NMR Evidence of the Fröhlich Mode in $Rb_{0.30}MoO_3$

P. Ségransan,(1) A. Jánossy,(2),(3) C. Berthier,(1) J. Marcus,(2) and P. Butaud(1)
(1) *Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble, 38402 St. Martin d'Hères, France*
(2) *Laboratoire d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, 38042 Grenoble, France*
(3) *Central Research Institute for Physics, H-1525 Budapest, Hungary*
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Current-voltage characteristics, voltage oscillations, and NMR on a $Rb_{0.3}MoO_3$ crystal at 77 K are presented. The $\frac{1}{2}$, $-\frac{1}{2}$ transition at $\nu_0 = 80$ MHz of ^{87}Rb nuclei, broadened by the charge-density-wave modulation, is motionally narrowed for bias currents exceeding threshold for nonlinear conduction. Calculation of the line shapes, on the assumption of a partial depinning of the sample, leads to excellent agreement with experiment. The ratio of average current density to voltage oscillation frequency in the depinned region agrees roughly with phenomenological models. The phase-correlation time of single domains is deduced to be $\tau = 200$ μs.

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In the last decade a number of few-dimensional conducting systems have been discovered[1] in which a unique mode of charge transport occurs. In these systems the high-temperature metallic state is unstable against formation of a periodic lattice distortion coupled to a charge-density-wave (CDW) state of the electrons. Below the ordering temperature of the CDW's a gap opens in the electron spectrum. For fields above a threshold which may be as small as a few millivolts per centimeter, a "nonlinear" current appears[2] in addition to the current of normal excitations above the Peierls gap. This current has remarkable properties: E.g., like superconductors, it carries only very little heat.[3] Also, it is accompanied by large voltage fluctuations referred to as "noise."[4]

Theories attempting to explain this phenomenon are based on Fröhlich's idea[5] of a collective motion of the electrons which may be envisaged in its simplest form[6] as a rigid sliding motion of the CDW coupled to an oscillating coherent motion of the lattice. For incommensurate systems the sliding is hindered by impurities only, and for crystals of high perfection it may set in at very low electric fields. Noise in this picture is due to the periodicity of the potential hindering the sliding motion of the CDW. Although these ideas are generally accepted, a direct proof of a motion of the electron condensate as a whole under an electric field has been lacking. Unsuccessful attempts by NMR in Rb blue bronzes have been reported.[7] Recently two NMR experiments were performed[8] with results interpreted as evidence for CDW motion.

In this paper we present the main results of a study of the electric conductivity, noise, and nuclear magnetic resonance of the blue bronze $Rb_{0.30}MoO_3$. The experiments are performed at 77 K on the same sample and unambiguously show that the appearence of the extra conductivity and noise above a threshold electric field[9] is accompanied by a sliding motion of the CDW. The width and shape of the NMR spectra are determined by the spatial modulation of the electric field gradient (EFG) at the observed Rb nuclei due to the CDW.[10] Roughly speaking, as the CDW sets in motion for a large enough bias current, the time average of the EFG at all nuclei becomes equal and the NMR spectra motionally narrows.

The sample was grown by electrolysis from a melt of MoO_3 and Rb_2MoO_4; it was 6 mm along the **b** axis (axis of high conductivity). Four contacts were deposited on a face 1.7×0.6 mm^2 polished in the plane perpendicular to **b** (Fig. 1). Current-voltage characteristics shown in Fig. 1 were determined *in situ* in the NMR coil by our passing current through each half of the crystal and measuring voltage across the other half. A pulsed-current method was used to verify that up to the highest currents applied in all measurements reported in this paper Joule heating was negligible. The two halves had nearly equal Ohmic resistances but somewhat different characteristics in the non-Ohmic

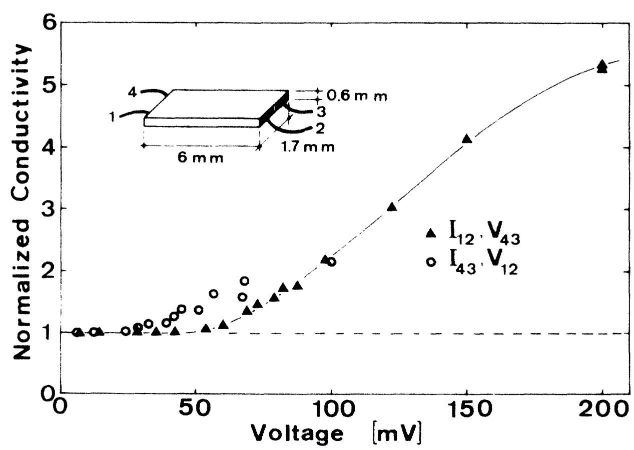

FIG. 1. Conductivity normalized to Ohmic conductivity σ_0 vs voltage across the sample. Inset: The geometry of the four contacts. Circles and triangles correspond to results on the two halves of the sample which have different threshold fields.

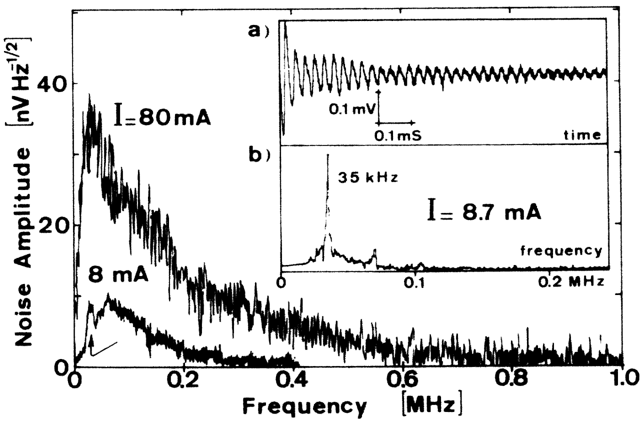

FIG. 2. Typical frequency distributions of noise amplitude (square-root of noise power). For currents slightly above threshold, well defined noise peaks appear as shown for $I = 8$ mA by the arrow. Correspondingly well defined oscillations appear in the voltage response to current pulses as shown in the inset. For large currents as shown for $I = 80$ mA a broad distribution of noise power is observed. For the noise power spectra, currents are extrapolated for the whole sample although these are taken only on one half as a four-probe method was used. The real-time measurements are done by two probes; a smooth background was subtracted.

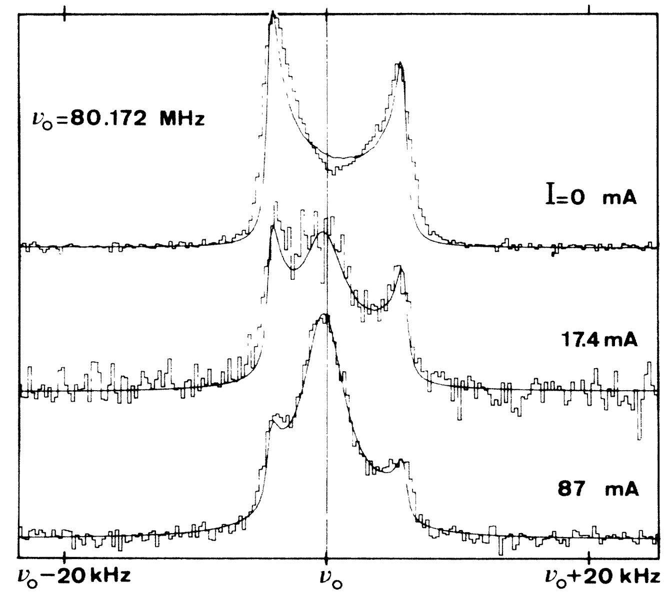

FIG. 3. ^{87}Rb nuclear magnetic resonance spectra without bias current and with two different bias currents. Solid curves are fits to the spectra calculated from (2) and (4). The central peak arises from the "dynamic fraction" of the sample in which the CDW is depinned; its width is due—in addition to the dipolar interaction—to a finite CDW phase correlation time.

regime. The conductivity increase of a factor of 6 for a field of $E/E_T = 4$ shows that for these fields the CDW current was, by far, larger than the Ohmic one.

We believe that the better than usual contacts ensured a more homogeneous current distribution in this sample. The NMR data below show, however, that even in this sample the current was inhomogeneous. For higher currents, anomalies occur in the I-V characteristics due to a normal current induced by the depinned CDW and flowing in the opposite direction. We do not discuss them here and have included in Fig. 1 results up to fields in which the characteristics are "normal."

A large increase of the voltage noise was observed as the field increased above threshold. This noise has been analyzed both by use of a HP71100A spectrum analyzer and by detection of well defined oscillations in the voltage response to a current step. In Fig. 2 we show oscillations which despite an averaging over 840 pulses decrease only slowly in time. The frequency of these oscillations varies linearly with the nonlinear current in a limited current range; at higher currents a new set of oscillations with much lower frequency appeared. Comparing the Fourier transform of these oscillations to the steady-state noise spectrum at similar currents, we find a well defined peak (and its harmonics) at the same frequency. These oscillations with well defined frequencies in the blue bronze are not only transients,[11] but continue indefinitely in agreement with findings[12] in $NbSe_3$. Most of the spectral density in our sample comes from a broad-band noise; at large currents no oscillations in the pulse response nor any narrow-band peaks in the noise spectra are observed. The average frequency and the noise power integrated over 0 to 1 MHz increase steadily with current.

The free-induction decay of the $(\frac{1}{2}, -\frac{1}{2})$ transition of ^{87}Rb (most likely[13] at site 1) was recorded at 80.2 MHz by a Brucker CXP-100 spectrometer with a rotating rf field $H_1 = 50$ G. Receiver dead time was less than 4 μs, signals were averaged and Fourier transformed with a Nicolet LAS 12/70 signal analyzer monitored by a HP 9836 computer. The static magnetic field was perpendicular to the $(\mathbf{b}, \mathbf{a} - 2\mathbf{c})$ plane and H_1 was along $\mathbf{b}$. Several spectra were taken with bias currents between 0 and 165 mA injected through the whole sample by shortcircuiting the pairs of contacts 1-4 and 2-3 (Fig. 1), respectively. The bias currents were pulsed with pulse lengths of 10 ms and a duty cycle of 0.33 Hz. The $\pi/2$ rf pulse was applied 2 ms after the onset of the bias pulse. Typical spectra are shown in Fig. 3.

To calculate the NMR line shape in the presence of a pinned CDW with wave vector $\mathbf{q}$, we recall that the frequency of the $(\frac{1}{2}, -\frac{1}{2})$ transition is spatially modulated. Neglecting higher-order terms, we have

$$\nu_{1/2,-1/2}(\mathbf{R}) = \nu_0 - \tfrac{3}{16}[(\nu_Q^0)^2/\nu_0 + \Delta\nu_{1/2,-1/2}(\mathbf{R})]f(\theta), \quad (1)$$

where ν_0 is the Larmor frequency, $\nu_Q^0 = e^2qQ/2h$ is the quadrupole frequency in absence of the CDW modulation ($\nu_Q^0 \simeq 4.5$ MHz), and $f(\theta)$ depends on the orientation of the electric-field-gradient (EFG) tensor principal axis with respect to the static magnetic field. $\Delta\nu_{1/2,-1/2} = 2\Delta\nu_Q(\mathbf{R})\nu_Q^0/\nu_0$ is a frequency shift due to the spatial modulation of the EFG; we assume it to be expressed as[10]

$$\Delta\nu_{1/2,-1/2}(\mathbf{R}) = (\omega_1/2\pi)\cos(\mathbf{q}\cdot\mathbf{R}+\Phi) + (\omega_2/2\pi)\cos^2(\mathbf{q}\cdot\mathbf{R}+\Phi). \quad (2)$$

The tensor nature of the EFG and local effects are neglected. The line shape was calculated numerically from (1) and (2) with the fitting parameters $\omega_1/2\pi = 4.9$ kHz and $\omega_2/2\pi = 0.7$ kHz and with the dipolar broadening taken into account by convolution with a Lorentzian of HWHM $\omega_D/2\pi = 0.3$ kHz. The fit is independent of $\mathbf{q}$ provided that $\mathbf{q}$ is incommensurate and numerical simulations show that any model which assumes widely spaced discommensurations in a commensurate CDW is inconsistent with our data.[10]

The theory of the NMR line shape in the presence of a uniformly sliding CDW was derived by Kogoj, Zumer, and Blinc.[14] Assuming the CDW to slide with a constant velocity v so that $\Phi = -\Omega t$, $\Omega = v/\lambda_{\mathrm{CDW}}$ throughout the whole sample, we find the line shape:

$$\mathscr{L}_D(\omega) = \sum_{n=-\infty}^{n=+\infty} [J_n(\omega_1/\Omega)]^2\delta(\omega - n\Omega) * h(\omega), \quad (3)$$

where $h(\omega)$ is a Lorentzian line shape corresponding to the secular spin-spin interaction and J_n is the nth order Bessel function; the asterisk denotes convolution. We neglected for simplicity in (3) terms in ω_2, although they were taken into account in the final analysis. It follows from (3) that well defined sidebands appear at $\omega = \pm n\Omega$ for a uniform motion of the CDW. However, if there is a distribution in v, these sidebands will be smeared and hidden by the noise. The main effect of the CDW motion on the line shape is then the appearance of a central line corresponding to $n=0$ in (3). The position and the width of the central line $n=0$—in contrast to the sidebands—is independent of v. Moreover, as our calculations show, for $\Omega/\omega_1 > 2$, 90% of the intensity is included in the central line. The effect of a finite value for ω_2 is a shift by $\omega_2/2\pi$ of the position of the central line.

The NMR spectra contain a static component which decreases with increasing bias current but does not disappear even for the largest current. The voltage noise spectra (Fig. 2) show, on the other hand, that below 10 kHz (i.e., $2\omega_1$) the noise power sharply decreases. Thus a consistent picture requires the assumption that even for large currents the CDW remains pinned in part of the sample. To take this into account we fitted the NMR spectra under bias currents by the expression

$$I(\omega) = f_s\mathscr{L}_s(\omega) + (1-f_s)\mathscr{L}_D(\omega - \omega_2/2), \quad (4)$$

where f_S is the static fraction of the sample. The central line $\mathscr{L}_D$ is a Lorentzian which we fitted with a HWHM $\omega_D/2\pi = 1.5$ kHz for all spectra. (We shall discuss the origin of this width later.)

Figure 4 shows the dynamic fraction $f_D = 1 - f_S$ as a function of the bias current. Although in our sample the current is quite inhomogeneous, it is still better than samples usually used. Thus extreme care should be taken even when qualitative results are to be obtained on blue bronze. In our view previous failures to obtain motional narrowing in blue bronze was caused by the inhomogeneity of the current.

One of the most debated questions of CDW dynamics is the origin of voltage fluctuations. The ratio of the CDW current to the washboard frequency according to the phenomenological model[6] is $J_{\mathrm{CDW}}/\nu = 2epn_\perp$, where $n_\perp$ is the density of conducting chains, and p the degeneracy of the conduction band. In blue bronze[15] $p=2$ and $J_{\mathrm{CDW}}/\nu = 80$ A/MHz$\cdot$cm^2 is expected. Attempts to determine J_{CDW}/ν experimentally used the current dependence either of peaks in the noise spectrum[16] or of the frequency of transients.[11] These methods use very uncertain values of J_{CDW} as the voltage oscillations with well defined frequencies arise from single domains extending over only a fraction of the sample. This is exemplified by the 35-kHz oscillations of Fig. 2 which are due to a CDW coherent phase domain which is at most 1% of the sample as deduced from f_D and its spectral weight in the noise power spectrum. To have an idea of the value of J_{CDW}/ν we calculated the average value of J_{CDW} by correcting for the unpinned regions, and the average value of ν from a weighted average of the noise power spectra. We obtained $J_{\mathrm{CDW}}/\nu = 50$ A/MHz$\cdot$cm^2 within a factor of 3. This value is in

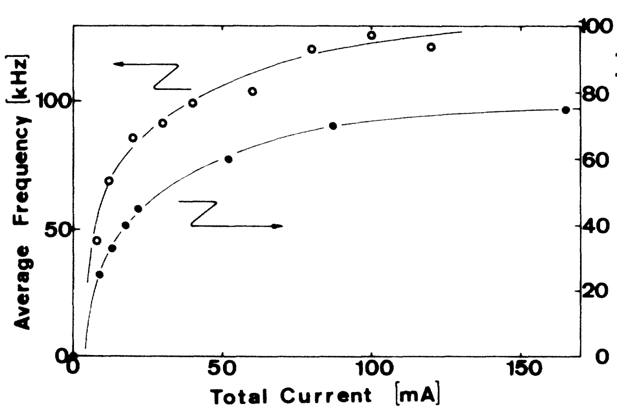

FIG. 4. Average voltage noise frequency (open circles) and dynamic fraction (solid circles) f_D as functions of bias current.

agreement with the washboard frequency of the phenomenological model.

The picture which emerges from our data is that at threshold only a small part of the sample becomes depinned. At large currents the CDW is depinned in almost the whole sample, but a widespread distribution of velocities occurs corresponding to a large number of CDW domains, each of them with a given velocity v. The width of the central peak of the NMR spectra shows, however, that within each domain the phase of the CDW does not vary strictly periodically; it has a finite correlation time. The width of the central peak is not affected by the distribution of the velocities. We find it, however, to be 1.5 kHz, a value much larger than the dipolar linewidth, which is at most 0.8 kHz, the room-temperature value. We attribute the increase of the central linewidth to a finite correlation time of the order of 200 μs, which arises from the fluctuation of the velocity of the CDW within single domains. This value is of the same order as the width of the peak in the noise spectrum of Fig. 2.

The main result of our study in an unambiguous proof of the sliding of an incommensurate CDW in blue bronze for currents above threshold, causing the motional narrowing of quadrupole distribution associated to a static CDW. As a result of the inhomogeneity of the current density, the onset of the Fröhlich mode is not simultaneous in the whole sample; for currents near threshold, the sliding of CDW gives rise to well defined voltage oscillations in some domains. For larger currents, a broad distribution of velocities occurs, and although voltage oscillations of individual domains cannot be discerned, analysis of the NMR line shape shows that the correlation time of the phase within domains remains long.

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