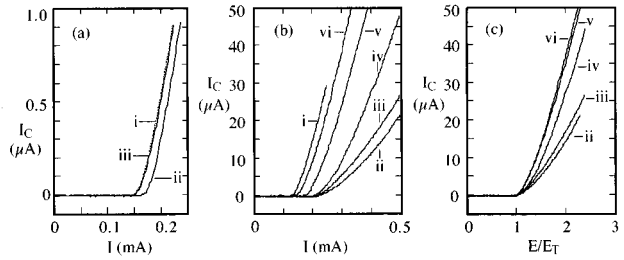

FIG. 2. Relation between CDW current I_C and applied field E (or current I), at $T\approx 115$ K. Records (a) are from specimen No. 5: (i) before intercalating In; (ii) after intercalation, using waveform (a) of Fig. 1 for I; and (iii) using waveform (b) with $I_P\approx 1.3I_{T0}$. Records (b) are from specimen No. 14: (i) before intercalation; (ii) after intercalation, using waveform (a); and (iii)–(vi), using waveform (b) with I_P, respectively, about 7.5, 15, 23, and 30 I_{T0}. In (c) the records of (b) are redrawn as a function of E/E_T.

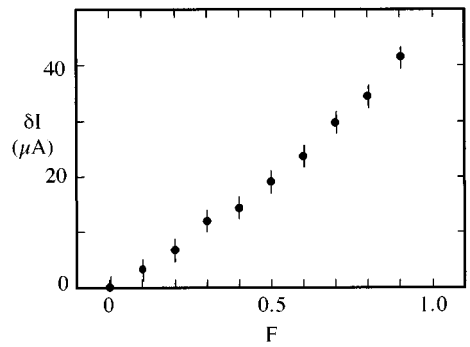

FIG. 3. The dependence of the pinning effect of intercalated In on the relative timing of the pulses I_P and I_O in waveform (c) of Fig. 1. $F=1-(t_d+2t_p)/t_r$ is the fraction of the time spent by the CDW in the state established by I_O. The contribution δE_T of the In to E_T is represented by the difference $\delta I(F)=I_O(F)-I_O(0)$, between values of I_O corresponding to the same I_C. The increase of δI with F is approximately linear.

Figures 2(a) and 2(b) show, for two representative specimens (Nos. 5 and 14), the relation between I_C and I_O recorded, using various waveforms of I, as I_O was increased slowly so as to maintain effectively steady-state conditions. Record (i) in each figure was obtained before any In was added, with I_O applied as short pulses [waveform (a) of Fig. 1]. The threshold current I_T and field E_T in this case are denoted I_{T0} and E_{T0}, respectively. Similar records were obtained using waveforms (b) and (c), if I_C was read after the decay of any transient (such as the pulse-sign memory ''overshoot'' [19]) due to rearrangement of the CDW by I_O.

Records (ii) show the response to waveform (a) after the addition of In. Nonlinear conduction now first appears at a larger value of I, showing that the In increases either E_T for the bulk CDW, or the contribution to V from the voltage V_{ps} needed to induce phase-slip. In the latter case the In may increase V_{ps} by inhibiting phase-slip at the current terminals, or it may cause the whole of V_{ps} to appear in V by pinning the CDW at the voltage terminals so that phase-slip also occurs there. To account for the increased threshold current in Fig. 2(b) (and in some other specimens) would require both phase-slip at the voltage terminals, and an increase in V_{ps} by an order of magnitude. Measurements on several specimens have shown neither of these to occur: interchanging the current and voltage terminals invariably led to an increase in V for given I_C, which would not happen if phase-slip already occurred at the inner terminals, and the increase [then approximately V_{ps} (Ref. 18)] was not significantly greater than before the addition of In. It is concluded that the differences between records (i) and others in Figs. 2(a) and 2(b) are indeed the result of increases in the bulk threshold field E_T. These increases will be denoted δE_T, and the ratio $\delta E_T/E_{T0}$ measured using waveform (a) will be denoted Γ. Unless otherwise stated, the quoted value of Γ will be that at 115 K, respectively, 0.11 and 0.81 in Figs. 2(a) and 2(b). It is adopted as a measure of the effect of the In on E_T, if not of its actual concentration. The effect on V_{ps} appears to be small compared with that on E_T: measurements on a specimen having $l\approx 40$ μm, not listed in Table I, revealed a barely significant increase $(8\pm 4)\%$ in V_{ps} whereas Γ was 0.38.

The effect of In is much smaller when $I(=I_O+I_P)$ is present almost continuously, as in waveform (b). Record (iii) in Fig. 2(a) was obtained with $I_P=1.3I_{T0}$ in the same direction as I_O; I_T is now almost indistinguishable from the initial I_{T0}. Qualitatively similar behavior, if overshoot transients are avoided, is observed with I_P opposite to I_O. The reduction of δE_T by waveform (b) is seen also in Fig. 2(b), where the sequence of records (iii)–(vi) shows the effect of increasing I_P in the same direction as I_O. In this case, with larger Γ, a much greater I_P ($\approx 30I_{T0}$) is required to reduce δE_T to near zero.

The increase in E_T, which in Fig. 2(a) leads to no obvious change in the relation between I_C and $E-E_T$, is accompanied in Fig. 2(b) by a large reduction in the rate of rise of I_C. This is very noticeable in specimens having $\Gamma>0.5$, and evidently is associated with large concentration of In. The slow rise of I_C is not simply a result of E scaling with E_T: Fig. 2(c), in which records (ii)–(vi) of Fig. 2(b) are plotted as a function of E/E_T, shows that when δE_T is greatest, I_C for given E/E_T is about 0.4 of its value when $\delta E_T\approx 0$. The possible significance of this will become apparent in Sec. V.

The reduction of δE_T when current flows continuously is not a direct result of the CDW then being in motion, for it can also be achieved by applying I_P as short pulses (duration t_P), as in waveform (c). The effect of the pulses depends on their sign, and also on their timing in relation to those of I_O: δE_T is reduced more as the interval t_d between I_P and the next following pulse of I_O increases. The apparent paradox, that I_P has its greatest effect on the response to I_O when most distant in time from it, has been resolved by varying the pulse repetition period t_r. The factor governing δE_T proves to be the fraction F of the time which the CDW spends at rest in the state left after I_O ceases, which here is $1-(t_d+2t_p)/t_r$. Figure 3 shows the approximately linear relation between δE_T and F, recorded from specimen No. 7, with I_P opposite to I_O and of magnitude $1.2I_{T0}$. The linear dependence of δE_T on F is also observed with pulsed I_P in the same direction as I_O, though then a much greater I_P ($\approx 30I_{T0}$) is required to reduce the minimum δE_T to near zero.

The phenomena described above have been observed, at temperatures T between 90 and 135 K, in all the specimens examined. The quantity Γ decreases slowly with increase in T, becoming too small to detect above 135 K: below 90 K its

measurement is impracticable, on account of the very slow diffusion of the In, to be described in Sec. II G.

F. Attribution to pinning by mobile impurities

To account for the behavior of δE_T in terms of the pinning effects of diffusing In impurities, as outlined in Sec. I, the following assumptions appear necessary.

(a) When the CDW is at rest, the In atoms tend to become distributed so that their pinning effect is greatest. This process, involving local increases and decreases of In concentration, will be referred to as the *accumulation* of pinning.

(b) When the CDW is in motion, the distribution of In reached when it is at rest diffuses toward a uniform (or more uniform) distribution. This process will be termed the *dispersion* of pinning.

(c) The configuration of the CDW at rest depends uniquely on its previous velocity and direction of motion. If the same motion is resumed, the CDW repeatedly passes through that configuration, or through one similar to it at least where the pinning accumulated.

(d) The moving CDW does not necessarily approach the rest configuration left after motion in the opposite direction, or even in the same direction with very different velocity.

Assumptions (a) and (b) provide for a greater δE_T being established when the CDW is at rest than when it is in motion; (c) is necessary so that the pinning accumulated at rest exerts a pinning force also on the moving CDW; and (d) ensures that dispersion may be induced using pulsed, as well as continuous, I_P. Provided that the accumulation and dispersion processes occupy many repetition intervals t_r, the observed dependence of δE_T on the relative timing of pulses of I_P and I_O then follows.

G. Time dependence of E_T

The development of E_T following a change in I (usually in I_P) has been studied, as a function of time t, by recording I_C for successive I_O pulses of constant amplitude. When Γ is small (<0.1), $I_O(t)$ effectively measures $-\delta E_T(t)$. With larger Γ, the transition from accumulation to complete dispersion (which may require $I_P \gg I_{T0}$) is complicated by the nonlinearity of the relation between I_C and $E-E_T$, and its dependence on δE_T. Only if I_P is reduced so that dispersion remains suitably incomplete is $I_C(t)$ then a measure of $-\delta E_T(t)$.

The variation of $I_C(t)$ will be described by functions $g(t)=[I_C(t)-I_C(\infty)]/[I_C(0)-I_C(\infty)]$. The time scale and form of $g(t)$, which relaxes monotonically, will be specified by a characteristic time τ_2 and shape factor $s=(\tau_4-\tau_2)/\tau_2$, where the τ_n's are defined by $g(\tau_n)=1/n$. Values 4, 2, 1, and 0.5 for s arise, respectively, when $g(t)$ decays as $1/\sqrt{(1+t)}$, $1/(1+t)$, $\exp(-t)$ and $1-t(t\leqslant 1)$, when the units of t are chosen appropriately.

As with the steady-state behavior, the time dependence of I_C depends on the In concentration. Figure 4 shows records typical of small concentration, obtained at $T=113$ K from specimen No. 3 ($\Gamma\approx 0.07$). Dispersion (I_C increasing with t, by about 13%) follows a change in the waveform of I from

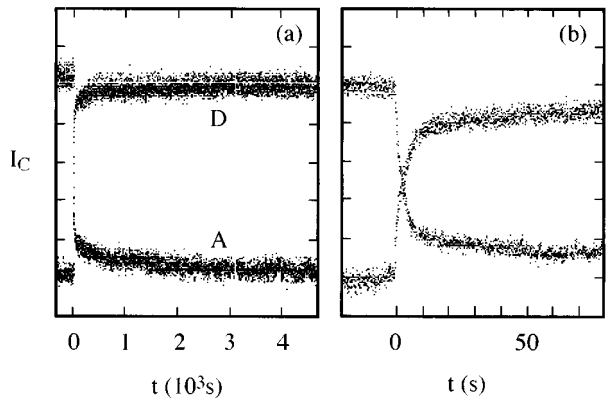

FIG. 4. Dispersion (D) and accumulation (A) transients in a specimen (No. 3) containing a small amount of In, at $T\approx 113$ K. In (a) and (b) the variation of I_C (effectively of $-\delta E_T$) is shown on two scales of time t. Data points show I_C recorded from individual pulses of I_O. The decrease of δE_T in D follows the replacement of current waveform (a) by (b); the increase in A follows the replacement of (b) by (a).

(a) to (b), with $I_P=3I_{T0}$ in the same direction as I_O; the reverse change [(b) to (a)] leads to accumulation (I_C decreasing). The corresponding $g(t)$, referred to below as dispersion and accumulation transients, are denoted $g_D(t)$ and $g_A(t)$. Essentially similar transients were observed using larger I_P, and also using waveform (c) instead of (b).

Figure 4 shows both $g_D(t)$ and $g_A(t)$ to decay at a rate which becomes extremely slow when t is large. The decay of $g_D(t)$ begins with a sudden step (about 15% being completed before the first sampling by I_O), but thereafter is smooth. No initial step is present in $g_A(t)$, but its later stages are confused by BBN, the amplitude of which increases as pinning accumulates. In each case the parameter s is close to 4. That value appears to be the maximum, approached in the limit of small Γ: Table I [in which s refers to $g_D(t)$, measured with I_P a few times I_{T0}] shows $s\approx 4$ only for specimens having $\Gamma<0.1$; in no case has a value significantly greater than 4 been observed.

Of the possible forms of $g(t)$ consistent with the value $s=4$, $1/\sqrt{(1+t/\tau)}$, in which a single adjustable parameter τ sets the time scale, is the simplest. Also deserving consideration is the ''stretched exponential'' $\exp\{-(t/\tau)^{\beta}\}$, which certain relaxations in CDW systems have followed quite closely;[20] a second parameter β (<1) determines the shape of the decay, $s=4$ requiring $\beta=\ln 2/\ln 5\approx 0.43$. An alternative, which has been fitted to relaxation roughly linear in $\ln(t)$,[21] is $\ln\{\tanh(t/\tau+\gamma)\}/\ln\{\tanh(\gamma)\}$;[21] this gives $s=4$ when $\gamma\approx 1.96\times 10^{-3}$.

In Fig. 5(a) the first two of these forms are compared with the observed $g_D(t)$, plotted versus t on a logarithmic scale. The data points are derived from means of those in Fig. 4 with $I_C(\infty)$ estimated from the final stages of the record, omitting the initial step. Throughout the observed range $0<t<2000\tau$, the data lie close to the line representing $g=1/\sqrt{(1+t/\tau)}$, with $\tau=1.6$ s. The data depart significantly from a stretched exponential form: if fitted, as shown, to the early stages of the decay, by choosing β so that $s=4$, it fails to reproduce the very slow relaxation when t/τ is large; if

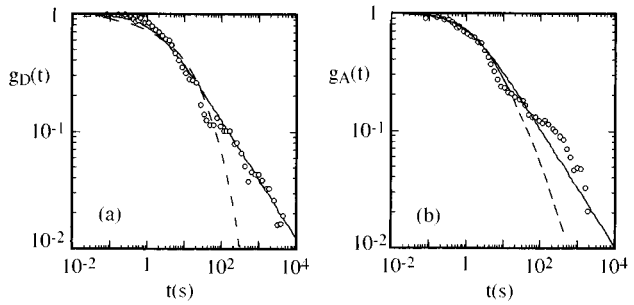

FIG. 5. The transients of Fig. 4 expressed as the functions $g_D(t)$ and $g_A(t)$ defined in Sec. II G. Data are means of those in Fig. 4. In (a) the continuous line represents $g_D(t)=1/\sqrt{(1+t/\tau)}$, with $\tau=1.6$ s; the broken line shows a stretched exponential having $s=4$. In (b) the continuous line represents $g_A(t)=1/\sqrt{(1+t/\tau)}$, with $\tau=1.0$ s; the broken line shows a form of $g_A(t)$ predicted in Sec. IV E.

fitted to the later stages, then s is very much greater than is observed [$\approx$100, if $g_D(t)$ is fitted between 0.1 and 0.01]. Qualitatively similar, but even larger, discrepancies arise in fitting $\ln\{\tanh(t/\tau+\gamma)\}/\ln\{\tanh(\gamma)\}$ to the data.

Figure 5(b) shows $g_A(t)$ as a function of t. In this case large fluctuations due to broadband noise make the later stages of the decay erratic, the data wandering either side of the continuous line, which represents $1/\sqrt{(1+t/\tau)}$ with $\tau=1.0$ s. Although further from the broken line, which indicates a decay form predicted in Sec. V, the discrepancy may not be significant, as the difference between the two lines is of the same order as the fluctuations.

When Γ is large, even if $\delta E_T(t)$ is measured by leaving dispersion incomplete, the forms of $g_D(t)$ and $g_A(t)$ differ greatly from those when Γ is small. The values of s quoted in Table I, which for large Γ were measured with I_P insufficient to produce complete dispersion, decrease rapidly as Γ rises. Figure 6 shows an example of the $g(t)$ for large Γ, measured with $I_P \approx I_O$ in a specimen (No. 14) having $\Gamma=0.81$. Both transients now decay almost exponentially [$s=0.8$ for $g_D(t)$, 1.1 for $g_A(t)$], with no initial step in $g_D(t)$. The times τ_2 are 3.5s and 1.4s, respectively, for $g_D(t)$ and $g_A(t)$, rather less than the values 4.8s and 2.7s ($=3\tau$) for small Γ.

As I_P increases, and complete dispersion is approached, the transients when Γ is large change both in shape and time

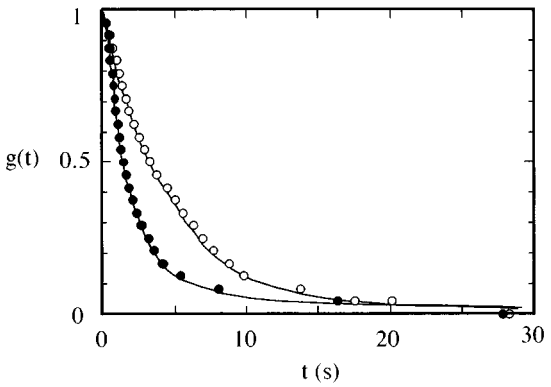

FIG. 6. Transients in a specimen (No. 14) containing a larger concentration of In, at 113 K. Symbols ○ show $g_D(t)$ during incomplete dispersion (δE_T reduced by about 30%); $g_A(t)$ during the opposite process of accumulation is shown by ●.

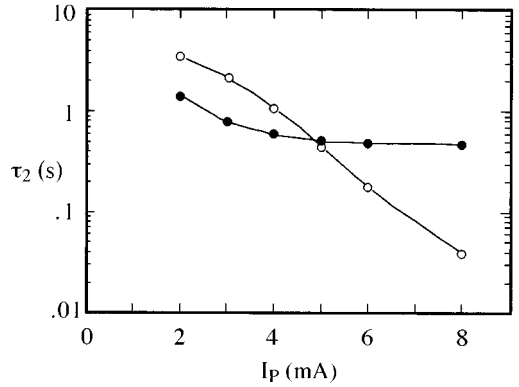

FIG. 7. The influence of current on the decay of $g_D(t)$ and $g_A(t)$ in specimen No. 14, at 113 K. The times τ_2 for $g_D(t)$ (○) and $g_A(t)$ (●) to decay to $\frac{1}{2}$ are shown as a function of I_P. As I_P increases, τ_2 for $g_D(t)$ decreases indefinitely, whereas τ_2 for $g_A(t)$ is reduced only by a factor $\approx$2.

scale: the changes in τ_2 for specimen No. 14 are shown in Fig. 7. In the case of $g_A(t)$, the asymptotic reduction in τ_2, and an accompanying increase in s, may be attributed to the nonlinear relation between δE_T and I_O; correction for this restores τ_2 and s to the values measured with small I_P, which are taken to describe $\delta E_T(t)$. With $g_D(t)$, however, τ_2 approaches zero as I_P increases, and s approaches 0.5, corresponding to a linear decay. These changes, which are not observed when Γ is small, are opposite to, and much greater than, any expected from the nonlinear relation between δE_T and I_C.

Measurements on nine of the specimens have shown that for $g_A(t)$, and for $g_D(t)$ if Γ is small or the dispersion far from complete, the variation of τ_2 with the temperature T is of the form $\tau_2=\Omega\exp(\theta/T)$, with Ω of the order of 10^{-12} s, and $\theta=(3200\pm200)$ K. Figure 8 shows this in the case of $g_D(t)$ for the specimens (Nos. 3 and 14) which provided Figs. 5–7. Clearly, the redistribution of In involved in $g_D(t)$ and $g_A(t)$ is through thermally activated diffusion.

The effect of the diffusion will depend on how the In responsible for the pinning is distributed, which in turn depends on the way in which the In couples to the CDW. The

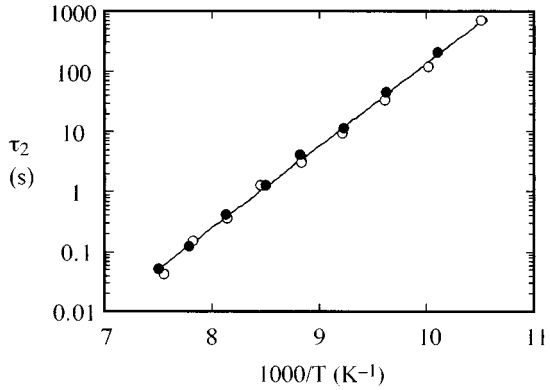

FIG. 8. The dependence of the characteristic time τ_2 on temperature T. Symbols ● and ○ refer to $g_D(t)$, respectively, from specimen No. 3, and from specimen No. 14 (with incomplete dispersion, as in Fig. 6). The line shows the activated form $\tau_2=\Omega\exp(\theta/T)$, with $\Omega=2.9\times10^{-12}$ s and $\theta=3150$ K.

identification of this is best attempted from the results for small Γ, where diffusion appears to be the dominant factor determining the $g(t)$. As the experiments show $g_D(t)$ to decay as $1/\sqrt{(1+t)}$, rather than as the alternatives considered, the explanation of that form is the main objective of Secs. III and IV. As mentioned in Sec. I, it is concluded in Sec. IV that the In exerts its pinning effect through dislocations in the CDW, and in Sec. V that these occur at the boundaries between the moving CDW and regions where it remains pinned.

As the behavior of $g_D(t)$ when Γ is large clearly is not solely a result of diffusion, it is of interest to ask whether a variation in the size of the immobile regions, and thus in the cross-sectional area A_M of the moving CDW, is also present. A measurement of the influence of mobile impurities on the ratio $I_C/\nu = \rho_0 e \lambda A_M$, where I_C is the current carried by the CDW and $2\pi\nu$ is the time-averaged phase winding rate $\langle \partial\phi/\partial t \rangle$, is therefore next described.

H. Synchronization phenomena in the presence of pinning by mobile impurities

Although the direct measurement of ν, from the narrow-band noise, proved impracticable on account of the large amplitude of broadband noise, synchronization (''mode locking'') between ν and an applied alternating field of appropriate frequency ν_{ac} could be observed even in specimens containing large concentrations of In. The results from one such specimen are presented here.

The phenomenon of mode locking, in CDWs driven by superposed direct and alternating fields, has already been studied in detail in $NbSe_3$.[22] Ideally, when ν, which varies with I_C, is sufficiently close to $(p/q)\nu_{ac}$, where p and q are integers, the time-averaged value of the periodic pinning force adjusts I_C so that ν becomes locked to $(p/q)\nu_{ac}$. Being determined by ν_{ac}, I_C then remains constant as E varies, and a ''Shapiro step'' appears in the I_C-E characteristic. In practice, dI_C/dE becomes zero only in unusually perfect crystals, and when p and q are small: more commonly dI_C/dE is reduced to $(1-f)(dI_C/dE)_0$, where $(dI_C/dE)_0$ is the value far from synchronization, and the ''mode-locked fraction'' f is less than 1. It is important to note that for f to be 1, $\langle \partial\phi/\partial t \rangle$ need be uniform only where the CDW is moving: complete mode locking is not prevented if some regions remain stationary, provided that elsewhere the CDW moves coherently.

In studying mode locking in the presence of pinning by mobile impurities, the dispersing effect of the alternating field was minimized by applying it only during the observing pulses I_O, whose duration t_p and repetition period t_r were, respectively, 5 and 80 ms. The four-terminal technique of Sec. II C was used to measure I_C, with the bridge system adapted to reject ν_{ac}. To measure dI_C/dE, the (pulsed) direct current I_O was reduced slightly for the final 1 ms of each pulse, and the resulting change in I_C obtained by sampling before and during the reduction. As in Sec. II C, the pinning could be dispersed by the quasicontinuous current I_P.

The experimental results presented here were obtained from specimen No. 12. To keep I_O, and thus its influence on the pinning, as small as possible, a small value of ν_{ac} (4 MHz) was used. The value of I_C for mode locking with various p and q was measured at temperatures between 70 and 140 K, before and after intercalation. Measurements in the presence of In were made both after pinning had accumulated in the absence of I_P, and also with pinning partly dispersed by $I_P \approx 2I_T$ opposite to I_C, reducing δE_T roughly by half (with $\Gamma = 0.52$, complete dispersion required inconveniently large I_P, especially when parallel to I_O).

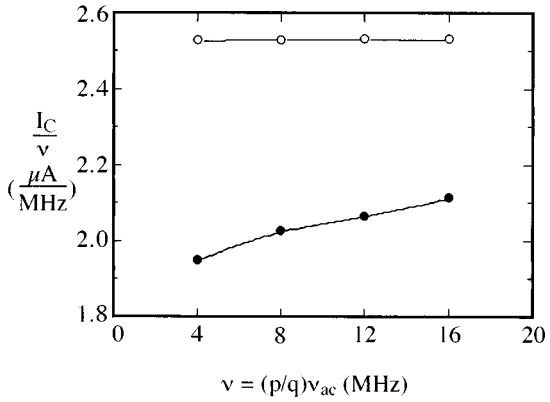

FIG. 9. The ratio between CDW current I_C and phase-winding frequency ν, before (○) and after (●) intercalation of In, at 120 K. A pulsed current I_O was used to observe mode locking between ν and an alternating field of frequency $\nu_{ac}=4$ MHz. Before intercalation, I_C/ν is independent of ν over the range observed. After intercalation, pinning by the In reduces I_C/ν to an extent which decreases as I_C rises.

In favorable conditions of temperature (120 K or thereabouts), amplitude of alternating field, and p/q (1/1 or 2/1), complete mode locking ($f=1$) was observed both before and after intercalation of In. However, most of the data presented below were obtained with f between 0.5 and 1 for $p/q=1/1$, and smaller for other p/q. The incomplete locking, which is evidence that the spectrum of ν is distributed about the measured value $(p/q)\nu_{ac}$ is probably the result of temporal fluctuations in the velocity of the moving CDW, rather than spatial nonuniformity in its average value. Splitting of the Shapiro steps, into components associated with independent regions, was not seen. It is interesting that when In is present, if I_O is set at the value appropriate to a particular Shapiro step, the parameter f (if not 1 already) rises to a slightly higher value in a time of the order of τ_2, evidently as further pinning accumulates.

Values of $I_C/\nu (= qI_C/p\nu_{ac})$ measured for complete or partial mode locking are shown in Figs. 9 and 10. Figure 9 illustrates, for a representative temperature, the behavior of I_C/ν as E increases: the data were obtained with $q=1$ and $p=1$–4, corresponding to a range of E roughly from $1.3E_T$ to $2E_T$. Over this range of E, no variation of I_C/ν is apparent before the intercalation of In. After intercalation, and when pinning has accumulated, I_C/ν is significantly smaller, and increases markedly with E. Both the reduction of I_C/ν, and its dependence on E, are less pronounced when the pinning is partly dispersed. These effects were seen at all temperatures of measurement above 90 K; at lower temperatures pinning took inconveniently long to accumulate.

The effect of the accumulated pinning on the magnitude of I_C/ν (measured for $q/p=1/1$) is shown for a range of temperature T in Fig. 10. The right-hand scale shows the effective electron density $\rho_{eff} = I_C/(\nu e \lambda A)$ transported by the

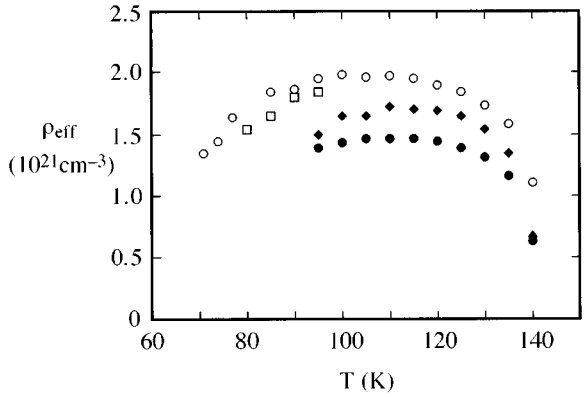

FIG. 10. The influence of pinning by mobile In impurities on the effective electron density $\rho_{\rm eff}=(I_C/\nu)/(\lambda A)$ transported by the CDW. Measurements at various temperatures T were made with ν=4 MHz. Values before intercalating In are shown by ○. Values after intercalation are shown by ● when pinning has accumulated in the presence of I_O; by ♦ when the pinning has been partly dispersed by I_P; and by □ when measured before pinning has had time to accumulate.

CDW over the cross section A of the specimen. In the absence of In, I_C/ν passes through a broad maximum near 105 K, corresponding to $\rho_{\rm eff}\approx 2.0\times 10^{21}$ cm^{-3}, and decreases rapidly as T approaches T_P=144 K, and also as T decreases below 90 K. This behavior has already been reported by others.[4,23]

Figure 10 shows that I_C/ν is reduced by about 25% when, with In present, pinning has accumulated to its greatest extent. The reduction of I_C/ν becomes less when the pinning is partly dispersed, by approximately the same factor as δE_T is reduced (0.4 at 100 K, 0.6 at 120 K). The presence of In has little effect on I_C/ν at 90 K and below, since the diffusion is too slow for appreciable pinning to accumulate during the experiment. At 95 K, where $\tau_2\sim$10 min, a measurement made within 2 min of first applying I_O provided the data point close to that measured in the absence of In, whereas those for the accumulated and partly dispersed states were obtained after allowing 45 min for steady conditions to be approached.

It is hard to see how the reduction in $\rho_{\rm eff}$ which attends the accumulation of pinning could result from a change in the electron density concerned in the CDW. The direct effect of the In on ρ_0, of the order of 1%, is too small to be noticeable, and varies only locally as pinning accumulates. The ''backflow'' of electrons, suspected of causing the decrease in $\rho_{\rm eff}$ at low temperatures,[23] might be affected if the In were to modify the electron pockets left by the CDW, but the minor effect of the In on the resistivity below T_P suggests that any change will be very small. In any case, it is not obvious that the backflow would be sensitive to the accumulation of pinning, which merely redistributes In without changing its mean concentration.

A conclusion that the changes in $\rho_{\rm eff}$ result from changes in the cross-sectional area A_M of the moving CDW thus seems inescapable. Although the mode locking shows that elsewhere its motion is essentially coherent, a substantial part of the CDW, which increases in volume as pinning accumulates, evidently remains at rest. Clearly, in order to reduce A_M by 25%, as in Fig. 10, at least 25% of the cross-sectional area A of the specimen does not participate in the motion. It is also evident from Fig. 9 that the effect of the pinning, in increasing the volume which remains at rest, becomes smaller as I_O increases.

III. COUPLING BETWEEN MOBILE IMPURITIES AND THE CDW

A. Coupling mechanisms

As there is no evidence of the ordering seen in heavily intercalated materials,[11] and no obvious structural barrier to motion parallel or perpendicular to the $NbSe_3$ chains, the In atoms will be assumed to move independently in three dimensions, hopping thermally between their preferred sites between the chains. The electron transfer associated with intercalation is expected to leave them positively charged (as In^+), and the resulting increase in electron density ρ_0 in the CDW is presumed responsible for the 1% increase in T_P mentioned in Sec. II D. From the magnitude of the increase, and the negligible broadening of the transition, it is concluded that the In in that heavily doped specimen was distributed uniformly, with concentration approximately 0.01 ρ_0, of the same order as was detected by microprobe analysis (Sec. II B).

In the FLR and most other treatments of pinning, the coupling between a charged substitutional impurity and a CDW is represented by a potential $V\cos\Phi_i$, where $\Phi_i=\mathbf{Q}\cdot\mathbf{r}_i+\phi(\mathbf{r}_i)$, and $\mathbf{r}_i$ is the position of the impurity. Although of electrostatic origin V is not the result simply of the Coulomb interaction between the impurity and the modulation of conduction electron density in the CDW, it is thought to arise from the matching of the latter to the Friedel oscillations induced in screening the impurity charge.[24]

While intercalated impurities also may couple to the CDW in this way, the coupling is expected to be much weaker than for substitutional impurities. The Coulomb interaction between the CDW and a charged impurity between the $NbSe_3$ chains is likely to be negligible, as the macroscopic distribution of charge on the chains is unaffected by the combined modulation of the densities of conduction electrons and of ion cores, respectively, by the CDW and the periodic structural distortion which accompanies it. The amplitude of Friedel oscillations induced by such an impurity is also likely to be small, because of the wide spread of screening charge along the chains. However, although this may result in the coupling to Φ_i being negligible, the screening charges contribute to the electron density concerned in the CDW, and thus to its equilibrium wave vector. This allows nonuniformity in the density of impurities to couple to the longitudinal component of the strain $Q^{-1}\nabla\phi$ in the CDW. Which form of coupling is the more consistent with experiment is now examined.

B. Coupling to Φ_i

Suppose a mobile In impurity has available sites, equivalent in the absence of the CDW, in which its potential energy is $-V\cos\Phi_i$. The CDW gap Δ (Δ_0 when T=0) sets an upper limit to V of the order of 20 meV in $NbSe_3$,[4] and similar to k_BT in the present experiments. For intercalated impurities one may assume $V\ll k_BT$, so that in thermal equi-

librium site occupancies are approximately proportional to $[1+V\cos\Phi_i/k_BT]$, and the energy of an In atom has an expectation value $-V^2/2k_BT$. As the In atoms diffuse far too slowly to move with the CDW, they are equivalent to strong pinning centers of strength $V^2/2k_BT$ (though the energy is minimized by adjusting the $\mathbf{r}_i$ rather than by distorting the CDW). Their contribution to E_T is then $(C_0Q/e\rho_{\rm eff})(V^2/2k_BT)$, where C_0 is the average density of In atoms coupled to the CDW, whose effective electron density at temperature T is $\rho_{\rm eff}\approx\rho_0(\Delta/\Delta_0)$.[2] Taking $\rho_{\rm eff}=0.5\rho_0$ at $T=115$ K, $\rho_0=2\times10^{21}$ cm^{-3}, $C_0=0.01\rho_0$, and $Q=4.5\times10^7$ cm^{-1}, a coupling strength $V\approx0.05$ meV would account for $\delta E_T\approx0.1$ V cm^{-1}, as observed in the more heavily doped specimens.

Although this value of V, being smaller than for substitutional impurities[4] by about two orders of magnitude, seems not inappropriate for intercalated impurities, it is easy to see that coupling to Φ cannot account for the decay of $g_D(t)$ as $1/\sqrt{(1+t)}$ seen when $\Gamma\ll1$. With $V\ll k_BT$, the modulation of impurity concentration by $V\cos\Phi$ is almost linear, and the defect-density wave which develops in equilibrium is expressed, in a continuum approximation, by

$$\delta C=C_0(V/k_BT)\cos\Phi, \tag{1}$$

where $\delta C=C-C_0$, and C is the local concentration of In. If motion of the CDW reduces the local average of $V\cos\Phi$ to zero, this sinusoidal distribution necessarily decays exponentially, in accordance with

$$\delta C(t)=\delta C(0)\exp(-D_zQ^2t), \tag{2}$$

where t represents time, and D_z is the diffusivity in the z direction. As δE_T is proportional to δC, $g_D(t)$ also must decay exponentially, in striking disagreement with observation. An exponential form also applies if the impurities occupy discrete sites.

It is interesting that if the impurities were initially in equilibrium in a potential $-V\cos\Phi$ with $V\gg k_BT$, their pinning effect *would* decay as $1/\sqrt{(1+t)}$. The distribution $C(z,t)$ of impurities in equilibrium at time $t=0$ is then expressed by

$$C(z,0)\approx(C_0/Q)(4\pi\alpha)^{1/2}\exp[-\alpha z^2], \tag{3}$$

where $\alpha=(VQ^2/2k_BT)\gg Q^2$, and distance z is measured from the nearest maximum at $\Phi=2n\pi$. It is easily shown[25] that, as this Gaussian distribution broadens as a result of diffusion along z, its maximum value $C(0,t)$, and therefore δE_T, decays according to

$$C(0,t)=C(0,0)/\sqrt{(1+t/\tau)}, \tag{4}$$

where $\tau=1/(4D_z\alpha)$, until t/τ approaches $(\pi^2/2)(V/k_BT)$, and $C(0,t)$ its final value C_0. However, to account in this way for the observed $g_D(t)$ following this form until $t\approx2000\tau$ would require $V\approx10^3k_BT$ (≈10 eV), which clearly is out of the question.

Thus the decay of $g_D(t)$ as $1/\sqrt{(1+t)}$, rather than as a simple exponential, appears to be conclusive evidence that the In is not coupled appreciably to the argument Φ of the electron-density modulation. The alternative is that it couples to the strain $Q^{-1}\nabla\phi$.

C. Coupling to $\nabla\phi$

As already noted, intercalated atoms couple to $\nabla\phi$ as a consequence of their contributing electrons to the conduction band. It will be assumed that $\nabla\phi$ varies on a macroscopic scale, on which electrical neutrality is preserved. A continuum approximation then applies, in which the effects of individual atoms may be ignored.

Consider an ideal quasi-one-dimensional band, in which conduction electrons of density ρ_0 support a CDW having wave vector $Q_0=2k_F$, where the Fermi wave vector k_F is parallel to the chain axis z. Now suppose that In atoms in concentration C each contribute one electron to the band; if C has the uniform value C_0, the added electrons increase the equilibrium wave vector to $Q_1=Q_0(1+C_0/\rho_0)$. In the present experiments Q_1 is assumed to remain incommensurate, as for the CDW of interest Q_0 is about 3% less than the commensurate value, and C_0 is though not to exceed 0.01 ρ_0.

When $C=C_0$, a wave vector $Q\neq Q_1$ corresponds to longitudinal strain $e_{zz}=Q/Q_1-1$ in the CDW, and is associated with elastic energy $\frac{1}{2}K_{zz}e_{zz}^2$, where K_{zz} is the longitudinal elastic modulus of the CDW. The elastic energy vanishes, however, if $C=C_0+(\rho_0+C_0)e_{zz}$ as Q is then the equilibrium wave vector. This possibility of energy reduction enables the In atoms to couple to $e_{zz}=\nabla_z\phi/Q_1$, favoring an increase in C where e_{zz} is positive. The departure of C from uniformity is conveniently expressed by $e_C=(C-C_0)/(\rho_0+C_0)$, which is the strain whose elastic energy vanishes when the concentration of In is C.

The value of e_C in thermal equilibrium with a given e_{zz} at temperature T is now required. When $C\neq C_0$, the elastic energy density associated with e_{zz} is

$$W_{zz}=\tfrac{1}{2}K_{zz}[e_{zz}-e_C]^2. \tag{5}$$

As the addition of an In atom to any given volume increases its elastic energy by an amount $\delta W=dW_{zz}/dC$, the condition for thermal equilibrium is

$$C=C_0\exp(-\beta\delta W)=C_0\exp[(\beta K_{zz}/\rho_0)(e_{zz}-e_C)], \tag{6}$$

where $\beta=1/k_BT$, and it is assumed that $C_0\ll\rho_0$. From this, and in the high-temperature case $\beta|\delta W|\ll1$, the value of e_C in thermal equilibrium is

$$e_{Ce}=\frac{b}{1+b}\,e_{zz}, \tag{7}$$

where $b=\beta K_{zz}C_0/(\rho_0)^2$. The contribution of e_{zz} to the free-energy density is then

$$\Delta F=W_{zz}+\beta^{-1}\frac{(C-C_0)^2}{2C_0}=\tfrac{1}{2}Ke_{zz}^2\frac{1}{1+b}, \tag{8}$$

so that in thermal equilibrium the CDW behaves as though its elastic modulus were $K_{zz}/(1+b)$.

The values of $\beta|\delta W|$ and b in the present experiments will first be estimated using a mean-field model.[26] In that approximation, the high-temperature assumption $\beta|\delta W|\ll1$ appears to be valid: when $T\approx0.8T_P$, as in the experiments, the elastic limit on macroscopic strain restricts $|\delta W|$ (which cannot exceed the energy gap Δ) to about $0.1\Delta_0$, where $\Delta_0=1.76k_BT_P$, so that $\beta|\delta W|<0.2$. This, as

$|e_{Ce}|<\beta|\delta W|C_0/\rho_0$, implies that C nowhere departs from C_0 by more than 20%. The parameter b, which is a convenient measure of the coupling between the CDW and In, is also small even in the specimens containing the most In: if one takes for K_{zz} the mean-field value $2\rho_0\varepsilon_P(\Delta/\Delta_0)^2$ (about 60 J cm^{-3} with $\Delta=0.7\Delta_0$, $\rho_0=2\times10^{21}$ cm^{-3}, and Fermi energy $\varepsilon_F=0.2$ eV, corresponding to the free-electron mass), then $b\approx0.2$ when $C_0/\rho_0=0.01$.

However, these estimates require revision in view of the experimental evidence that K_{zz} (Ref. 27) and Δ_0,[28] respectively, are about 2.5 and 5 times their mean-field values. This leads one to expect $\beta|\delta W|\approx1$ when the strain approaches its limiting value (if that is unchanged) and $b\approx0.5$ in the most heavily doped specimens. Even when $\beta|\delta W|=1$, however, expression (7) is not seriously in error: e_{Ce} is given within $\pm15\%$ for any b if $|e_{zz}|\leqslant0.01$ and $C_0/\rho_0=0.01$. The effects of coupling between the In and the various strains expected in CDW's are examined next.

IV. STRAINS IN CDW'S AND THEIR COUPLING TO MOBILE IMPURITIES: EXPECTATIONS AND EXPERIMENT

A. Conditions for the observed threshold behavior

Only in certain circumstances can the redistribution of mobile impurities in response to CDW strain lead to threshold behavior of the kind observed. The redistribution may contribute to E_T in two distinct ways.

(1) As the minimization of free energy effectively reduces K_{zz}, it enhances any FLR weak pinning by fixed impurities, for which E_T depends inversely on K_{zz}.

(2) The impurities also pin the strain pattern in which the free energy was minimized. This contributes to E_T only if the motion requires that pattern to be translated, or otherwise modified, so as to raise the energy above its value with the CDW at rest.

If the resulting contributions δE_T to E_T are to behave in the manner observed, the strain in the CDW has to satisfy two further conditions.

(a) As (c) in Sec. II F implies, the moving CDW must repeatedly surmount the energy barrier which determines δE_T. In the case of enhanced FLR pinning (1), repetition is ensured by the spatial periodicity of the coupling of fixed impurities to Φ in the moving CDW. For δE_T to arise from the pinning of a strain pattern by mobile impurities, as in (2), the pattern itself must repeat spatially, as well as moving when the CDW is in motion.

(b) Both in (1) and (2), in order that continued motion of the CDW eventually reduces δE_T by allowing the mobile impurities to disperse, the effective strain pattern in which the impurities diffuse must be averaged by the motion.

The principal strains expected in CDWs are (i) the random strains associated with FLR pinning to fixed impurities; (ii) the longitudinal strain due to the obstructing effect of current terminals, by which phase-slip there is induced; (iii) longitudinal and shear strains due to irregularities in the shape and structure of the crystal; (iv) strains associated with discommensurations; and (v) strains due to dislocations in the CDW. The extent to which these satisfy the requirements just outlined is now considered.

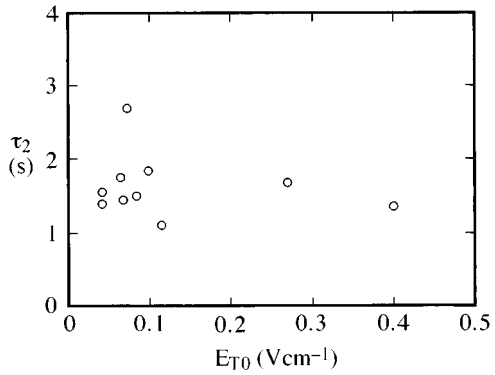

FIG. 11. A comparison between E_{T0} and the characteristic time τ_2 obtained from $g_A(t)$, measured at $T\approx113$ K from the ten specimens in Table I from batches II and III.

B. Strains associated with FLR pinning

In a moving CDW in the FLR model, once the unique configuration discussed by Middleton[9] has been established, the pattern of strain is stationary on scales much larger than Q^{-1}. As a stationary pattern does not satisfy condition (a), there is no contribution of type (2) to E_T from the pinning of the FLR strain pattern by mobile impurities.

A contribution of type (1) is possible from FLR weak pinning, however, as condition (a) is satisfied and E_T varies as $K_{zz}^{(1-d)/2}$, where d is the dimensionality.[4] The reduction of K_{zz} by the mobile impurities in equilibrium increases E_T by a factor $(1+b)^{(d-1)/2}$; if $b=1$, as seems possible in the specimens containing the most In, this would account for $\Gamma=0.7$ or 1, according to whether $d=2$ or 3, which is of the order observed in such specimens.

However, while the magnitude of δE_T can be accounted for, its suppression by motion of the CDW cannot, for the stationary strain pattern does not satisfy condition (b). Although δE_T may be modified by motion, as the strain in the moving CDW need not be the same as when it is at rest, there is no reason to expect it to vanish, nor even necessarily to decrease.

Confirmation that δE_T does not arise from an enhancement of FLR weak pinning is provided by the characteristic times τ_2 which describe its relaxation. As it is determined by diffusion, τ_2 is expected to be proportional to ζ^2, where ζ is a length characteristic of the strain distribution. For weak pinning ζ will be the Lee-Rice phase correlation length L_ϕ, and as E_T is proportional to L_ϕ^{-2}, τ_2 should vary inversely with E_T (with some dependence on dimensionality).

In Fig. 11, τ_2 and E_T are compared for ten specimens, from batches II and III. The wide range of E_T, roughly a factor 10, is the result of differences in thickness d. The values of τ_2 show some scatter, attributed to dependence on Γ and the conditions of measurement [to reduce the effect of this, the τ_2 are taken from $g_A(t)$ rather than $g_D(t)$]. No cor-

relation is evident, τ_2 being essentially independent of E_T. Similar τ_2 were measured in specimens from batch I.

It is clear from this that δE_T is not the result of coupling between the In atoms and strains involved in FLR pinning. However, if b is as large as supposed, and the pinning is weak, the addition of In should result in a significant increase in E_T, which motion of the CDW would not remove. That no increase has been apparent is probably a consequence of the very long times required for diffusion over lengths L_ϕ of several μm, which amount to many hours at 135 K and to weeks at 115 K, if the diffusivity is as estimated in Sec. V A.

C. Macroscopic strains associated with obstacles to motion

Except where phase continuity is broken, in which case the strain field is modified by dislocations [(v) in Sec. IV A], a stationary distribution of strain develops in the moving CDW as a result of such obstacles to motion as current terminals, and irregularities in the shape or content of the specimen, respectively, (ii) and (iii) in Sec. IV A. As neither (a) nor (b) in Sec. IV A is satisfied, the redistribution of impurities in response to this strain does not contribute to δE_T.

D. Discommensurations

Discommensurations (DC's) appear when the lattice potential, favoring a commensurate value Q_C, prevents the CDW wave vector from adopting its preferred incommensurate value Q. A mean value Q_M between Q and Q_C may then be achieved by the alternation of commensurate regions, and DC's in which Φ changes relative to $Q_C z$ by $2\pi/p$, which corresponds to the lattice spacing, where p is an integer (and would be 4 in $NbSe_3$). Relative to Q_C, strain in the CDW is concentrated around parallel planes, normal to **Q**, with spacing $\ell = (2\pi/p)/|Q_M - Q_C|$.

This strain pattern, whose translation through $p\ell$ advances the CDW through its wavelength $\lambda = 2\pi/Q_M$, satisfies conditions (a) and (b) in Sec. IV A. Its coupling to mobile impurities, as in (2), should therefore provide a contribution δE_T to the threshold field exhibiting accumulation and dispersion phenomena qualitatively as observed. Although no evidence of DC's has been found in $NbSe_3$, it is of importance to enquire whether their pinning by In might account for the behavior of δE_T, and notably for the decay of $g_D(t)$ as $1/\sqrt{(1+t)}$.

The form of $g_D(t)$ expected from the pinning of an array of DC's depends on the distribution of In in equilibrium, which is available from e_{Ce} and is related to the strain e_{zz} through expression (7). The avoidance of an exponential form for $g_D(t)$ requires the width w of the DC's to be small compared with their separation ℓ, so that e_{zz} does not approximate to a sinusoid. It is not difficult to show, in a continuum approximation,[29] that when $w \ll \ell$ the two quantities are related through

$$(\delta - \delta_C)/\delta_C \sim 4(1 + 2\ell/w)\exp(-2\ell/w), \tag{9}$$

where $\delta = |Q - Q_C|$, and δ_C is its critical value for ''lock in,'' below which $Q_M \equiv Q_C$. Relative to the preferred wave vector Q, the strain in a DC centered at $z=0$ is then expressed by $e_{zz} = Q_C/Q - 1 + 2\sqrt{(V_C/p)}\,\mathrm{sech}\{z\sqrt{(pV_C)}\}/Q$, where V_C specifies the strength of the lattice potential relative to K_{zz}. From this, the width of the DC is defined as $w = 2/\sqrt{(pV_C)}$.

The e_{Ce} expressing the distribution of In in equilibrium with the DC array is concentrated in layers normal to z and roughly of thickness w. If at time $t=0$ the array is set in motion, so that the average strain at any point approaches zero, diffusion (effectively in one dimension) causes $e_C(z)$ in each layer to approach a Gaussian form in a time $\tau \approx w^2/16D$. Thereafter the central value of e_C declines as $1/\sqrt{(1+t/\tau)}$, where D is the diffusivity, until t/τ approaches $(\ell/w)^2$, after which the decay is approximately exponential.

While it is tempting to suppose that this might explain the decay of $g_D(t)$ as $1/\sqrt{(1+t/\tau)}$, that is not so: when t/τ is large the pinning effect of $e_C(z)$, and thus δE_T, is proportional to the maximum value of $\partial e_C/\partial z$, rather than of e_C. As the width of the Gaussian $e_C(z)$ increases as $\sqrt{(1+t/\tau)}$, $g_D(t)$ then decays approximately as $1/(1+t/\tau)$, which differs significantly from the experimental data in Fig. 5(a).

Even if δE_T were proportional to the maximum of e_C, its relaxation as $1/\sqrt{(1+t/\tau)}$ could hardly continue until $t/\tau > 2000$, as has been observed for $g_D(t)$. According to expression (9), the value (≈ 45) required for ℓ/w would imply that $|\delta - \delta_C|/\delta_C < 10^{-36}$. Although the ''lock-in'' transition of real DC's tends to be less sudden than expression (9) suggests, it is clear that the required ℓ/w could occur only over an extremely narrow temperature range preceding lock-in. However, the relaxation as $1/\sqrt{(1+t/\tau)}$ is seen throughout the range 90–130 K, in which Q varies slowly with no sign of locking to any Q_C.[30] Moreover, if ℓ were as large as $45w$, DC's would surely have been detected in NMR studies.[31] Their failure to appear indicates that $\ell < 1.5w$, corresponding to a near-sinusoidal strain profile, and relaxation close to a simple exponential.

E. Dislocations

Dislocations in CDW's (which, unlike discommensurations, are topological defects) have been discussed at length by Feinberg and Friedel.[8] Here the concern is with edge dislocations, as only these involve longitudinal strain capable of coupling to mobile impurities. Such a dislocation is illustrated later, in Fig. 12(a): the amplitude of the CDW vanishes along the line of the dislocation (there the x axis), and is reduced within a region whose radius along y (normal to **Q**) is the appropriate amplitude coherence length, but along z (parallel to **Q**) is likely to be larger, as the ability of the CDW to sustain longitudinal strain is limited. Except within the ''core'' where it is modified by the collapse in amplitude, the strain field is expressed by

$$\begin{aligned} e_{zz} &= Q^{-1}(\eta y)/[(\eta y)^2 + z^2], \\ e_{yz} &= Q^{-1}(\eta z)/[(\eta y)^2 + z^2], \end{aligned} \tag{10}$$

where e_{zz} and e_{yz} are longitudinal and transverse (shear) strains, with respective elastic moduli K_{zz} and K_{yz}, and $\eta = (K_{zz}/K_{yz})^{1/2}$. The elastic energy per unit length of the dislocation, ignoring the small contribution from the core, is

$$U_0 = \pi Q^{-2}(K_{zz}K_{yz})^{1/2}\ln(R/r_{\mathrm{core}}), \tag{11}$$

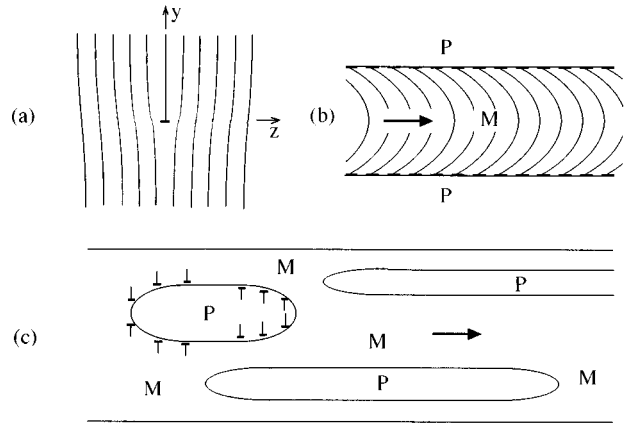

FIG. 12. (a) A CDW dislocation (⊥). The lines represent surfaces of constant phase Φ, at intervals of 2π. (b) Arrays of dislocations at the boundaries between moving (M) and pinned (P) regions of CDW. Shear inducing the dislocations to glide, and associated with curvature of the surfaces of constant phase in M, is indicated. (c) Pinned regions (P) embedded within a multiply connected moving CDW (M). The generation of dislocation loops at the ends of a region P, and their subsequent motion over its surface, is illustrated. Longitudinal strains in P and M determine whether (as shown) opposite loops appear at the two ends of P, and annihilate between them, or loops of a single sign appear at one end and collapse at the other.

where the strain field extends over a range R, and $r_{\rm core}$ is the effective radius of the core.

Although a single dislocation does not provide the spatially repetitive strain pattern needed to satisfy condition (a) of Sec. IV A, an array of parallel dislocations can satisfy both conditions (a) and (b). Provided that motion of the CDW involves motion of the array, their pinning by mobile impurities then gives rise, through (2), to δE_T exhibiting accumulation and dispersion phenomena. The time dependence of δE_T will first be examined in the simple case where motion of the CDW requires the dislocations to move on the surface in which the array lies. The dislocations then pass exactly through the sites occupied when at rest, and δE_T is proportional to the maximum force exerted on them by pinning accumulating in, or dispersing from equilibrium with, the strain fields of dislocations in those positions. The resulting $g_D(t)$ and $g_A(t)$ will first be found for $b \ll 1$, assuming the dislocations to move (''glide'') parallel to the chain axis z. The pinning of dislocation arrays in other situations will be discussed in Sec. V.

The pinning arises because the impurities lower the elastic energy of the dislocation, by an amount which decreases as its center is displaced from the position in which the impurities accumulated. To detach the dislocation of Fig. 12(a) from the pinning, the threshold force to be exerted per unit length is

$$F_T = \max\{\partial U(z_1)/\partial z_1\}, \tag{12}$$

where $U(z_1)$ is the elastic energy per unit length when the dislocation is centered at $(0,z_1)$, and the maximum is taken with respect to z_1. Because $b \ll 1$, $\partial U(0,z_1)/\partial z_1$ can be obtained by appropriate integration of the term $-K_{zz}e_{zz}e_C$ in W_{zz} (5), with e_{zz} given by (10); this ignores terms of the order of b^2, which arise because e_{zz} and e_{yz} are modified by the effective reduction in K_{zz} evident in (8).

The core of the dislocation, where expressions (10) do not apply, and at whose center W_{zz} vanishes, must be omitted from the integration. An empirical allowance for the omission is made by multiplying K_{zz} by a ''core'' function $M(y,z)$, such that $M=0$ at the center, and $M=1$ far outside the core.

The accumulation and dispersion of the pinning are the result of the diffusion of impurities in the effective potential $\mathscr{V}(y,z)$ exerted by the dislocation. When the latter is stationary, $\mathscr{V}(y,z)=\delta W \approx -(K_{zz}/\rho_0)M(y,z)e_{zz}(y,z)$; for the moving dislocation it is assumed that $\mathscr{V}=0$. After a change in $\mathscr{V}$, a diffusion equation $\partial C/\partial t = \boldsymbol{\nabla}\cdot[D\{\boldsymbol{\nabla}C+\beta C\boldsymbol{\nabla}\mathscr{V}\}]$, where D is the diffusivity tensor, governs the adjustment of impurity concentration C. When $|\beta\mathscr{V}| \ll 1$ (which, according to Sec. III C, seems to apply even near the core of the dislocation), and taking y and z to be principal axes of D, this can be linearized to

$$\partial(e_C - e_{Ce})/\partial t = (D_y\partial^2/\partial y^2 + D_z\partial^2/\partial z^2)(e_C - e_{Ce}), \tag{13}$$

where $e_{Ce} \approx -(C_0/\rho_0)\beta\mathscr{V}$ is the value of e_C in equilibrium with $\mathscr{V}$. When a stationary dislocation centered at the origin provides $\mathscr{V}$, and $b \ll 1$, $e_{Ce} = bMe_{zz}$, with e_{zz} given by (10); this will be denoted e_{C0}.

During dispersion, following $\mathscr{V}$ becoming zero at time $t=0$, the decay of e_C from e_{C0} towards e_{Ce} (now zero) is expressed by

$$e_C(y,z,t) = e_{C0}(y,z) \otimes S_y(y,t) \otimes S_z(z,t), \tag{14}$$

where the symbol $\otimes$ denotes convolution, and $S_k(k,t) = \exp(-k^2/4D_k t)/\sqrt{(4\pi D_k t)}$ expresses the spread, due to diffusivity D_k along an axis k $(=y,z)$, of a distribution initially localized at $k=0$. Expression (12) then becomes

$$F_T(t) = K_{zz} \max\left\{ \iint [-e_C(y,z,t)\partial\{M(y,z)e_{zz}(y,z)\}/\partial z_1] \times dydz \right\}, \tag{15}$$

where M and e_{zz} refer to the dislocation centered at $(0,z_1)$, and the maximum is taken with respect to z_1.

The core function M, by introducing a characteristic length $r_{\rm core}$ into the problem, sets both the initial magnitude of F_T, and the time scale of its decay. If $r_{\rm core}$ were zero, so that $M \equiv 1$, then (15) could be written

$$F_T(t) = \frac{bK_{zz}}{\pi Q^2} \frac{1}{\sqrt{(\eta^3 Dt)}} I_{\max}, \tag{16}$$

where $D = \sqrt{(D_y D_z)}$, and $I_{\max}$ is the maximum, with respect to z_1, of

$$\int\int\int\int \frac{y'}{y'^2 + (z'+z_1)^2} \frac{yz}{(y^2+z^2)^2} \times e^{-[(1/A)(y-y')^2 + A(z-z')^2]} dy'dz'dydz, \tag{17}$$

where $A=\eta\sqrt{(D_y/D_z)}$. $I_{\max}$ is roughly $2.5/\sqrt{A}$ when $A\gg 1$, and $5.4\sqrt{A}$ when $A\ll 1$.

The effect of r_{core} being nonzero is, approximately, to replace t in expression (16) by $t+\tau_c$, where $\tau_c = r^2_{\text{core}(k)}/4D_k$, that being the time in which the width of S_k would approach the core radius $r_{\text{core}(k)}$, measured in the direction k in which such an approach first occurs. Then

$$F_T(0)=\varepsilon(0)\,\frac{2bK_{zz}}{\pi Q^2 r_{\text{core}(k)}}\,\kappa, \tag{18}$$

where $\kappa\approx 2.5/\eta^2$ or $5.4/\eta$, according to whether $D_k=D_y$ or D_z, and

$$F_T(t)=\frac{\varepsilon(t)}{\varepsilon(0)}\,F_T(0)\,\frac{1}{\left(1+\dfrac{t}{\tau_c}\right)^{1/2}}, \tag{19}$$

where $\varepsilon(t)$ expresses the departure from variation as $1/\sqrt{(1+t/\tau_c)}$, and depends on the structure of the core function M, rather than its scale which determines τ_c. As $\varepsilon(t)=1$ once diffusion has eliminated the variation of e_C on the scale of r_{core}, and otherwise is never far from 1 for any reasonable choice of M,[32] the decay of $F_T(t)$ during dispersion is for practical purposes as $1/\sqrt{(1+t/\tau_c)}$. An analogous derivation (in which inclusion of the core removes a weak divergence in the integral corresponding to $I_{\max}$, as well as the singularity in $1/\sqrt{t}$), leads to the same form for the pinning force opposing dislocation motion (''climb'') in the y direction.

It is easy to see that, for F_T to become proportional to $1/\sqrt{t}$ when $t\gg\tau_c$, one requires e_{zz} to vary as $1/r$ when r is large. As dislocations are the only plausible source of strain varying in that manner, the decay of F_T as $1/\sqrt{(1+t/\tau_c)}$ appears to be characteristic of their pinning by mobile impurities.

The relaxation as $1/\sqrt{(1+t/\tau_c)}$ is, however, restricted to the case where the dispersion proceeds to completion. The distribution e_C then broadens indefinitely as t increases, and the integral in (15) is maximum for a steadily increasing value of z_1. If the dispersion remains incomplete, then that value becomes independent of t as e_C approaches its asymptote $e_{Ce}\neq 0$, and $F_T(t)$ approaches its equilibrium value as $1/t$, rather than as $1/\sqrt{t}$. In the limit when e_{Ce} is close to e_{C0}, the computed relaxation has τ_2 about 0.44 of the value for $e_{Ce}=0$, and $s\approx 2.8$. These values also apply to relaxation in the opposite sense, i.e., accumulation toward e_{C0} from an initial $e_C\approx e_{C0}$. Accumulation from the completely dispersed state is only slightly different. The growth of e_C from zero toward e_{C0} is expressed by

$$e_C(y,z,t)=e_{C0}(y,z)-e_{C0}(y,z)\otimes S_y(y,t)\otimes S_z(z,t), \tag{20}$$

whose final term decays in the same way as e_C during dispersion proceeding to completion. Again, e_{C0} sets the appropriate z_1 in (15) when t is large, and $F_T(t)$ approaches its final value as $1/t$. The computed τ_2 is about 0.62 of that for dispersion with $e_{Ce}=0$, with $s\approx 3.0$. The predicted form of $g_A(t)$ in this case is shown by the broken line in Fig. 5(b).

In the absence of any plausible alternative, it is concluded that the decay of the dispersion transient $g_D(t)$ as $1/\sqrt{(1+t/\tau)}$, observed when Γ is small, follows that of the pinning force F_T arising from the coupling of In to the strain fields of dislocations in the CDW. Whether $g_A(t)$ follows the growth of F_T as pinning accumulates is less clear: relative to $g_D(t)$, both τ_2 and $\tau_4=(s+1)\tau_2$ are roughly as predicted, but the later stages of the decay of $g_A(t)$ are not as $1/t$, though the discrepancy may perhaps be a result of broadband noise. With Γ large, however, neither transient is at all close to the form predicted, whether or not allowance is made for the dispersion being incomplete. While not implying that δE_T arises other than from the pinning of dislocations, this shows that a more elaborate model will be required to account fully for the experimental results.

V. MODELS

Several factors in addition to the form of the pinning force $F_T(t)$ have to be considered if the effect of In on the threshold behavior is to be modeled by the pinning of arrays of CDW dislocations. So that F_T may contribute to the threshold field, the dislocations must be so arranged that motion of the CDW requires them to escape from the pinning. Although the evidence in Sec. II H that part of the CDW remains at rest suggests a possible arrangement, it has to be confirmed that the pinning is capable of accounting for the magnitude of δE_T, and for the characteristic time of its variation as the pinning accumulates or disperses. The dispersion of pinning by finite I_P, and especially the use of pulsed I_O to monitor the changes in δE_T during accumulation, also require examination. These matters are considered below. Although no unique model is developed, certain essentials of the CDW motion are identified, in reaching a picture of CDW motion which is at least qualitatively consistent with experiment.

A. Origin and magnitude of δE_T, and time scale of its variation

Consider, as in Sec. IV E, an array of parallel dislocations which move, by gliding parallel to the chain axis z, over the surface in which the array lies. That surface separates regions a and b in which the z component of the CDW wave vector takes the slightly different values Q_a and Q_b. The spacing of the dislocations is then $2\pi/(Q_a-Q_b)$, and if the velocity of the CDW in the two regions is v_a and v_b, the dislocations move with respect to the lattice with velocity $(Q_a v_a - Q_b v_b)/(Q_a-Q_b)$. Pinning which prevents the dislocations from moving with respect to the lattice equalizes the phase winding rates $Q_a v_a$ and $Q_b v_b$, without necessarily requiring v_a and v_b to be zero.

The effect of such pinning on the threshold behavior depends on the circumstances. If the dislocations were fixed in the CDW, so that $v_a=v_b$, then pinning them to the lattice would be equivalent to pinning the CDW, giving $v_a=v_b=0$, and F_T would contribute directly to δE_T. However, that possibility may be discounted, for the shear stress needed to induce dislocations to glide through the CDW, unless opposed by pinning, is expected to be very small.[8] If a difference in E_T causes v_a and v_b to differ slightly, then pinning the dislocations, no matter how strongly, merely causes E_T to exceed its average value by the small amount required to induce glide. If, however, region b is already so heavily pinned as to be immovable, so that $v_b=0$, the observed E_T is that for region a, whose motion relative to b requires the

dislocations to escape from the pinning. The force F_T, now a Peach-Koehler force provided by a threshold shear stress $\sigma_T = F_T/\lambda$, then contributes to δE_T and increases indefinitely as the dislocations become more firmly pinned. Unless glide is much more difficult than has been supposed, such immobile regions are essential if the pinning of dislocations is to contribute substantially to E_T.

It is reasonable to conclude that these immobile regions make up that part of the CDW which, in the experiments of Sec. II H, was found to remain at rest while the CDW elsewhere moved coherently. The increase detected in the volume remaining at rest, as pinning accumulates, then corresponds to an increase in the size (or possibly the number) of immobile regions. The manifestations of this in the threshold behavior will be discussed in Sec. V E. Of more immediate interest is whether the pinning of dislocations at the boundaries of the immobile regions can account for the magnitude of δE_T.

An estimate of δE_T can be made by assigning plausible values to the relevant parameters. The anisotropy η is expected to be large: recent x-ray measurements of L_ϕ in $NbSe_3$ (Ref. 5) suggest that $\eta \approx 12$ when y and z correspond to the crystallographic directions c^* and b^*. With no obvious structural reason for the diffusivity D to be very anisotropic, A is assumed similar to η; the elongation of the dislocation strain field along z then ensures that diffusion is effectively in the y direction. From (18), the critical shear stress is then $\sigma_T \approx 2.5 K_{zz} b/(\pi^2 Q \eta^2 r_{\mathrm{core}(y)})$.

Consider now the situation illustrated in Fig. 12(b): a layer M of thickness L_y in which the applied field induces the CDW to move, is bounded on surfaces parallel to z by layers P in which it remains pinned. A lower limit on L_y is set by the phase correlation length L_ϕ, perhaps of the order of 1 μm in the transverse direction. To provide the critical shear stress at its boundaries, a field $\delta E_T = (\sigma_T/e\rho_0)S$ has to be applied to the layer M, where S (here $2/L_y$) is the surface area of P, per unit volume of M. Taking $K_{zz}(115\ \mathrm{K}) = 150\ \mathrm{J\,cm^{-3}}$, $Q = 4.5\times10^7\ \mathrm{cm^{-1}}$, $\eta = 12$, $r_{\mathrm{core}(y)} = 30$ Å (see below), $\rho_0 = 2\times10^{21}\ \mathrm{cm^{-3}}$, $L_y = 1$ μm, and $b = 0.5$ (the estimated maximum in the experiments), one obtains $\delta E_T \approx 600\ \mathrm{mV\,cm^{-1}}$. As this exceeds the largest value observed, it is clear that the pinning of CDW dislocations is fully capable of accounting for the magnitude of δE_T.

A more adaptable alternative to the planar geometry of Fig. 12(b) is for immobile regions P, elongated along z, to be embedded in a multiply connected moving region M, as in Fig. 12(c). As phase coherence may extend throughout M, the spacing L_P of the regions P transverse to z, if they occupy a small part of the volume, need not limit L_ϕ. For regions P having a circular cross section of radius r_P, a value $S = 2\times10^4\ \mathrm{cm^{-1}}$, sufficient to account for the observed δE_T (giving 600 mV cm^{-1} when $b = 0.5$), can be achieved, for example, with $r_P = 0.01$ μm, $L_P \approx 0.1$ μm, or with $r_P = 0.1$ μm, $L_P \approx 0.4$ μm (which would be consistent with the observation in Sec. II H that up to 25% of the cross section of the CDW was at rest).

The pinning of dislocations is consistent also with the time scale of the changes in δE_T. In the case of $g_D(t)$ when $\Gamma \ll 1$, and if $A \gg 1$, the time τ characterizing the decay as $1/\sqrt{(1+t/\tau)}$ may be identified with $\tau_c = r^2_{\mathrm{core}(y)}/4D_y$. The value of $r_{\mathrm{core}(y)}$ is likely to be close to $r_{\mathrm{core}(z)}/\eta$, and perhaps a few times greater than the lower limit set by the chain spacing. If one takes $r_{\mathrm{core}(y)}$ to be 30 Å, then the observed $\tau \approx 10^{-12} \exp(3200\ \mathrm{K/T})$ s corresponds to $D_y \approx 0.02 \exp(-3200\ \mathrm{K/T})\ \mathrm{cm^2\,s^{-1}}$. As both the prefactor and exponent are quite representative of the diffusion of In in transition element chalcogenides,[11] the conjecture that τ is set by a length scale of the order of 30 Å appears to be justified. Such a scale could hardly arise except as the transverse dimension of a dislocation core.

B. Possibility of complete dispersion

While a stationary dislocation array clearly will accumulate pinning, it is less obvious that this can be dispersed completely by motion of the array, as was assumed in deriving the form of $g_D(t)$ in Sec. IV. The following argument suggests that dispersion will become complete if the velocity of the CDW exceeds a critical value, dependent on the strength of the pinning.

Suppose that, in Fig. 12(b), the CDW in layer M moves in the z direction with average velocity v, and that the dislocations are detached from their pinning sites when the shear strain e_{yz} reaches a critical value e_T. During the ensuing glide, e_{yz} relaxes toward zero until the CDW next to the boundary has advanced through a wavelength λ, when the array again becomes pinned. For simplicity, assume that during the relaxation e_{yz} decays exponentially, with characteristic time τ_d. As the mean displacement of the CDW in M, relative to its edges, is $e_{yz}L_y/6$, the time t_g taken to glide from one pinning site to the next satisfies

$$\lambda = v t_g + (e_T L_y/6)\cdot(t_g/\tau_d) \tag{21}$$

where $e_T L_y/6$ is assumed much larger than λ, so that $t_g \ll \tau_d$. If e_T in the steady state is proportional to the fraction of the time for which the dislocations are pinned, namely $1 - v t_g/\lambda$, then

$$e_T = e_{T0}[1 - v/v_c], \tag{22}$$

where e_{T0} is the value of e_T in equilibrium when $v = 0$, and $v_c = L_y e_{T0}/6\tau_d$ is a critical velocity at which dispersion becomes complete. It appears that in the experiments, a nearly continuous current I_P a few times greater than I_T was sufficient to ensure that $v > v_c$ when Γ was small.

C. Effect of the observing pulse I_O

In the experiments, the changes in δE_T were monitored using the repetitive short ''observing'' pulses I_O. While these have a negligible effect on dispersion, they may be expected to influence δE_T during accumulation. The immediate effect of I_O is to induce dispersion for the duration t_P of the pulse, so that accumulation does not proceed to completion; however, this reduces δE_T only by a fraction t_P/t_r, easily arranged to be negligible. A more serious problem is that, as each pulse of I_O displaces the CDW along z by a distance of the order of 10^3 wavelengths, it is not obvious that, when the CDW comes to rest after I_O ceases, accumulation can be resumed with the same sites occupied by dislocations. It is clear, however, that the sites occupied after

successive pulses are correlated to some extent, for otherwise the I_O pulses would lead to complete dispersion, with pinning distributed uniformly.

The extent to which I_O inhibits accumulation has been investigated experimentally by interrupting the sequence of pulses, and varying their repetition period, during the accumulation process. In specimen No. 3 ($\Gamma=0.07$), the steady δE_T reached with pulses having $t_P \ll t_r \ll \tau_2$ present continuously was increased by about 10% when they were interrupted for an interval much greater than τ_2, allowing pinning to accumulate with the CDW at rest. That δE_T is reduced only slightly by the pulses shows that, after each application of I_O, the sites occupied by dislocations are almost unchanged. While the tendency of repeated pulses to translate the CDW through an integral number of wavelengths[33] may be partly responsible, the main reason for the sites being reoccupied is probably that, after I_O ceases, the relaxation of shear strain [such as is illustrated in Fig. 12(b)] allows glide to continue until the dislocations are captured by the pinning previously accumulated with the CDW at rest. However, exact repetition of the previous configuration requires that the remaining shear stress, which displaces the dislocations with respect to the pinning already present, relaxes completely before appreciable diffusion has occurred. Incomplete relaxation of the stress, leading in the steady state to a distribution of pinning somewhat broader than if the CDW were always at rest, is a likely cause of the reduction of δE_T when I_O is applied repeatedly.

Since the width of the distribution governs the time for its accumulation and dispersion by diffusion, its broadening by I_O is expected to lead to a minor increase in τ_2 for $g_A(t)$ and $g_D(t)$, by an amount of the same order as that in δE_T. The broadening probably accounts also for the tendency, noted in Sec. II H, for mode locking to be enhanced as extra pinning accumulates. As perfect mode locking causes the configuration of the CDW to repeat exactly at the frequency v, even partial locking reduces the broadening due to I_O, allowing pinning to accumulate further, exerting a stronger potential and increasing the mode-locking parameter f.

However, the effect of applying repeated pulses of I_O is not limited to broadening and slight dispersion of the distribution of pinning. It has been found that when I_O is applied after being absent for an interval much longer than τ_2, after which accumulation should be nearly complete, the δE_T recorded depends on the value last measured, and can be less than is reached with the pulsed I_O present continuously. An explanation is suggested in Sec. V E.

D. Pinning by impurities in large concentration

Before discussing the effect on δE_T of the expansion of the immobile regions as pinning accumulates, which is expected to be more prominent when the concentration of In (and hence b and Γ) is large, it is useful to outline the predicted behavior in that situation of the pinning force F_T, which applies to dislocations moving in a fixed plane.

The calculation of F_T for large b is straightforward, though tedious. The reduction in effective modulus K_{zz} causes the strain field of the dislocation in Fig. 12(a) to expand in the y direction, in effect replacing η in (10) by $\eta/\sqrt{(1+b)}$, in accordance with (8). The inequality $\beta|\mathscr{W}|\ll 1$ is retained, so that e_{Ce} is now $Me_{zz}b/(1+b)$, from (7), and (13) continues to describe the diffusion. A major complication is that, in order to find $U(z_1)$, the strain field for the dislocation displaced to z_1 in the presence of e_C has to be found numerically. During dispersion e_C is given, as before, by (14). During accumulation, e_C and the strain field evolve as a coupled system, whose development can be followed by alternately obtaining e_{zz} and e_{yz} for given e_C, and advancing e_C, in accordance with (20), toward equilibrium with the strain field then existing.

Computations along these lines have been made for a range of values of b, with $A \gg 1$. As the results bear little resemblance to experiment, only their main features will be described. The increase with b of the pinning force F_T in equilibrium, at first linear, becomes slow when $b \gg 1$, as parts of the dislocation nearest the core escape from the pinning first. As might be expected from the expansion of the strain field in the y direction, the characteristic times τ_2 associated with dispersion and accumulation both increase with b. For dispersion, the increase when $b=1$ is only about 5%, and reaches 50% when $b=10$. For accumulation, the increase is already 50% when $b=1$, making τ_2 roughly the same as for dispersion. In form the transients are little changed: for dispersion the parameter s remains close to 4 for $b<10$, and for accumulation increases from 3 when $b \ll 1$, to 5 when $b=10$.

It is clear from this that the departure, when Γ is large, of $g_D(t)$ and $g_A(t)$ from the forms predicted for $F_T(t)$ in Sec. IV E cannot be attributed to any dependence of $F_T(t)$ on b, especially as b probably did not exceed 1 in any specimen measured. Neither is it likely that the discrepancies arise from inadequacy of the assumptions underlying the calculation of F_T. Failure of the high-temperature assumption $\beta|\delta W| \ll 1$ cannot be responsible, as the $g(t)$ would be affected irrespective of Γ. The implicit assumption that r_{core} is unaffected by the impurities is perhaps questionable, as the reduction of elastic energy might allow the core to contract when b is large, but that would reduce τ_2 with little effect on s, whereas s is reduced while τ_2 is little changed. Ordering of the In when C_0 is large is also a remote possibility, but it is not obvious that ordered regions, in which C is practically constant, would have a noticeable effect on E_T.

From this it is clear that the observed forms of $g_D(t)$ and $g_A(t)$ when Γ is large are not explicable in terms of the accumulation or dispersion of pinning by dislocations moving along a fixed path. The possibility that the large departures from prediction are a result of the variation in size of the immobile regions, apparent in Sec. II H, is next discussed.

E. Variation in size of immobile regions, and its effects on threshold behavior

The observed tendency of the immobile regions in the CDW, such as those denoted P in Fig. 12, to expand as pinning accumulates at the dislocations on their boundaries is to be expected, for two reasons. As the pinning reduces the effective elastic modulus, the attraction between dislocations on opposite sides of P, which favors contraction, becomes less. Also, if P is embedded in the moving region M, as in Fig. 12(c), dislocations are generated at its ends, and trace out its surface through a combination of climb and glide, the relative velocities of which govern the cross-sectional radius

r_P of the immobile region. With resistance to climb likely to be determined largely by the interchain separation, and glide opposed mainly by pinning, the velocity of climb relative to glide, and thus r_P, increases as pinning accumulates.

Figure 9 shows that the extent to which pinning increases the volume of the immobile regions becomes less as the current inducing CDW motion increases. It seems unlikely that the pulsed current used in the measurement disperses the pinning sufficiently to account for this effect, which might alternatively be a result of the velocity of glide increasing more rapidly with current than that of climb. The tendency of r_P to increase with pinning, to an extent that is reduced by current, appears to explain, at least qualitatively, the various departures of the threshold behaviour from that predicted when the path of the dislocations is fixed.

One expects the effects of changes in r_P to be most obvious when Γ is large. In specimen No. 14 ($\Gamma=0.81$), the reduction in the cross section A_M of the moving CDW as pinning accumulates, which is likely to be rather greater than the 25% measured in Sec. II H with $\Gamma=0.52$, provides a ready explanation for the reduced rate of increase of I_C with $E-E_T$, evident in Fig. 2(b). If the velocity of the CDW is assumed to be a function only of E/E_T, the rescaling in Fig. 2(c) indicates that A_M is reduced by about 60%. Although this may be too simple an interpretation, it is clear that the accumulation of pinning renders immobile a substantial part of the CDW in that specimen.

While the effect of this on $g_D(t)$ and $g_A(t)$ cannot yet be calculated, the records in Fig. 3(b) suggest that their forms will be determined more by the change in r_P, and thus in A_M and S (defined in Sec. V A), than by that in the pinning force F_T opposing motion of the dislocations, which itself is modified as their path varies. Large departures from the predictions of Sec. IV are to be expected, though how closely it will prove possible to account for the near-exponential decays of Fig. 6 remains to be seen.

Changes in r_P also provide a simple explanation for the drastic acceleration, as I_P increases, of the decay of $g_D(t)$, which is shown in Fig. 7 and was observed for large Γ. Suppose that I_P becomes large enough either to reduce r_P, so that the dislocations pass within the accumulated pinning, or even to depin the ''immobile'' regions, sweeping the dislocations from the system. When the next observing pulse I_O is applied dislocations, created if necessary by I_O, then follow a path largely free of pinning, and $g_D(t)$ is reduced accordingly. It is to be expected that in the limit of small Γ, when the pinning has negligible effect on r_P, the dislocations encounter pinning already accumulated, and $g_D(t)$ decays purely as a result of diffusion. However, even when $\Gamma=0.07$ (specimen No. 3), the reduction of r_P by I_P appears to be detectable in the slight fall in δE_T at the commencement of dispersion, observed when $I_P>I_O$, and evident in Fig. 4 but omitted from $g_D(t)$.

A further probable symptom of the influence of pinning on r_P is the dependence of δE_T on the value last measured, mentioned in Sec. V C. In specimen No. 3, δE_T reached by undisturbed accumulation from the completely dispersed state was about 10% smaller than when accumulation was initially almost complete. The value ultimately reached by F_T when pinning accumulates at a stationary dislocation can hardly depend its initial distribution, which must influence δE_T through r_P and S. It seems that, although the equilibrium value of S increases as pinning accumulates, the dislocations remain in their original positions until caused to move by I_O or I_P. Dislocations originally in equilibrium when pinning was negligible then retain the initial value of S as pinning accumulates in the absence of I_O, but reach another equilibrium, in which S and δE_T are greater, when I_O is applied repeatedly as accumulation proceeds. As expected, this effect is more pronounced when Γ is large: in specimen No. 14, the value reached by δE_T when sampled repeatedly by I_O was more than 50% greater than when accumulation from a (partly) dispersed state was uninterrupted.

It is clear that in specimen No. 3, the variation in S can have only a small effect on $g(t)$, which are close to the forms of $F_T(t)$ predicted in Sec. IV. It is to be expected, however, that the later stages of the decay of $g_A(t)$ will be rather slower than predicted for $F_T(t)$, as S, and thus the asymptotic value of δE_T, gradually increases as pinning accumulates. During dispersion an opposite tendency is expected, as the decrease in S assists the decay of $g_D(t)$, but the effect on the later stages will be small, as δE_T becomes less sensitive to the path of the dislocations as the distribution of pinning broadens. Whether this accounts for the slight discrepancy between observation and prediction in Fig. 5, where the later stages of the decay of $g_A(t)$ are slower than expected, while $g_D(t)$ accords with prediction, is not yet known. It is concluded that a model in which immobile regions are embedded in the moving CDW, and dislocations at their boundaries are pinned by the coupling of their strain fields to mobile impurities, can account at least qualitatively for the influence of intercalated In on the threshold behavior of $NbSe_3$.

VI. DISCUSSION

The conclusion that substantial regions of the CDW remain pinned in fields many times greater than E_T appears to be widely (and perhaps universally) valid, for the pinning effects of In were observed in every specimen examined. While the experiments do not prove that such regions exist in the absence of In, their presence when the concentration of In is small, and the accumulation of pinning increases their size negligibly, makes it most unlikely that they are merely a product of the intercalation.

While the present results provide ample evidence for the coexistence, even in fields $E\gg E_T$, of moving and pinned regions of CDW in $NbSe_3$, there have been several earlier experimental indications. The clearest are to be found in the observation of Richard, Chen, and Artemenko[23] that, even when the NBN has a single spectral component, I_C/ν increases slowly with E between E_T and $10E_T$; and in the NMR data of Ross, Wang, and Slichter,[31] who concluded that as much as 10% of the CDW did not participate in the motion when $E\approx 25E_T$. The NMR measurements of Butaud *et al.*[34] led to a similar conclusion with respect to the CDW in $Rb_{0.3}MoO_3$.

Both in the present and earlier experiments, however, it is possible that the inhomogeneity in E_T which allows some regions to remain pinned results from some macroscopic imperfection of the crystal. An imperfection in most $NbSe_3$ crystals, which frequently prevents the CDW from depinning

as a whole, is nonuniformity in the thickness d. This leads to nonuniformity in E_T for weak pinning, which depends inversely on d in the common two-dimensional situation $d<L_\phi$.[4] However, thickness variations could hardly account for the wide range of E over which immobile regions persist in the present experiments, or for their presence and variable size in a specimen so perfect as to exhibit complete mode locking. The immobile regions seem not to be associated with the crystal surface, for their effects showed no pronounced dependence on d, over a range exceeding 30:1. The evidence in Sec. II that the bulk E_T is modified shows them not to be associated with terminals, except perhaps as a supply of dislocations. While they might conceivably be associated with other macroscopic defects, it is not clear what those could be: they would have to be present in all the specimens examined, and support immobile regions occupying up to 25% or more of the total volume.

The alternative is that the immobile regions result from the failure of the FLR model to describe the motion of a CDW even over randomly distributed impurities. That the FLR model must fail, at least for a weakly pinned CDW in an infinite crystal, was mentioned in Sec. I: as E approaches E_T, and local depinning occurs over an increasing fraction of the total volume, the maximum stress exerted on the regions remaining pinned increases indefinitely.[6] Ultimately the CDW ceases to behave elastically, and the stress is relieved through processes of phase-slip not included in the FLR model.

Coppersmith and Millis[7] have examined the statistics of this phase-slip at zero temperature. They find that, in three dimensions, continuous motion becomes possible in a connected region of CDW at a threshold identifiable as E_T, but that there are inevitably a few isolated regions, where the pinning is unusually weak, in which motion occurs below E_T, and also more abundant regions of stronger pinning, embedded in the moving CDW, which remain at rest when E is greater than E_T. In these heavily pinned regions, clusters of impurities happen to occupy sites where each reduces the energy of the undistorted CDW. With the pinning then in effect strong, the force required to depin the region may exceed that needed to induce phase-slip at its boundary. Although uncertainty regarding the pinning force and elastic limit of the CDW makes the size of these regions difficult to estimate, it is obvious that, even if each requires only a few impurities in nearby sites, they amount to a very small part of the total volume, since impurities typically occupy fewer than 0.1% of the available sites. Clearly, the strongly pinned regions proposed by Coppersmith and Millis are not the immobile regions, occupying up to 25% of the total volume, detected in the present experiments.

However, the two may not be wholly unrelated. When $T=0$ the elastic limit of the CDW is well defined, and unlikely to be reached except near small strongly pinned regions. Longitudinal stresses below the elastic limit are not expected to lead to continuous phase-slip, for although they may lead to dislocation generation at Frank-Read sources, those tend to be removed by motion of the CDW.[35] The situation is quite different when $T>0$: dislocation loops can then be nucleated thermally[36] wherever the CDW is stressed. Any region pinned more strongly than its surroundings may remain at rest in an applied field insufficient to depin it directly, provided that the surrounding CDW moves slowly enough for the nucleation to provide adequate phase-slip. In practice, although there is no critical stress for phase-slip, the velocities typical of moving CDWs are such that only regions where the pinning is much stronger than usual are likely to remain at rest. Measurements on $NbSe_3$ (Ref. 27) show that at 90 K the strain required to induce typical rates of phase-slip at current terminals is about an order of magnitude greater than the average ($\sim\lambda/2L_\phi$) involved in FLR pinning, though it will be less at higher temperatures. Even at 90 K, where immobile regions are likely to require pinning an order of magnitude stronger than average, such regions may, however, not be unusual: calculations by Abe[37] indicate that the pinning energy density of FLR domains is distributed over two orders of magnitude. It is not altogether surprising, therefore, that substantial parts of the weakly pinned CDW in $NbSe_3$ remain at rest when $E>E_T$.

A further complication is that, while the distribution of pinning strength determines whether immobile regions will occur, the appearance of the dislocation loops may induce changes in that distribution. After nucleation the loops, by a combination of climb and glide, trace out the surface of the immobile region. As the phase of the CDW inside (and in the plane of) a loop differs by $\pi/2$ from that outside, the phase within the region can be adjusted independently of its surroundings by suitably arranging sufficient dislocation loops on its surface.[38] The loops, being free to glide, then effectively decouple the immobile region from the surrounding CDW. As such decoupling tends to strengthen the FLR weak pinning by reducing the effective dimensionality, it seems possible that the dislocation loops, once formed, enhance the pinning which caused their nucleation. Conceivably this enhancement of pinning allows stable immobile regions to extend indefinitely from the original domains at which phase-slip is initiated, increasing both the fraction of the CDW remaining pinned, and the value of E/E_T required for complete depinning.

This picture of weak pinning, in which thermally generated dislocations allow substantial regions of the CDW to remain at rest when the rest is in motion, is consistent not only with the present experimental results. Clearly, it can account qualitatively for the presence of broadband noise, and accompanying frequency modulation of the narrow-band noise: both may be attributed to variation in the number of dislocations moving, and thus in the current carried by the CDW. Its consequences for the dependence of E_T on T, and I_C on E, neither of which is satisfactorily explained by the FLR model, have yet to be explored. As regards E_T, the present picture offers at least a qualitative explanation of its puzzling increase at low temperature. With E_T now marking the onset of motion in a connected region of the CDW, and of thermally induced phase-slip at the boundaries of regions which remain pinned, it would be expected to increase as T falls, for greater stress is then required to generate dislocations at a given rate. Also expected is the observed tendency of E_T to become less well defined at low temperatures. The form of $I_C(E)$, which at low temperatures commonly varies as $\exp[-E_0/(E\sim E_T)]$, where E_0 depends on T, also seems qualitatively explicable, in terms of the dependence of the

rate of phase-slip on stress.[36]

Although differing fundamentally from the FLR model, the present picture of weak pinning retains its length scales L_ϕ. As the immobile regions develop from FLR domains, their cross-sectional dimensions are expected to be similar. In the remaining connected region of CDW's, FLR pinning may operate with only minor modification. The success of the FLR model in accounting for the dependence of E_T on the specimen thickness d, and its consistency with the observed phase correlation lengths, are therefore not incompatible with the present picture. Whether that picture will lead to a useful model of CDW transport remains to be seen.

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