

NMR Study of the Charge-Density Wave in $\text{Rb}_{0.30}\text{MoO}_3$ Single Crystal

P. Butaud, P. Ségransan, and C. Berthier

Laboratoire de Spectrométrie Physique, associé au Centre National de la Recherche Scientifique, Université Scientifique et Médicale de Grenoble, 38402 Saint-Martin d'Hères Cedex, France

and

J. Dumas and C. Schlenker

Laboratoire d'Etudes des Propriétés Electroniques des Solides, associé à l'Université Scientifique et Médicale de Grenoble, Centre National de la Recherche Scientifique, 38042 Grenoble-Cedex, France

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We present the first NMR study of the quasi one-dimensional conductor $\text{Rb}_{0.30}\text{MoO}_3$. From the line shape of the ^{87}Rb first-order quadrupole satellite, we have studied the onset of the incommensurate charge-density wave at $T_I = 184$ K and the temperature dependence of the order parameter. Our results demonstrate the crucial role played by impurities on both the normal-incommensurate and the incommensurate-commensurate transitions and give evidence for an interaction between the charge-density wave and mobile defects around T_I .

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Despite their layered structure,¹ the so-called "blue bronzes" $\text{K}_{0.30}\text{MoO}_3$ and $\text{Rb}_{0.30}\text{MoO}_3$ have recently been recognized as quasi one-dimensional conductors through their electrical and optical properties.² These compounds undergo a Peierls transition at about 180 K observed both by x rays³ and neutron scattering.⁴⁻⁶ The component of the wave vector of the distortion along the monoclinic **b** axis has been found temperature dependent from 180 to about 100 K: Below this temperature, it stays constant and very close to the commensurate value $q_c = 0.75b^*$, thus giving rise to a controversy on the existence of a genuine incommensurate-commensurate transition (ICT). Besides, these compounds exhibit nonlinear transport properties⁷ associated with the depinning of the charge-density wave (CDW), as well as metastability^{8,9} and memory effects.¹⁰

Our interest in studying the NMR of the ^{87}Rb in $\text{Rb}_{0.30}\text{MoO}_3$ was manifold: First, pulsed NMR in single crystals has proved to be a powerful tool for studying at a microscopic level the static and dynamic properties of CDW¹¹⁻¹³ and, more generally, of incommensurate systems¹⁴; this technique is particularly appropriate to the study of the ICT.^{14,15} Second, there has been a strong temptation for a few years to study by NMR the depinning of CDW under an applied dc electric field and the related so-called "narrow-band noise."

Three classes of compounds, exhibiting both CDW on one hand and non-Ohmic transport properties associated with the depinning of CDW on the other, offer this possibility: the trichalcogenides of transition metals (NbSe_3 , TaS_3),¹⁶ the halogenated transition-metal tetrachalcogenides^{13,17} (TaSe_4)₂I, (NbSe_4)_{10/3}I, and the blue bronzes.

However, clean experiments require the study of a

truly single crystal, necessary for a clear interpretation of both NMR and transport measurements. In the case of NbSe_3 , the natural size of crystals is so small that up to now NMR studies have been restricted to pseudomonocrystals¹⁸ (a bunch of crystals aligned along the **b** axis), or nuclear quadrupole resonance in powders.¹⁹ Among the halogenated tetrachalcogenides of the transition-metal family, the onset of a CDW has been studied by NMR in a single crystal of (NbSe_4)_{10/3}I, but the interpretation of the spectra is made difficult by the existence of a large number of inequivalent Nb sites above the Peierls transition. As far as the blue bronzes are concerned, the size of the crystals can be easily varied to meet an optimum between resistivity and NMR requirements. Although the only nuclei one can study are the alkali ions (^{87}Rb), which do not belong to the conducting chains and thus provide an indirect picture of the CDW, $\text{Rb}_{0.30}\text{MoO}_3$ seems to be the most promising candidate for an NMR study of CDW under applied dc current. In this spirit, we present preliminary NMR results on the static properties of the CDW in this compound and particularly on its interaction with impurities.

The samples were prepared by electrolytic reduction of a $\text{Rb}_2\text{MoO}_4\text{-MoO}_4\text{-MoO}_3$ melt. Three different crystals were investigated weighing respectively 80, 40, and 110 mg (No. 1 and No. 2 belonged to the same batch). In all experiments, the Bruker CXP-100 spectrometer was operated at 83 MHz and the external magnetic field H_0 lay in the (**b**, **a** + 2**c**)¹ plane of the crystal. Most of the spectra were obtained from the Fourier transform of half of a solid echo. The complex Fourier transform (without apodization) was performed after averaging over a few hundred echoes (depending on the temperature) using a Nicolet LAS 12/70 transient analyzer. Final phase adjustments

were achieved on a HP 9836 computer, and no further mathematical filtering was applied to the resulting spectra. The crystal and the homemade probe head were placed in a CF-200 Oxford cryostat, and the temperature was monitored to better than 0.1 K.

In the unit cell of $\text{Rb}_{0.3}\text{MoO}_3$ there are two inequivalent Rb sites, with respective populations in the ratio 1:2.¹ Although their local symmetry is relatively high, neither of the two sites is axial. ^{87}Rb has a spin $I = \frac{3}{2}$, and one thus expects two different sets of first-order quadrupole satellites in the normal metallic phase. When \mathbf{H}_0 is perpendicular to the \mathbf{b} axis we observed that the $(\frac{1}{2}, \frac{3}{2})$ transition gives rise to two distinct quadrupole satellites, but those corresponding to the $(-\frac{1}{2}, -\frac{3}{2})$ transition are unresolved, although the linewidth at 329 K is as small as 6 kHz. The separation between the central line and the lower satellite is 270 kHz at 245 K. In the following, we shall not discuss further the electric-field gradient tensors experienced by the two Rb sites in absence of CDW, but we shall concentrate on their variation due to the onset of CDW and we shall restrict our analysis to the temperature dependence of the line shape of the lower satellite.

In Fig. 1, we show the temperature dependence of the $(\frac{1}{2}, \frac{3}{2})$ transition line shape in the temperature range 250–140 K. One can observe two regimes: Above 184 K, a pretransitional broadening occurs which will be discussed in more detail later on. Below 183 K, the broadening becomes much more pronounced, and the line shape becomes double horned, as expected from an incommensurate single- q CDW. The interpretation is quite straightforward, provided a number of simplifying assumptions are made. At the onset of the CDW the charge perturbation gives rise to a spatial distribution of electric-field gradient tensors at the Rb sites. An eventual distribution of Knight shifts can be neglected, since neither the position nor the line shape of the $(\frac{1}{2}, -\frac{1}{2})$ transition is modified in the same temperature range. We shall assume, neglecting the asymmetry of the tensors and the non-local effects of the charge distribution, that the change of the first-order quadrupole splitting at site \mathbf{R} can be

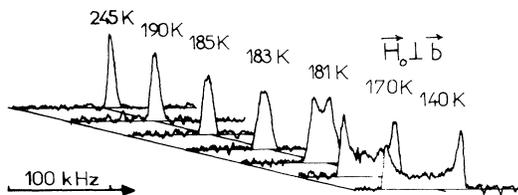


FIG. 1. Typical spectra recorded by Fourier transform of half a solid echo in the temperature range 250–140 K.

expressed as a power expansion of the order parameter η leading to

$$\Delta\nu_Q(\mathbf{R}) = \alpha \cos(2\mathbf{k}_F \cdot \mathbf{R} + \phi) + \beta \cos^2(2\mathbf{k}_F \cdot \mathbf{R} + \phi), \quad (1)$$

where α and β are coupling constants in kilohertz (respectively proportional to $|\eta|$ and $|\eta|^2$), and where we restrict ourselves to the plane-wave approximation. The extraction of the resulting line shape $g(\nu)d\nu$ reduces to a straightforward calculation of density of states and has been analyzed in great detail by Blinc.¹⁴ In our case, the positions of the singularities are characteristic of a dominant linear coupling. So in our computer fits of the line shape, we only used the parameter α , although setting $\beta \neq 0$ leads to a better agreement, especially as far as the asymmetry of lines is concerned. We thus extracted the temperature dependence of the order parameter (Fig. 2), which compares well with that obtained from neutron-⁴ and x-ray scattering.⁶ This allows the determination of $T_I = 184$ K. As we shall see later, the behavior of η close to T_I is dominated by defects and the thermal history of the sample; as a consequence, we did not try to extract a critical exponent from our data.

When one is approaching the ICT, the CDW can no longer be described as a plane wave, but as a regular array of discommensurations or solitons, separating commensurate domains.²⁰ As far as the NMR spectrum is concerned, one expects the continuous distribution of Fig. 1 to be replaced by a set of discrete lines, corresponding to the finite number of inequivalent sites in the commensurate domains. The lines will grow at the expense of the continuum background because of nuclei in the discommensurations width.¹⁴

In our case, a discontinuous change of the line shape between 95 and 90 K (Fig. 3) was observed in the first two runs (separated by a few months) in sample No. 1.

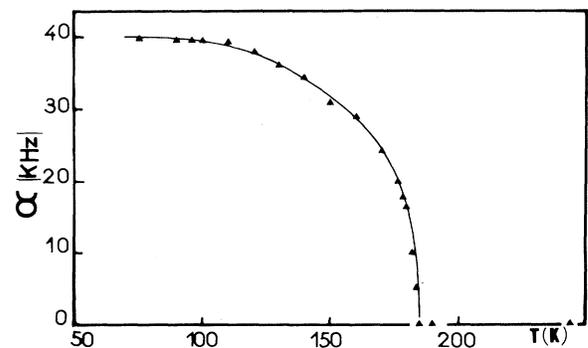


FIG. 2. Temperature dependence of the amplitude of CDW, on the assumption that the quadrupole splitting is linearly dependent on the amplitude α of a plane wave.

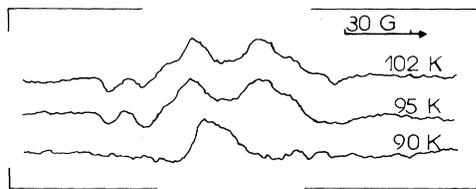


FIG. 3. Change of the line shape attributed to the incommensurate-commensurate transition in sample No. 1 (first heating-cooling cycle). The line shape was obtained by analog Fourier transform, using a boxcar integrator and sweeping the magnetic field H_0 .

This disappearance of the double peak in the spectrum (which was less marked in the second run) can be taken as qualitative evidence for an ICT in the sample. But these spectra do not represent the real line shape, since the repetition rate of the pulse sequence was too fast ($R_R = 3.3$ Hz). In subsequent experiments, careful recording of the line shape in the temperature range 140–150 K did not reveal any ICT, whatever the repetition rate (varied between 0.1 and 10 Hz). Suspecting that the repeated heating-cooling cycles could introduce new defects in the crystal, thus quenching the ICT, we repeated the same type of measurements in samples No. 2 and No. 3, neither of which displayed ICT, even during the first cooling cycle. Possible explanations could be the following:

(i) The ICT is very sensitive to and can be quenched by charged “impurities” which play a major role in the blue bronzes. These impurities might be the result of a stoichiometry defect, and therefore be alkali vacancies.

(ii) The “impurity content” is time dependent even in the absence of a heating-cooling cycle, which suggests a slow oxidation process which, for example, increases the number of Rb vacancies.

Our computer simulations²¹ show that low-temperature line shape in absence of ICT cannot be interpreted in the framework of a multisoliton lattice, except if one assumes solitons’ width of the same order of magnitude as their interspacing.

As observed in Fig. 1, the broadening of the $(\frac{1}{2}, \frac{3}{2})$ transition starts well above $T_I = 184$ K, determined from the computer line-shape analysis. Such a pre-translational broadening in the temperature range $(T_I, 2T_I)$ was already observed in $2H\text{-NbSe}_2$.¹¹ As in this two-dimensional compound, it does not result from dynamic fluctuations of the order parameter, but from an anomalous screening (Friedel oscillations) of impurities due to the divergence of the electric-response function $\chi(\mathbf{q} = 2\mathbf{k}_F)$ with $T - T_I$. At $T = 200$ K, the whole line is broadened, which means that all the nuclei in the crystal feel these overlapping CDW clouds. This seems to indicate that at least in our samples, the weak-coupling theory²² must be applied.

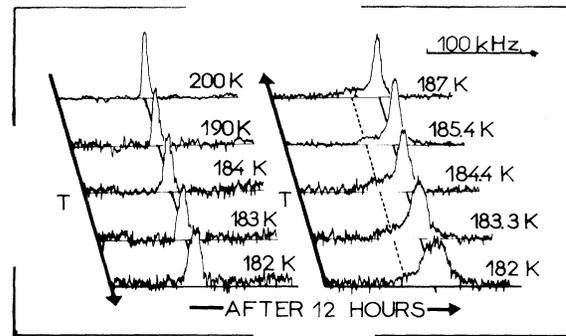


FIG. 4. Variation of the line shape along a cooling-heating cycle around T_I . The interaction of the CDW with mobile defects leads to an increase of the linewidth by a factor of 2 on a time scale of 12 h. Because of the partial ordering of the defects, a remanent CDW persists above T_I in part of the sample.

Such a long-range coupling between charged impurities and the order parameter leading to overlapping clouds of CDW above the long-range-order transition temperature T_I seems to be a unique feature of low-dimensional conductors, and has not yet been reported in incommensurate dielectric systems.¹⁴

Another “impurity” effect, which is now time dependent, is shown in Fig. 4. A cooling-heating cycle around the T_I was performed, including one night at 182 K. Two features should be noted: Firstly, after the sample was kept for over 12 h at 182 K, the linewidth, i.e., the order parameter, increased by a factor of 2! This broadening is not homogeneous, since a still broader underlying line can be observed. This we interpret as the first observation of an interaction between CDW and mobile defects. Such a coupling has been observed in incommensurate dielectrics, such as thiourea²³, for example, and proposed to explain memory effects in these systems. Recently, a large time dependence of the order parameter just below the normal incommensurate transitions has been observed by x ray and birefringence in barium sodium niobate,²⁴ in great similarity with our case. Those authors also considered alkali vacancies as the mobile species. Lederer, Montambaux, and Jamet²⁵ have made some predictions concerning defect-density wave resulting from the interaction between CDW and mobile defects. They predicted an increase of the order parameter when $T < T_I$, which we have indeed observed, and also a large positive shift $T_I \approx 2c_0 V_0^2 / T_I$ where c_0 is the impurity concentration and V_0 the coupling strength. On the right side of Fig. 4, corresponding to the signal after about 12 h relaxation at 182 K subsequent to heating, one can note a broad line persisting well above $T_I = 184$ K, corresponding to about one half of the nuclei. This we interpret as domains of remanent long-range-ordered CDW in the tempera-

ture range ($T_I, T_I + \Delta T_I$). From our experiments, ΔT_I is about 10 K; the variation of the line shape on the right-hand side of Fig. 4 is reversible as long as the temperature is kept lower than 200 K.

This latter effect has to be taken into account in the interpretation of the resistivity data, which are found to be time dependent even in the Ohmic regime^{8,9,26}; we believe that it contributes to memory and thermoremanent effects present in these compounds. Moreover, it is clear that the presence of mobile defects, giving rise to different quenched configurations at low temperature, is a source of metastable states.²⁷ This raises a series of questions:

(i) How much are these (charged) defects mobile under the applied dc electric field?

(ii) To what extent are they related to the very low frequencies present in the narrow-band noise observed in these compounds,²⁸ and also to the low-frequency behavior of the dielectric susceptibility²⁹?

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