Solid State Communications, Vol. 43, No. 7, pp. 583–586, 1982.
Printed in Great Britain.

0038–1098/82/310583–04$03.00/0
Pergamon Press Ltd.

NONLINEAR CONDUCTIVITY AND NARROW BAND NOISE IN $NbSe_3$

M. Weger

The Racah Institute of Physics, The Hebrew University of Jerusalem, Israel

and

B. Horovitz*

Institute for Theoretical Physics, University of California, Santa Barbara, CA 93106, U.S.A.

(*Received* 26 *October* 1981; *in revised form* 8 *February* 1982 *by A.A. Maradudin*)

A charge density wave system near commensurability and with strong damping is considered, as a model for $NbSe_3$. The observed threshold field is associated with depinning of a commensurate part of the charge density, while the excess charge, in form of phase kinks, contributes just to the ohmic conductivity. The characteristic length associated with the frequency generation is one lattice constant.

NIOBIUM TRISELENIDE, $NbSe_3$, is of considerable interest as a system with Fröhlich conductivity due to sliding charge density waves (CDW) [1]. The conductivity is strongly non-ohmic when the electric field E exceeds a critical value E_c [2], and well defined frequencies appear in a d.c. field [3]. These phenomena are associated with a depinning of the charge density wave; however the depinning mechanism is not yet understood. It has been suggested that the depinning is a result of quantum tunneling [4, 5] or of depinning from impurities [6–10].

We suggest here that the depinning field is an intrinsic effect due to lattice pinning. The CDW wavevectors are [11] $\mathbf{q}_1 = (0, 0.243 \pm 0.005, 0)$ for the transition at $T_1 = 142$ K and $\mathbf{q}_2 = (0.5, 0.263 \pm 0.005, 0.5)$ for the transition at $T_2 = 59$ K. The corresponding band is almost 1/4 filled and the CDW is therefore 4-fold commensurate with the lattice, except for relatively small regions where the excess charge is localized as phase kinks or discommensurations [12–14].

In the absence of impurities phase kinks lead to Fröhlich type conductivity [15, 16]. We assume here that in the presence of impurity or phonon scattering the conductivity of the phase kinks is essentially ohmic and that there is no sharp depinning field associated with their motion. In contrast, parts of the CDW are pinned by the lattice commensurability and their motion requires a field stronger than some well defined depinning field E_c. The distinction between the motion below and above E_c is made more precisely below.

The contribution of the phase kinks to the current is bounded due to their limiting velocity and various damping effects. Therefore for strong enough fields the whole CDW must move; in particular the motion of charge far from centers of phase kinks requires passing through a commensurability barrier. This is illustrated in Fig. 1: The states ψ_n are degenerate ground states, while $\tilde{\psi}_n$ require higher energies. In presence of an electric field $\psi_n \to \tilde{\psi}_n \to \psi_{n+1}$ as function of time with the field overcoming the loss in commensurability energy.

Consider a CDW of the form $\Delta \cos(\mathbf{Q}\cdot\mathbf{r} + \phi)$ where $\mathbf{Q}$ is a commensurate wavevector and Δ is the corresponding gap in the electron spectrum. The phase ϕ is space dependent since $\int \phi'(y, t)\, dy \neq 0$ (y is the chain direction) measures the deviation from commensurability or the phase-kink density n_k. If the phase is also time dependent it describes an electric current. This current has a component with a rapid spacial variation (periodicity $\sim Q_y^{-1}$) and a slowly varying component associated with the drift velocity $\sim \dot{\phi}(y, t)$ of the whole Fermi sea [16]. For example, if $\phi(y, t) = \phi_1(y) - Q_y vt$ then the CDW is propagating with a uniform velocity v; the corresponding current is uniform ($\sim v$) plus oscillations on a microscopic scale. In the d.c. measurements which we consider here [2, 3, 7] the contacts are distributed over a length of order 10^{-2} cm while the CDW wavelength is of order 10^{-7} cm. Therefore the microscopic oscillations average to zero and the measured current J is a space average of the drift velocity $J \sim \int \dot{\phi}(y, t)\, dy$. Hence only time variations in the velocity can give rise to a time dependence in the measured current.

We describe the ohmic regime by a moving solution $\phi(x - vt)$ with velocity v and the corresponding current is $\sim v \int \phi'(x - vt)\, dx \sim vn_k$. Since the velocity v is

* On leave from the Department of Nuclear Physics, The Weizmann Institute of Science, Rehovot, Israel.

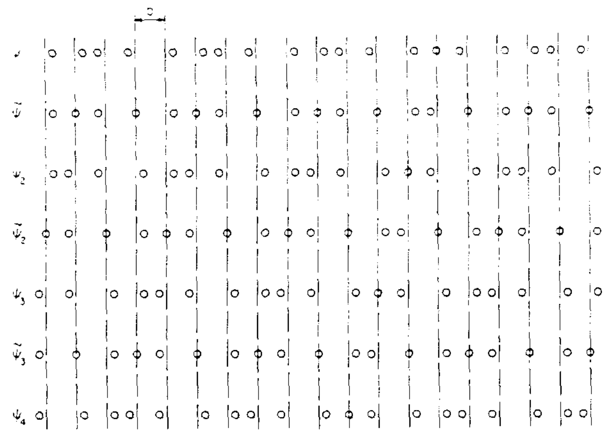

Fig. 1. Ion positions in a nearly commensurate CDW. Dashed lines are the ion positions in the absence of the CDW, defining the lattice constant b. In presence of an electric field $\psi_n \to \tilde{\psi}_n \to \psi_{n+1}$ depinning the CDW as well as moving the phase kink.

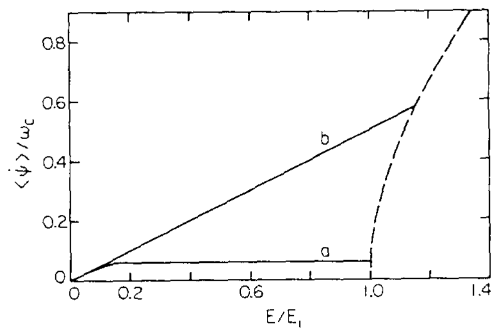

Fig. 2. Schematic current field curve for low soliton density $n_k \xi = 0.1$ with (a) low damping $\omega_0/\omega_c = 0.1$ (see [21]) and (b) strong damping $\omega_0/\omega_c \gtrsim 1$. The intersections with the dashed line [equation (4)] define the critical field, E_c.

limited, above some critical field E_c the solution $\phi(x, t)$ will not be a moving type. This definition of E_c, as a transition from moving to non-moving type solution, has two consequences: (a) The moving solution involves the low phase kink density n_k, while the non-moving solution involves all the electronic charge. (b) A moving solution cannot generate a time dependent current since $\int \phi'(x - vt)\,dx$ is independent of time. Thus only for $E > E_c$ a time dependent current can be generated.

To demonstrate these ideas we proceed with the following model. In presence of an electric field the current is written in the form [15–17]

$$J = \rho_{eff} e \frac{\langle \dot{\phi} \rangle}{\pi S}, \tag{1}$$

where $\langle \dot{\phi} \rangle$ is the space average of $\partial\phi/\partial t$ and S is the area per conducting chain. The coefficient ρ_{eff} gives the fraction of the total charge which is carried by the electric field. The total electron density is given by the volume enclosed by the Fermi surface in the absence of the CDW. Here we allow for the possibility that only a fraction $\rho_{eff} \leqslant 1$ of this total density contributes to the CDW current and determine ρ_{eff} by experimental data. If ρ_c is the fraction of condensate electrons [6] then $\rho_{eff} > \rho_c$ since also normal electrons are dragged by the moving CDW. Note that the CDW wavevector Q' pairs any two degenerate states at k and $k + Q'$ over the whole Brillouin zone, even if only part of these states are at the Fermi level. Therefore a moving CDW drags the normal electrons and ρ_{eff} can be close to 1. In particular $\rho_c \to 0$ as $T \to T_{CDW}$ but ρ_{eff} can remain constant.

Although a two fluid model is not strictly valid in the presence of free carriers [18], we assume that the CDW motion can be described by a phase equation with a phenomenological damping constant Γ [19]. In presence of 4th order commensurability this equation has the form [15, 17]

$$\frac{M^*}{m}\ddot{\phi} + \Gamma\dot{\phi} - v_F^2\phi'' + \frac{8\Delta^4}{\lambda W^2}\sin 4\phi = \tfrac{1}{2} v_F e E \frac{\rho_{eff}}{\rho_c}, \tag{2}$$

where M^*/m defines the Fröhlich mass, W is the bandwidth, v_F the Fermi velocity and λ is the dimensionless electron–phonon coupling constant. Each term on the left-hand side of equation (2) may involve a different condensate density, which can be absorbed in the relevant parameters. Also thermal fluctuations are neglected in equation (2), since the system is rather 3-dimensional and phase kinks are in fact 2-dimensional walls.

The characteristic parameters in the problem are: The unit length $\xi = v_F W\sqrt{\lambda}/(4\sqrt{2}\Delta^2)$ which satisfies $\xi \gg b$ since $\Delta \ll W$ (b is the lattice constant); the pinning frequency $\omega_0 = (2m/M^*\lambda)^{1/2} 4\Delta^2/W$, the crossover frequency $\omega_c = 32\Delta^4/(\Gamma\lambda W^2)$ and the field $E_1 = 16\Delta^4\rho_c/(ev_F\lambda W^2\rho_{eff})$. With these definitions equation (2) for $\psi = 4\phi$ becomes

$$\frac{\ddot{\psi}}{\omega_0^2} + \frac{\dot{\psi}}{\omega_c} - \xi^2\psi'' + \sin\psi = \frac{E}{E_1}. \tag{3}$$

This equation has been studied in the context of Josephson junctions [20, 21]. In the commensurate situation, where ψ is independent of x, there is a depinning field which is $E_c = E_1$ for $(\omega_c/\omega_0)^2 < 0.703$, while for larger values of $(\omega_c/\omega_0)^2$, E_c is decreasing [20]. For $NbSe_3$ the a.c. conductivity data [22] (see below) shows that $\omega_c \ll \omega_0$, so that $E_c = E_1$, if the system were commensurate. For $\omega_0/\omega_c \to \infty$ the time average $\langle \dot{\psi} \rangle_t$, which determines the d.c. current, is related to the field by

$$E = E_1(1 + \langle \dot{\psi} \rangle_t^2/\omega_c^2)^{1/2}. \tag{4}$$

Equation (3) in the presence of a phase-kink lattice has been investigated by Marcus and Imry [21]. For a given phase kink density n_k (i.e. n_k^{-1} is the mean distance over which ψ changes by 2π) they show that a propagating kink lattice of the form $\psi(x - vt)$ is a solution of equation (3). The current is then determined by $\langle \dot{\psi} \rangle = \int \dot{\psi}(x - vt)\, dx/L = -2\pi v n_k$, where L is the length of the system. The velocity v is in the range $0 \leqslant v \leqslant \omega_0 \xi$ corresponding to fields $0 \leqslant E \leqslant E_c$. At E_c the second order derivatives in equation (3) cancel each other so that the solution must satisfy equation (4). Since at $E = E_c$ also $\langle \dot{\psi} \rangle = -2\pi\omega_0 \xi n_k$, we obtain

$$E_c = E_1[1 + (2\pi n_k \xi \omega_0/\omega_c)^2]^{1/2}. \tag{5}$$

The current–field curves are shown in Fig. 2. For law fields the current is ohmic; the velocity (for low kink density, $n_k\xi \lesssim (2\pi)^{-1}$) is found from a linear response analysis [21]

$$v = \tfrac{1}{4}\pi\omega_c \xi E/E_1. \tag{6}$$

The kink conductivity is then

$$\sigma_k = \rho_{eff}\pi e n_k \xi \omega_c/(8SE_1). \tag{7}$$

In the weak damping case, $\omega_0 < \omega_c$ the velocity v in equation (5) approaches the limiting velocity $\omega_0\xi$ (i.e. the phason velocity) for some $E < E_1$ and then the kink conductivity becomes nonlinear (curve a in Fig. 2).

For strong damping equation (6) yields $v \ll \omega_0 \xi$ even at $E = E_1$ and non-linearity in the kink conductivity appears at most in the range $E_1 < E < E_c$ which is narrow for sufficiently low kink density $2\pi n_k \xi \omega_0/\omega_c \lesssim 0.5$ (curve b in Fig. 2). Therefore for strong damping and low soliton density the kink conductivity is essentially linear for $E < E_c$.

Note that for very strong damping $\omega_c \ll \omega_0$ the velocity $\omega_0\xi$ is high and higher order damping terms in equation (2) may be important. In fact, if ω_0 is the pinning frequency, it is estimated that $\omega_0 \simeq 10^2\omega_c$ [7]. In this case equation (5) is not reliable; however we may still use it, considering ω_0 as a phenomenological parameter which sets an upper bound on the kink velocity which is not necessarily related to the phason velocity.

The propagating kink lattice solution is possible only for $E < E_c$; for $E > E_c$ the solution changes qualitatively, involving $\psi(x, t)$ which changes slowly in space relative to the change with time. We approximate this situation by a space independent solution, and consider the overdamped case

$$\dot{\psi}(t)/\omega_c + \sin\psi(t) = E/E_1. \tag{8}$$

The solution (up to an integration constant) is

$$\dot{\psi}(t) = \frac{\omega_c(E_1/E)[(E^2/E_1^2 - 1]}{1 + (E_1/E)\sin(\omega_c t\sqrt{(E_1/E)^2 - 1})}. \tag{9}$$

The time average yields equation (4) and the d.c. current [equation (1)] is

$$J_{CDW} = \rho_{eff}\frac{e\omega_c}{4\pi S}\sqrt{(E/E_1)^2 - 1}. \tag{10}$$

Equation (9) shows that a d.c. field above threshold $E > E_c$, leads to a time dependent current. This time dependence is due to the commensurability energy which changes with time as the field drives the phase $\psi(t)$. The fundamental frequency of equation (9) is $\Omega(E) = \omega_c[(E_1/E)^2 - 1]^{1/2}$ and is therefore proportional to the current

$$2\pi J_{CDW}/(e\Omega) = \rho_{eff}/(2S). \tag{11}$$

These frequencies have indeed been observed experimentally [3, 23, 24]; the left-hand side yields $\sim 4 \times 10^{13}\,cm^{-2}$. The area of the unit cell, perpendicular to the b-axis, is 148 $Å^2$; there are however two equivalent chains in the unit cell which contribute to each CDW transition [25]. Therefore the area per contributing chain is $S = 74\,Å^2$ and equation (11) yields $\rho_{eff} \simeq 0.6$. Considering the experimental accuracy of $\sim 30\%$ this is rather close to 1, i.e. most of the electrons move with the CDW. Note also that the ratio of current to frequency is independent of temperature, even if $T \to T_{CDW}$ [23, 24]. This confirms our previous assertion that ρ_{eff} can be very different from ρ_c.

Equation (11) may also be understood as a current of particles with density n and drift velocity v_d so that $J_{CDW} = nev_d$. If a space periodicity Λ is now introduced then v_d becomes time dependent, a frequency $\Omega = 2\pi v_d/\Lambda$ is generated and $2\pi J_{CDW}/(e\Omega) = n\Lambda\rho_{eff}$. In our case the periodicity is generated by the lattice, i.e. $\Lambda = b$ and $n = (2bS)^{-1}$ corresponding to 1/4 electron per atom per spin for a 1/4 filled band.

In models based on impurity pinning [6–10] $\Lambda = \pi/k_F \simeq 4b$ where k_F is the Fermi wavevector. The corresponding density is $2k_F/(\pi S)$ so that $n\Lambda = 2/S$ which is a factor 4 higher than above. For impurity pinning of a phase-kink lattice, each kink has charge $e/2$ so that $n\Lambda = (2S)^{-1}$, same as in our model. Bak [26] has used this mechanism to deduce that the phase-kink charge $\rho_{eff}e/2$ is close to $e/2$. (Here however $\Lambda \simeq 30b$ and the corresponding drift velocity is larger by a factor ~ 30, e.g. of order $\sim 1\,cm\,sec^{-1}$ at $J_{CDW} \simeq 10\,A\,cm^{-2}$.)

The oscillating current in a d.c. field was also observed in TaS_3 [27], with the left-hand side of equation (11) being $\sim 2 \times 10^{14}\,cm^{-2}$. The area of the unit cell is 560 $Å^2$ but it contains 24 nearly equivalent chains, which is consistent with the Hall constant [28].

Therefore the area per contributing chain is 23 $Å^2$ which yields $\rho_{eff} \simeq 0.9$. Since TaS_3 is commensurate [29] our depinning mechanism is even more obvious.

Finally we comment on two additional features of the experimental data – temperature dependence of E_c and a.c. conductivity data. The critical field E_c shows a minimum near $T \sim 0.8\, T_{CDW}$ [1, 2]. In equation (5) $\Delta(T)$ and $\Gamma(T)$ indeed yield opposite temperature dependencies. As T increases, $\Delta(T)$ decreases, vanishing at T_{CDW}, while $\Gamma(T)$ increases (from the high field conductivity [1, 2]) as $\Gamma \sim T^x$ with $1 \lesssim x \lesssim 3$. However a more detailed microscopic derivation is needed for this analysis.

The a.c. conductivity shows a crossover behaviour as in a relaxation oscillator model [7, 8] with $\omega_c \simeq 10^8$ sec^{-1}. This corresponds to equation (3) with a time dependent field, space independent solution ($n_k = 0$) and $\omega_0 \gg \omega_c$. However the data shows [22] that the crossover region is very broad (from $10^7\, sec^{-1}$ to 10^9 sec^{-1}) and cannot fit a single crossover frequency. The conductivity in presence of phase kinks can be evaluated within linear-response theory, as done for the polarizability [30]. The effect of the phase kinks is to break translation invariance so that the a.c. field can couple to all extended phonon modes with wavevectors q. This introduces new crossover frequencies at $\omega_c(1 + \xi^2 q^2)$ which smear the crossover region, in qualitative agreement with experiment.

In conclusion, we have shown that lattice commensurability can explain the depinned CDW phenomena in $NbSe_3$. This is supported by the observation of the same phenomena in the similar but commensurate TaS_3.

Acknowledgements – We wish to thank S.E. Trullinger, A.R. Bishop, N.P. Ong, G. Gruner, M.C. Cross, P. Bak, S. Kivelson, J.R. Schrieffer and S. Shtrikman for valuable discussions. This research was supported in part by the National Science Foundation, Grant No. PHY77-27084.

REFERENCES

1. For recent reviews see *Proc. Int. Conf. on Low Dimensional Conductors*, in *Molecular Crystals and Liquid Crystals*. Gordon and Breach, New York (1982).
2. P. Monceau, N.P. Ong, A.M. Portis, M. Merschant & J. Rouxel, *Phys. Rev. Lett.* **37**, 602 (1976).
3. R.M. Fleming & C.C. Grimes, *Phys. Rev. Lett.* **42**, 1923 (1979).
4. K. Maki, *Phys. Rev. Lett.* **39**, 46 (1977).
5. J. Bardeen, *Phys. Rev. Lett.* **45**, 1978 (1980).
6. P.A. Lee & T.M. Rice, *Phys. Rev.* **B19**, 3970 (1979).
7. M. Weger, G. Gruner & W.G. Clark, *Solid State Commun.* **35**, 243 (1980).
8. G. Gruner, A. Zawadowski & P.M. Chaikin, *Phys. Rev. Lett.* **46**, 511 (1981).
9. J.B. Sokoloff, *Phys. Rev.* **B23**, 1992 (1981).
10. A.M. Portis in [1].
11. R.M. Fleming, D.E. Moncton & D.B. McWhan, *Phys. Rev.* **B18**, 5560 (1978).
12. W.L. McMillan, *Phys. Rev.* **B14**, 1496 (1976).
13. R. Bruinsmaa & S.E. Trullinger, *Phys. Rev.* **B22**, 4543 (1980).
14. V.J. Emery & D. Mukamel, *J. Phys.* **C12**, L677 (1979).
15. P.A. Lee, T.M. Rice & P.W. Anderson, *Solid State Commun.* **14**, 703 (1974).
16. D. Allender, J.W. Bray & J. Bardeen, *Phys. Rev.* **B9**, 119 (1974).
17. B. Horovitz & J.A. Krumhansl, *Solid State Commun.* **26**, 81 (1978).
18. T.M. Rice, P.A. Lee & M.C. Cross, *Phys. Rev.* **B20**, 1345 (1979).
19. S.N. Artemenko & A.F. Volkov, *JETP Lett.* **33**, 147 (1981).
20. D.E. McCumber, *J. Appl. Phys.* **39**, 3113 (1968).
21. P.M. Marcus & Y. Imry, *Solid State Commun.* **33**, 345 (1980).
22. G. Gruner, L.C. Tippie, J. Sanny, W.G. Clark & N.P. Ong, *Phys. Rev. Lett.* **45**, 935 (1980).
23. P. Monceau, J. Richard & M. Renard, *Phys. Rev. Lett.* **45**, 43 (1980).
24. W.G. Clark, G. Gruner & M. Weger (to be published).
25. J.A. Wilson, *Phys. Rev.* **B19**, 6456 (1979).
26. P. Bak, *Phys. Rev. Lett.* **48**, 692 (1982).
27. G. Gruner, A. Zettl, W.G. Clark & A.H. Thompson, *Phys. Rev.* **B23**, 6813 (1981).
28. N.P. Ong, in [1].
29. K. Tsutsumi, T. Sambongi, S. Kagoshima & T. Ishiguru, *J. Phys. Soc. Japan* **44**, 1735 (1978).
30. M.B. Fogel, S.E. Trullinger & A.R. Bishop, *Phys. Lett.* **59A**, 81 (1976).