Ultrasonic properties of quasi-one-dimensional blue bronze $K_{0.3}MoO_3$

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We report ultrasonic measurements on quasi-one-dimensional $K_{0.3}MoO_3$. Softening of the longitudinal modes along the *b* axis and the [102] direction has been measured at the Peierls transition. No electric field effect is observed on the sound velocity in the low-temperature phase.

Molybdenum blue bronze $K_{0.3}MoO_3$ is a quasi-one-dimensional conductor[1] which undergoes a Peierls transition at $T_p = 180$ K. Phonon softening at $2K_F$ (Fermi momentum) induces lattice modulations associated with an electron charge-density wave (CDW). The crystal structure is monoclinic and the crystallographic *b* axis is the highly electric conducting axis.[1,2] The anomaly in the electrical properties at T_p corresponds to a metal-semiconductor transition. At low temperatures the resistance becomes non-Ohmic if the measuring voltage exceeds a threshold value V_T and nonlinear properties are associated with the charge-density-wave motion.[1] Low-frequency elastic experiments[3] have been performed on this compound, and to our knowledge no experimental investigation with ultrasonic methods has been reported so far. Theoretical predictions on the electric field dependence of the elastic properties of charge-density-wave conductors have been given.[4-6]

In the present investigation we report ultrasonic measurements performed on a single crystal of $K_{0.3}MoO_3$ cleaved into thin plates of typical dimensions $5 \times 2 \times 0.5$ mm^3. The largest dimensions 5 and 2 mm are parallel to the *b* axis and the [102] direction, respectively. The acoustic measurements were performed on the same samples used with the electric measurements.[7] Because of the existence of a large number (13) of independent elastic constants related to the monoclinic symmetry, elastic measurements were performed only with longitudinal modes. Three longitudinal modes were generated along the *b* axis, the [102] direction, and the [201] direction perpendicular to the plate.[1] The standard pulse-echo technique[8] was used with $LiNbO_3$ transducers. The samples were small and the measurements were performed with the buffer-rod technique described by Mc Skimin[9] (the sample was bounded to one end of a buffer quartz rod). The sound-velocity change was measured by a phase-coherent detection.[8] The measurements related to the C_{22} mode along the *b* axis were performed with a transducer bounded directly on the sample with gold paint and conducting epoxy. The acoustic bond also served as one of the electrical contacts for the electrical field applied along the *b* axis. The electrical field effect on the travel time of an acoustic echo propagating along the *b* axis and the [102] direction was measured with the superposition of an electric pulse with electric field parallel to the *b* axis. Care was taken to avoid spurious effects

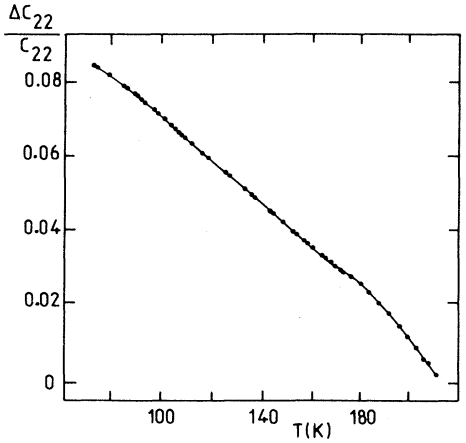

FIG. 1. Relative change of the elastic stiffness C_{22} measured at 15 MHz.

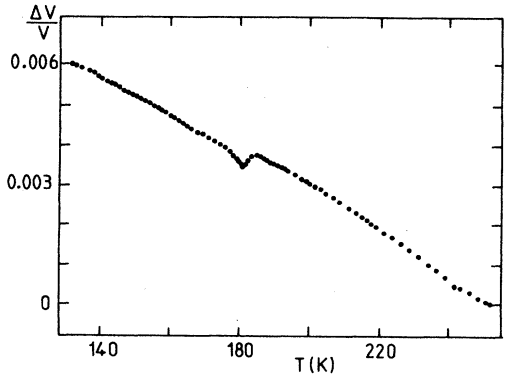

FIG. 2. Relative change of sound velocity of the longitudinal mode generated along the [102] direction at 46 MHz.

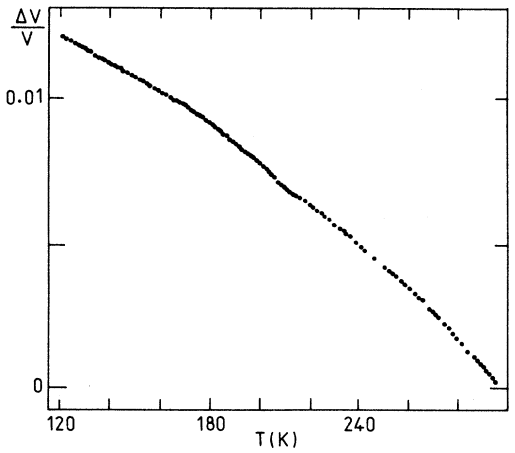

FIG. 3. Relative change of sound velocity of the longitudinal mode generated along the [201] direction at 46 MHz.

due to sample heating by the electric pulses. The experimental procedure was similar to that described in Ref. 10. A 30-μs-wide electric pulse was applied and its position was adjusted in order to cover completely the travel period T (about 8 μs) of a selected acoustic echo 1 μs wide. T was measured while the electric pulse was delayed progressively until the selected acoustic echo was outside the electric pulse.

Elastic stiffness constants were deduced from the sound-velocity results with the density[2] $d=4.3$ g/cm^3, $C_{22}=8.7\times10^{11}$ dyn/cm^2, and $C_\perp=4\times10^{11}$ dyn/cm^2 deduced from the velocities 4.5×10^5 and 3.1×10^5 cm/s of the longitudinal modes generated along the b axis and the [102] direction, respectively. The modes C_{22} (Fig.1) and $C_\perp$ (Fig. 2) have their modulus softened at T_p, but no anomalous behavior (Fig. 3) within the experimental accuracy is observed for the mode along the [201] directions. At T_p, after subtracting the thermal variation, a relative shift $\Delta C_{22}/C_{22}\simeq8\times10^{-4}$ is estimated (Fig. 1) and $\Delta C_\perp/C_\perp\simeq6\times10^{-4}$ (Fig. 2). $\Delta C_{22}/C_{22}$ is comparable with the results obtained at lower frequencies[3] but $\Delta C_\perp/C_\perp$ is 1 order of magnitude smaller than the decrease of the Young's modulus[3] perpendicular to the b axis. Softening of the $C_\perp$ mode at T_p can be analyzed with a power law of the reduced temperature $t=|T-T_P|/T_P$:

$$\frac{\Delta C_\perp}{C_\perp}\sim t^\rho . \tag{1}$$

A critical exponent $\rho\simeq1$ was determined in the temperature range $10^{-3}\le t\le10^{-2}$ above and below T_p. Thermodynamics analysis[11] of a second-order phase transition gives a discontinuity of the bulk modulus B related to the specific anomaly ΔC and the stress dependence $\partial T_c/\partial P$ of the transition temperature T_c:

$$\frac{\Delta B}{B}\sim-B\frac{\Delta C}{T_c}\left[\frac{\partial T_c}{\partial P}\right]^2 . \tag{2}$$

Using $\Delta B/B\simeq6\times10^{-4}$ and $\Delta C\simeq4\times10^4$ dyn/cm^2 K corresponding to the entropy change[1,3] 150 mJ/mol in $K^{0.3}MoO_3$, Eq. (2) gives $\partial T_c/\partial P\simeq2$ K/kbar, comparable to that observed in different CDW conductors.[3,12] No anomaly related to a lock-in incommensurate-to-commensurate transition[1] around 100 K is observed in the temperature dependence of C_{22}, in agreement with lower-frequencies results.[3] No electric field effect within the measurement resolution 3×10^{-6} was observed on the sound velocity of the C_{22} mode for applied voltages as high as $10V_T$ and $3V_T$ at 77 and 4.2 K. No change at 77 K was observed on the sound velocity of the $C_\perp$ mode with an applied voltage of $10V_T$, the electric field being parallel to the b axis. The values of the threshold voltages $V_T\simeq0.1$ and 9 V at 77 and 4.2 K, respectively, were deduced from electric measurements performed on the same sample used with the acoustic measurements. The low-temperature (4.2K) nonlinear I-V curve was similar to that reported in Ref. 7 with a threshold voltage $V_T\simeq9$V.

In conclusion, the present ultrasonic measurements point out a softening of the longitudinal elastic constants C_{22} and $C_\perp$ defined along the [102] direction at the Peierls transition in $K_{0.3}MoO_3$. The decrease $\Delta C_{22}/C_{22}$ is comparable with the decrease $\Delta C_{33}/C_{33}$ observed[13] along the highly electric conducting axis in $(TaSe_4)_2I$ and is 1 order of magnitude smaller than that observed[10] at the same frequency in TaS_3. Finally, no electric-field-induced softening of the modes C_{22} and $C_\perp$ is observed, in agreement with lower frequencies.[3] CDW depinning by application of electric fields greater than the threshold field does not affect the elastic properties of $K_{0.3}MoO_3$. This result confirms that the electron-phonon–coupling constant[4] in this system is smaller than that observed[14] in TaS_3.

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