Electromodulated Infrared Transmission in Blue Bronze

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The infrared transmittance of the quasi-one-dimensional charge-density-wave (CDW) material blue bronze ($K_{0.3}MoO_3$) is observed to be affected by an applied electric field. The effect is interpreted in terms of changes in free carrier absorption resulting from surprisingly large changes in the density of quasiparticles which screen the CDW polarization at electrical contacts. The magnitude of the screening charge has a maximum at 110 K, and is thermally activated below this temperature.

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Quasi-one-dimensional metals undergoing phase transitions into charge-density-wave (CDW) states, in which the lattice constant and conduction band charge are periodically modulated, exhibit a large array of unusual electronic properties [1]. In these materials, the equilibrium CDW is pinned to the crystal by a potential established by random defects. While most of the unusual properties are related to motion of the CDW in an applied electric field greater than the threshold needed to depin it, there are also unusual properties associated with the large number of metastable CDW states associated with different phase configurations in the random potential. These metastable states manifest themselves in a variety of properties such as history dependent "normal" (i.e., due to quasiparticles at fields below threshold) resistance and polarization phenomena associated with deformation of the CDW near electrical contacts [2–4]. While deformations have been observed with x-ray diffraction [5,6], the most common experimental probes of these metastable states are transport measurements. In the latter, it is difficult to separate the effects of changes in CDW density (n_c), quasiparticle density (n_{qp}), CDW mobility, and quasiparticle mobility [2–4].

In this paper, we report on changes in the infrared transmission near electrical contacts of the CDW material blue bronze ($K_{0.3}MoO_3$) [7,8]. The motivation of the experiment was to search for spectral changes expected as signatures of CDW deformation (spatially varying amplitude and/or phase) [9]. Instead, the changes observed are approximately independent of optical frequency over a wide spectral range. The electromodulated transmission appears for currents for which polarization of the CDW also becomes apparent. The changes (an increase in transmission at the positive contact and a decrease at the negative contact) are interpreted in terms of surprisingly large (approaching 100%) changes in the density of quasiparticles screening the CDW deformations at the contacts, and are the results of the huge CDW polarizability [1]. This is the first report of changes in optical properties due to deformation of a CDW. While electric field induced changes in free carrier absorption have been observed for conventional semiconductors [10], in the present case the ionized defects are not static impurities but reversible deformations of the CDW *created* by the small electric field.

Blue bronze is a quasi-one-dimensional metal which undergoes a CDW transition into a semiconducting state, with gap $\sim 1200\ \mathrm{cm}^{-1}$ at 180 K [7,8]. While the CDW is incommensurate near 180 K, its wave vector changes with temperature above 120 K, approaching the commensurate value (0,0.75,0.5), where **b** is the high-conductivity direction [11]. The threshold electric field for CDW depinning and non-Ohmic conduction is temperature and sample dependent, but in typical samples has a value of 0.1 V/cm at 80 K [1,8,12]. Hysteresis in the normal conductivity is observed between 45 and 145 K [13].

In the present set of experiments, crystals of blue bronze were cleaved to thicknesses of $\sim 5\ \mu$m. (All data shown in this paper are for a single sample, 1.1 mm$\times$0.5 mm, but qualitatively similar results were observed in other samples.) Two contacts were put on the ends of the sample by silver painting onto evaporated copper films. The sample was placed over a slit in an opaque, insulating thin film on a KRS5 substrate at the end of a cold finger at the focus of a grating infrared spectrometer with a globar source, and the transmitted light was refocused onto a Ge(Zn) photodetector. The diameter of the spot size at the sample was ~ 0.4 mm. The KRS5 cryostat windows and substrate limit our spectral range to $> 250\ \mathrm{cm}^{-1}$. In some experiments, apertures were placed over different portions of the sample. Transmission spectra were taken by chopping the light, while current induced transmission changes were searched for by applying (symmetric or biased) square wave voltages to the sample while illuminating the sample continuously. The ac detector signal (at either the voltage modulation frequency or chopping frequency) was measured with a two-phase lock-in amplifier. For the light intensities and currents used, heating of the sample was determined to be small, and had no significant effect on the results [14].

We observed that, depending on the placement of the aperture, the ir transmission was significantly modulated by the alternating voltage in the sample. The voltage dependence at 82 K, for a symmetric square wave voltage at 137 Hz, of $|\Delta\tau|$, the amplitude of the electromodulat-

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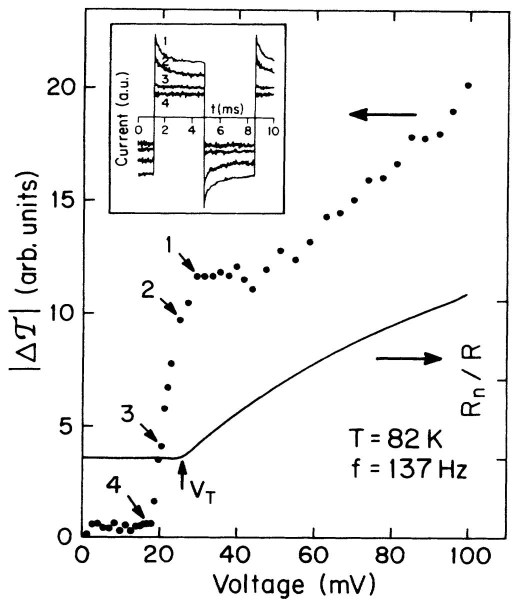

FIG. 1. The amplitude of the electromodulated response vs voltage for symmetric square waves. V_T is the CDW depinning threshold voltage. Also shown is the voltage dependence of the conductance, $1/R$, normalized to its value $(1/R_n)$ below threshold. The inset shows the shapes of the current wave forms for the voltages indicated by the numbered arrows.

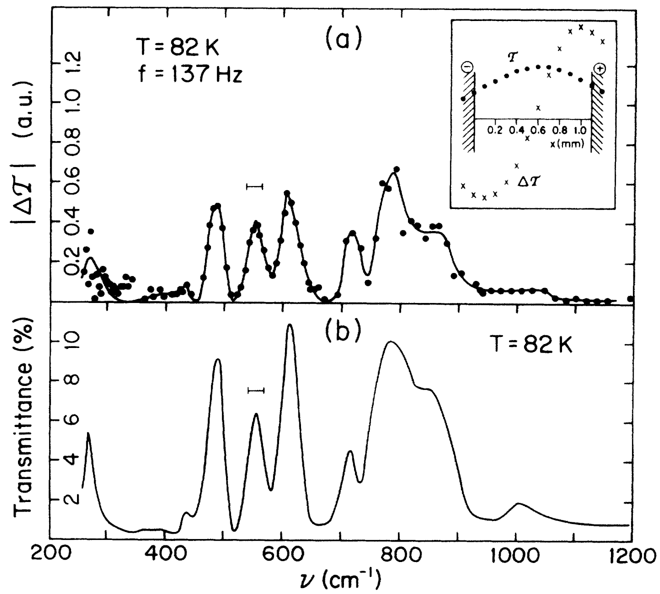

FIG. 2. The transmission (τ) spectrum (b) and the electromodulated transmission ($\Delta\tau$) spectrum (a) (the curve is a guide to the eye). The resolution is shown by horizontal bars. The inset shows the spatial dependence of both signals; the shaded vertical lines indicate the location of the contacts.

ed transmission, with one side of the sample blocked is shown in Fig. 1; also shown is the sample conductance. (In this experiment, the spectrometer was set so that the electromodulated response was integrated over the spectral range 250–700 cm^{-1}.) For small voltages, $\Delta\tau$ is below the noise level of the detector. $\Delta\tau$ grows rapidly out of the noise at a voltage somewhat smaller than V_T, the threshold for depinning, and has a local maximum near V_T. Also shown in the inset to Fig. 1 are the shapes of the current responses of the sample to the oscillating voltage; the spikes at the beginning of each half cycle (i.e., the "overshoot" effect [2]) are caused by repolarization of the CDW. The onset of the overshoot coincides with the onset of electromodulation. Thus it is natural to associate the electromodulation with the CDW polarization. Supporting this association is the observation that negligible ac electromodulated transmission is observed for unipolar pulses (for which the polarization is approximately fixed) [2].

In the inset to Fig. 2, the position dependence of $\Delta\tau(x)$ at 82 K and 460 Hz for a symmetric square wave (with amplitude $|V|=3.8V_T$) is shown. For these measurements, no aperture was placed on the sample and the (magnitude and sign) of the detector response "in-phase" with the modulating voltage measured. Also shown is the position dependence of the transmission τ at the same chopping frequency. $\Delta\tau(x)$ has opposite sign with respect to the voltage at the two contacts, so that no "average" signal, e.g., at the center of the sample, is seen. The spatial profiles for both the transmission and electromodulated transmission signals are clearly affected by the large (0.4 mm) spot size; however, the relative modulation, $\Delta\tau/\tau$, with a 100 μm aperture very near the contact was approximately double the value of $\Delta\tau/\tau$ for light illuminating half the sample, indicating that the spatial profile of the electromodulated signal is approximately linear. The sign of the electromodulation is such that the transmission increases at the positive contact and decreases at the negative. (At 110 K, the change in transmission is sufficiently large ($\sim 1\%$) that it can also be observed with a dc current.)

The transmission [7,15,16] and electromodulated transmission spectra are shown in Fig. 2. The electromodulated spectrum was, within our resolution, identical to that of the transmission spectrum; both signals are also approximately polarized perpendicular to **b** [15]. $\Delta\tau \propto \tau$ implies that $\Delta\alpha$ (the absorption coefficient) is independent of wavelength. Defect states associated with deformation of the CDW are expected to give rise to states within the CDW gap [9,15,17]; while these features may be broad, they should not fill the gap. The wide spectral range of the electromodulated spectrum suggests that it is due to a change in the free carrier absorption. A negative (positive) CDW will be compressed at the positive (negative) contact and rarified at the other, shifting the chemical potential [18,19] and concentration of quasiparticles. If these screening quasiparticles are electrons (holes), they will be compressed at the negative (positive) contact and rarified at the positive (negative). The phase of the electromodulated signal indicates that the mobile quasiparticles are electrons, consistent with the sign of the

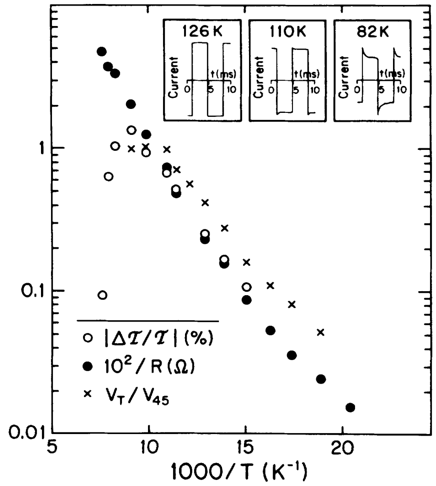

FIG. 3. The temperature dependence of the (low field) conductance, electromodulated transmission (near V_T), and "knee voltage," V_{45}, where the electromodulated response lags the applied voltage by 45° at 137 Hz (see Fig. 4). The insets show the current wave forms at a few temperatures.

Hall effect [20]. The large spatial extent of Δn_{qp} must be caused by a CDW deformation extending throughout the sample [5,19].

That the electromodulation is caused by the quasiparticles is also suggested by its temperature dependence, plotted in Fig. 3. (Plotted is $|\Delta\tau/\tau|$ at its local maximum near V_T.) For temperatures below 110 K, $|\Delta\tau/\tau|$ has an Arrhenius behavior similar to that of the conductance, also shown, suggesting that it is limited by the quasiparticle density. In the low-conductivity limit, appropriate to the transverse conductivity [8], the free carrier absorption is wavelength independent and proportional to the conductivity, $\alpha=(377\,\Omega)\sigma$. Assuming that the transverse mobility [8,20] and reflectivity are not significantly affected by the CDW deformation, we find that the change in electron density $\Delta n_{\mathrm{qp}}(T)\sim n_{\mathrm{qp}}(T)/2$ for $T<110$ K, where $n_{\mathrm{qp}}(T)=|1/eR_H(T)|$ and R_H is the low field Hall constant [20].

The charge density associated with the overshoot during a half period of the oscillation is much smaller. The current wave forms at several temperatures are shown in the Fig. 3 insets. For $T<110$ K, we measure

$$\Delta n\ (\text{overshoot})\sim\int\Delta I\,dt/e\Omega\sim 2\times10^{16}/\text{cm}^3\sim 4\times10^{-6}n_c$$

[20], where ΔI is the overshoot current and Ω the sample volume. Wang and Ong [3] have shown that, depending on sample history, the polarization may take several seconds to develop fully, in which case they obtain a maximum $\Delta n(\text{overshoot})\sim10^{-5}n_c$. In comparison, $\Delta n_{\mathrm{qp}}\sim n_{\mathrm{qp}}\sim10^{-3}n_c$ at 82 K. Therefore, our results indicate that the polarization is almost completely screened by the quasiparticles at temperatures above 80 K, so that the polarization charge observed in transport measurements is a small fraction of the total polarization of the CDW.

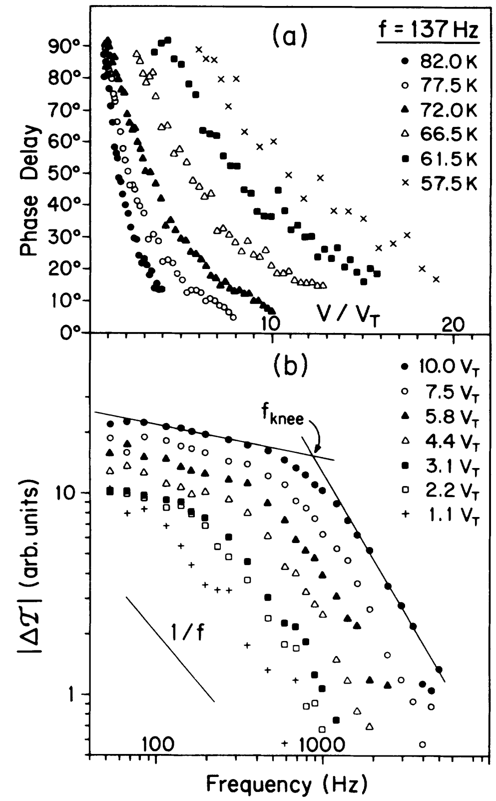

FIG. 4. (b) The amplitude of the electromodulated response vs frequency for several voltages at 72 K. The lines for $10V_T$ indicate how the knee frequency may be defined. (a) The phase delay of the electromodulated signal as a function of voltage for several temperatures at 137 Hz.

With decreasing temperature, of course, the screening by quasiparticles becomes worse.

The precipitous decrease in the electromodulated signal for temperatures above 110 K is mirrored in a decrease in the overshoot phenomena, as shown in Fig. 3. The lack of an electromodulated response indicates that the lack of an overshoot is not due to screening; instead we suggest that the polarization of the CDW cannot develop because thermally activated phase slip processes (i.e., local collapse of the CDW amplitude) can now occur readily [21]. Similarly, the lack of hysteresis at high temperature [13] indicates that metastable states are not accessed for macroscopic time scales, even though the CDW wave vector is temperature dependent here, so the optimum pinning configuration should also be.

We have also started measurements of the dynamics of the polarization associated with the electromodulation. For any square wave voltage, the electromodulated response decreases with frequency. In Fig. 4(b), the frequency dependences of $|\Delta\tau/\tau|$ for several voltages at 72 K are shown. For low frequency, the frequency dependence is much weaker than $1/f$. Above a knee frequency, which is approximately proportional to voltage, the frequency dependence becomes stronger, approaching $1/f^2$.

The typical time scale of $1/2\pi f_{\text{knee}} \sim 1$ ms is comparable to estimates of Wang and Ong [4] for repolarization and implies a typical propagation velocity of 1 mm/1 ms, similar to the velocity observed for voltage pulse propagation by Csiba, Kriza, and Janossy [22], and much greater than estimates of the CDW propagation velocity [12]. In Fig. 4(a), we plot the voltage dependence of the phase shift (at 137 Hz) for several temperatures. Below the knee frequency (i.e., for $V \gg V_T$), the electromodulated response is in phase with the modulating voltage, as expected. As V approaches V_T, the electromodulated response lags the applied voltage by 90°, indicating that the rate of repolarization, dP/dT, is approximately constant during a half cycle. The "knee" voltage, where the response lags the applied voltage by 45°, has an activation energy similar to that of the conductivity, as shown in Fig. 3. This Arrhenius behavior is similar to what has been observed for various transport properties [23], and is thought to reflect the fact that, in order to sample different metastable configurations (i.e., to repolarize), the CDW must be locally screened by the quasiparticles [18,23].

In conclusion, we have observed electric field induced changes in infrared transmission due to polarization (i.e., deformation) of the CDW in blue bronze. These are interpreted in terms of surprisingly large changes in population of the quasiparticles, approaching 100% of their thermal population over a large fraction of the sample length, indicating that transport measurements only reveal a small fraction of the polarized charge. Optical probes may therefore allow a direct measurement of the spatial distribution of the CDW deformation and its time and field dependence.

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