Interference Effects of the Charge-Density-Wave Motion in $NbSe_3$

P. Monceau, J. Richard, and M. Renard
Centre de Recherches sur les Très Basses Températures, Centre National de la Richerche Scientifique, F-38042 Grenoble, France

(Received 4 March 1980)

It is reported that steps are induced in the nonlinear $V(I)$ characteristic of $NbSe_3$ by a superposed rf current. The frequencies responsible for these steps are interpreted as the Fourier spectrum of the motion of the charge-density wave in an anharmonic potential created by the impurities. It is shown that the relation $\bar{J} = n\bar{e}v$ is verified for the excess current $\bar{J}$ carried by the charge-density wave, v being the velocity of the wave. The number of condensed electrons n below the charge-density wave at 59 K is found to be in good agreement with previous measurements.

PACS numbers: 72.15.Nj

One of the most intriguing properties of $NbSe_3$ is the nonlinear resistivity behavior just below $T_1 = 145$ K and $T_2 = 59$ K, temperatures at which two independent charge-density waves (CDW) occur.[1-3] Lee and Rice[3] (LR) have developed a model where the electric field displaces the CDW as a whole from the pinning centers. Fleming and Grimes[4] (FG) showed recently that nonlinearity is observed only above a critical field E_c where they observed a large increase of the voltage noise. Superposed on the broadband noise they also measured an ac voltage detected as discrete frequencies with high harmonic content.

In this Letter we report the "reciprocal effect," i.e., the observation of steps in the dc characteristic $V(I)$ induced in the nonlinear regime of $NbSe_3$ below the T_2 transition by superposing a rf current of constant amplitude and a given dc current higher than the critical one. Interference takes place between the rf field and the "entities" in motion in the crystal at well-defined frequencies as seen by an increase of the resistance of the sample for these frequencies. For more sensitivity we measure the differential resistance

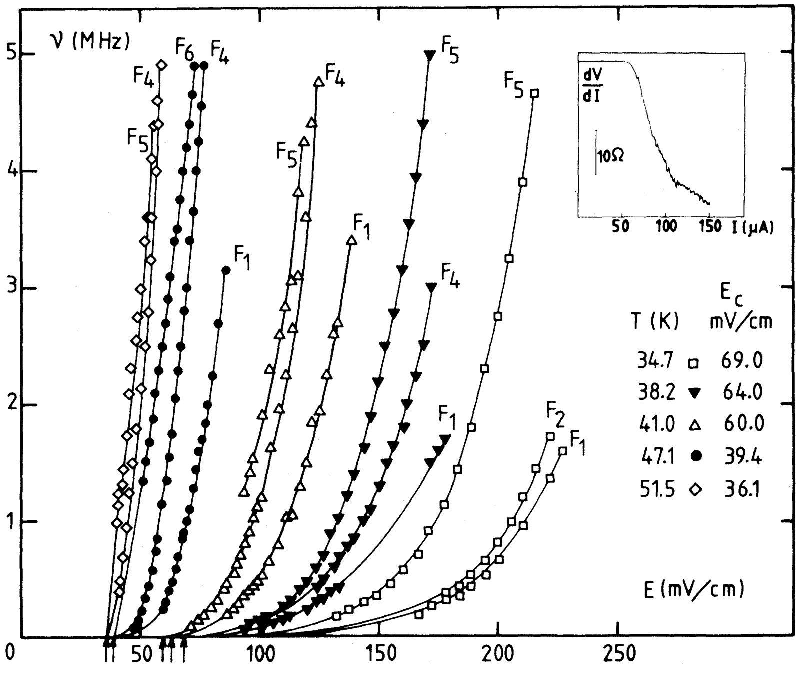

FIG. 1. Variation of the frequencies detected by noise spectrum analysis without rf field as a function of the electric field for different temperatures. The frequencies extrapolate to zero at the critical electric field indicated by the arrows. Inset: dV/dI at 33 Hz for the same sample which shows the onset of the noise above the critical current.

© 1980 The American Physical Society

dV/dI(33 Hz) and we observe a set of peaks by sweeping the rf frequency. We show that these resonant frequencies are the same as those measured by analyzing the spectrum of the noise at the same dc current and without rf field. We interpret these discrete frequencies as evidence of the staircase motion of the CDW in the pinning potential tilted by the electric field.

Measurements were performed on several $NbSe_3$ crystals from different batches. Contacts were usually made with silver paint.[5] The variation of dV/dI as a function of I is shown in the inset of Fig. 1 for the sample labeled B2 which has a resistance ratio of 80. The critical current I_c at 47 K is 57 μA ($E_c = 39.4$ mV/cm) above which dV/dI starts to decrease and where noise is generated in the crystal. As in FG, this noise has been frequency analyzed. Peaks for discrete frequencies up to 5 MHz were observed. In Fig. 1 we show the frequencies as a function of E for the sample B2 at different temperatures. We measure three or four frequencies which can be extrapolated to zero at E_c. We note that the frequency variation as a function of E is more and more rounded when T is decreased.

We put in evidence the "reciprocal effect" in Fig. 2, where dV/dI at 33 Hz for the sample B2 is shown as a function of the external rf frequency with a rms amplitude of 35 μA, for different dc currents above I_c. The current at 33 Hz for the ac bridge was 1 μA. The peaks correspond to an *increase* of the differential resistance; however, the latter never exceeds the low-field Ohmic value. We can account for the majority of the peaks with two frequencies F_1 and F_2 and their even harmonics and with a less well defined third one F_3. For $I = 2I_c$ at very small rf currents (8 μA), only the fourth harmonics which always have a predominant amplitude were detectable. As the rf current is increased, other harmonics and fundamentals became detectable. When visible, the frequencies corresponding to the peaks are independent of the rf amplitude between 8 μA and at least 45 μA, except very near I_c, where they are shifted to higher frequencies when the rf is increased. It should be noted that for about (3 to 4)I_c the peaks disappeared, and that only broadband noise is measured. The same experiment has been performed on three other samples and gave the same features.

A tentative interpretation is to associate these observations with the motion of CDW. It was shown that the current carried by a motion of CDW is[3,6]

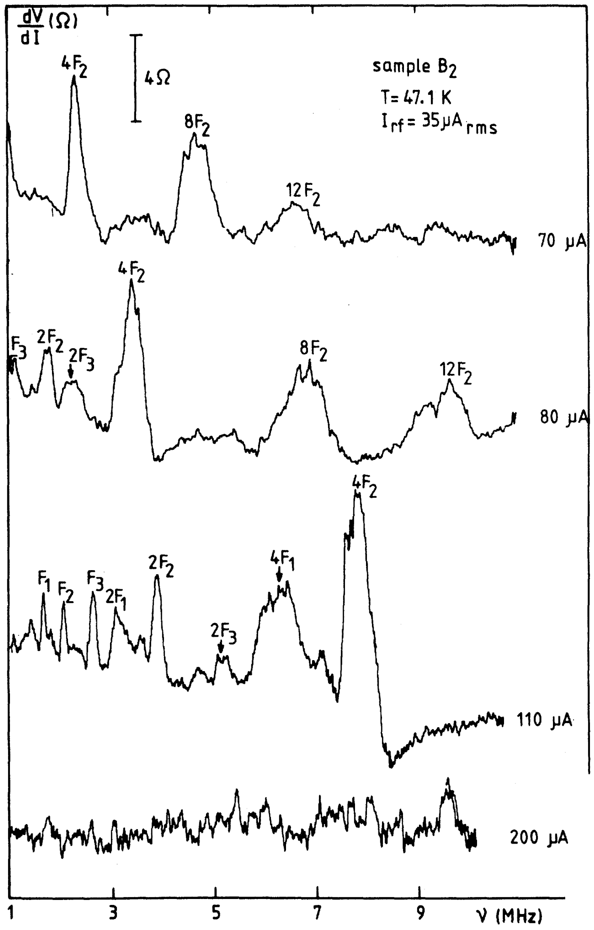

FIG. 2. Differential resistance dV/dI at 33 Hz of $NbSe_3$ at 47 K in sweeping the frequency of a rf current of constant amplitude superposed on the dc current above the critical current ($I_c = 59$ μA).

$$J_{CDW} = \rho_c n_0 e v, \tag{1}$$

where $\rho_c n_0$ are the condensed electrons under the gap, and v the velocity of CDW. The CDW can be thought of as a particle with mass, charge, and friction.[7,8] Its equation of motion contains also pinning forces which can reasonably be assumed to be periodic with the phase of CDW at the pinning centers. So the motion due to an external field is the superposition of a continuous drift, and a modulation due to pinning, at a recurrence frequency

$$\nu = (Q/2\pi) v_{\text{drift}},$$

where Q is the distortion vector. Since the pinning is strongly anharmonic, we expect many harmonics in the Fourier expansion of the velocity with the fundamental frequency given above. Hence the current is modulated at ν and its harmonics and gives rise to quasiperiodic noise. The fundamental frequency is expected to be

$$\nu = (Q/2\pi)\bar{J}_{\mathrm{CDW}}\rho_c n_0 e. \qquad (2)$$

At high enough electric fields, the velocity becomes more uniform, and the peaks decrease in amplitude. The current carried by CDW, $\bar{J}_{\mathrm{CDW}}$, can be obtained experimentally from the nonlinear $V(I)$ characteristics, if we assume that the conductivity of normal electrons is not affected. We get

$$\bar{J}_{\mathrm{CDW}} = J(1 - R/R_n), \qquad (3)$$

where J is the applied current density, R the actual resistance of the sample at J, and R_n the value when J decreases to near zero.

In Fig. 3 we have plotted the same frequencies as in Fig. 1 as a function of $\bar{J}_{\mathrm{CDW}}$ (Eq. 3). We have measured R and R_n at each temperature. In fact, we have plotted the lowest frequencies F_1 for different temperatures and one, F_4 or F_5, of the highest frequencies. All the curves $\nu(E)$ of Fig. 1 superpose on two straight lines, one for F_1, the other for F_4 and F_5. This result proves the validity of Eq. (2). In the same Fig. 3, for 47.1 K, we show the frequencies F_1 obtained by the synchronization experiment. These frequencies are in excellent agreement with those observed by noise analysis. This agreement indicates that we are dealing with the same frequencies in the two experiments and that the motion of the CDW inside the crystal can be synchronized by an external frequency.

The ratio of the two slopes of the $\nu(\bar{J}_{\mathrm{CDW}})$ lines is approximately 4. Thus F_4 and F_5 may be the fourth harmonics of low frequencies which are not too different from F_1 but which we were unable to see in the frequency analysis because of their weak amplitude. As seen in Fig. 2 the fundamental frequency F_1 is not unique but we have detected a group of two or three peaks. At this point of our experimental study, we consider the straight line with the smallest slope in Fig. 3 as the average of the variation of ν with $\bar{J}_{\mathrm{CDW}}$ of this group and the other line (corresponding to F_4 or F_5) as the fourth harmonics of the same group. If we assume Eq. (2), the slope of $\nu(\bar{J}_{\mathrm{CDW}})$ gives directly the fraction of consensed electrons if we know the normal electronic concentration (above the CDW formation). For calculating this latter we use either the assumption of Wilson[9] or the band calculations of Bullett[10] which show that there are two electrons to be shared on four niobium sites, i.e., four d bands $\frac{1}{4}$ full. Each $\frac{1}{4}$ band corresponds to 160 C/cm^3. However at the T_1 transition already about 20% of the electrons are condensed[2] and do not participate in the conduction. With $\nu = 2$ MHz for $\bar{J}_{\mathrm{CDW}} = 53$ A/cm^2 we finally find $\rho_c \sim 0.40$, a number which is in relatively good agreement with conductivity[2] and susceptibility[11] measurements.

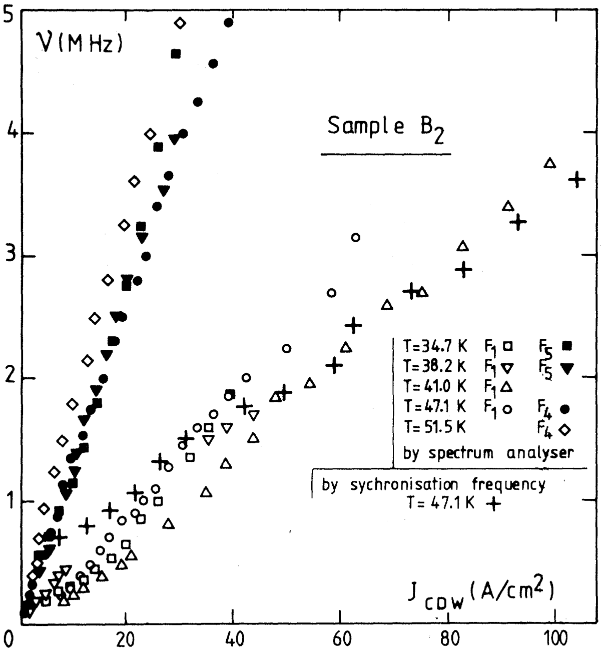

FIG. 3. Variation of the frequencies of Fig. 1 as a function of $\bar{J}_{\mathrm{CDW}}$, the current carried by the CDW as calculated in Eq. (3). The lowest set of data correspond to the frequencies F_1 at different temperatures of Fig. 1 which collapse onto a straight line when plotted as a function of $\bar{J}_{\mathrm{CDW}}$. The upper set of data corresponds to F_4 or F_5. The slope of ν vs J_{CDW} gives the number of condensed electrons below the CDW gap.

We do not understand the origin of the group of frequencies, and precise measurements of their variation with $\bar{J}_{\mathrm{CDW}}$ are necessary. Our experiments prove that the CDW can carry a current but we cannot say if the whole CDW moves or if the phase shift is carried by the motion of dislocations generated, for instance, by Frank-Read sources as suggested by LR. It can also be argued that the frequencies which we labeled fourth harmonics are in fact fundamentals and that the effect of the electric field is to generate subharmonics as it has been observed in turbulence experiments.[12,13]

In conclusion it seems that frequency generation in the noise above the critical electric field can be explained by the CDW motion in an anharmonic potential. We have shown that such a motion can be synchronized with an external rf field. Experimentally we find that the frequencies are proportional to the current carried by the CDW and that the fraction of condensed electrons is in quite good agreement with other experiments.

We are pleased to thank A. Meerschaut, L. Guemas, and J. Rouxel for providing us with the samples, J. L. Bret for his help with the electronics, and M. Papoular for stimulating discussions.

---

[1] P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, Phys. Rev. Lett. 37, 602 (1976).

[2] N. P. Ong and P. Monceau, Phys. Rev. B 16, 3443 (1977).

[3] P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).

[4] R. M. Fleming and C. C. Grimes, Phys. Rev. Lett. 42, 1423 (1979).

[5] The rectangular cross section of the crystals used in this experiment was measured with a scanning electron microscope. We obtain a room-temperature resistivity of about 250 $\mu\Omega\cdot$cm which is less than the previous values reported in Ref. 2.

[6] D. Allender, J. W. Bray, and J. Bardeen, Phys. Rev. B 9, 119 (1974).

[7] M. J. Rice, S. Strässler, and W. R. Schneider, in *Lecture Notes in Physics*, edited by H. G. Schuster (Springer-Verlag, Berlin, 1975), Vol. 34, p. 282.

[8] M. Papoular, Phys. Lett. 76A, 430 (1980).

[9] J. A. Wilson, Phys. Rev. B 19, 6456 (1979).

[10] D. W. Bullett, J. Phys. C 12, 277 (1979).

[11] J. D. Kulick and J. C. Scott, Solid State Commun. 32, 217 (1979).

[12] G. Ahlers and R. P. Behringer, Phys. Rev. Lett. 40, 712 (1978).

[13] J. Maurer and A. Libchaber, J. Phys. (Paris) Lett. 40, L419 (1979).

Enhanced Inelastic Light Scattering from Metal Electrodes Caused by Adatoms

A. Otto, J. Timper, J. Billmann, and I. Pockrand
Experimentalphysik III, Universität Düsseldorf, D-400 Düsseldorf 1, Federal Republic of Germany

(Received 4 February 1980)

The intensity of the continuous inelastic light scattering from a silver electrode in a ClO_4 electrolyte depends on the potential and the amount of redeposited silver. These experimental observations are consistently explained by the concentration of silver adatoms at the electrode surface.

PACS numbers: 78.35.+c, 68.45.Da

Since 1977 there has been an increasing interest in the phenomenon of surface-enhanced Raman scattering (SERS) from adsorbates on metals.[1] Billmann and Otto[2] present new experimental evidence for a local enhancement mechanism, in contrast to recent theoretical and experimental claims[3] for a nonlocal enhancement mechanism by electromagnetic resonances caused by roughness on a scale of 500 Å.

A local enhancement mechanism is the adatom hypothesis.[4,5] It predicts resonant Raman scattering from adsorbate vibrations for adsorbates chemisorbed to adatoms and a structureless background due to resonant electronic Raman scattering.[4,6] The resonance is caused by itinerant electron-hole pairs in the metal which are the intermediate state in the scattering process.[7-9] The adatom mediates strong coupling of the photon to metal electrons.

In this Letter we report new experimental evidence strongly supporting the adatom hypothesis. Then we describe the parameters which will influence the adatom concentration on an electrode (e.g., Ag adatoms on a silver electrode) and later show that the measured background intensity follows the expected concentration of adatoms.

In metallic crystal growth the important sites of atoms at the surface are the monoatomic step, the kink site within a step, and the adatom, which is an isolated atom on an atomically smooth surface.

The binding energy of a kink-site atom equals the cohesive energy of the metal (per bulk atom), whereas the binding energy of an adatom is twice the surface energy of the metal (per surface atom).[10] For all alkali, transition, and noble

© 1980 The American Physical Society