Brief Reports

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Conductivity mode in blue bronze

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We have extended far-infrared reflectance measurements of $K_{0.3}MoO_3$ to frequencies as low as 4 cm^{-1} using a Martin-Puplett interferometer and a ^{3}He-cooled bolometer. The new results, combined with other measurements, span an energy range from ~ 0.5 meV to 6 eV and reveal two optically active modes arising from charge-density waves, the lower of which is near a frequency of 3 cm^{-1} (corresponding to a thermal energy of 4 K, slightly above the sample temperature of 2 K in our experiment). We interpret the peaks as new evidence of pinned charge-density waves, in addition to the Raman-active mode previously seen at higher frequencies.

In this paper we present far-infrared reflectance measurements of blue bronze ($K_{0.3}MoO_3$) down to a frequency of 4 cm^{-1}. Our motivation was to fill in the gap between microwave frequency data,[1-3] which indicated a rising conductivity up to ~ 0.3 cm^{-1} (9 GHz), and optical data[4] which extended down only to 20 cm^{-1}. Our results strongly suggest a new peak at about 3 cm^{-1}, which we interpret as a pinned charge-density-wave (CDW) mode in addition to the two modes previously observed at higher frequencies. We also find that the lower of these two modes occurs at 22 cm^{-1}, rather than at 15 cm^{-1} as estimated by an extrapolation of previous optical data.

The new low-frequency mode is, in some respects, comparable to modes observed in other systems. Within analysis using the single-oscillator model, the relatively large damping frequency (5.5 cm^{-1}), compared to the maximum conductivity [130 $(\Omega\,cm)^{-1}$] indicates a large effective mass for the pinned mode ($10^4 m_e$). Systematic uncertainties involved in our analysis are estimated to be of the order of a factor of 2, although within our fitting procedure the random errors are only about 10%. Our results seem compatible with mm-wave measurements[5] on other inorganic compounds, $NbSe_3$ and TaS_3, both of which show a pinned mode at relatively low frequency ~ 0.3 cm^{-1} (~ 10 GHz).

We have used a Martin-Puplett[5] interferometer to probe the frequency region below 20 cm^{-1}. The light incident on the sample was polarized with the electric field along the *b* axis of the $K_{0.3}MoO_3$ single crystal. For our reference in the reflectivity measurements we used polished brass. After a single reflection the radiation was detected with a bolometer operating at a temperature of 350 mK.

Figure 1 shows the reflectance R for **E** $\|$ **b** at $T=2$ K. We find little noticeable difference in R for T up to 15 K. For comparison we have plotted the reflectance data from Travaglini and Wachter[4] for blue bronze of the same nominal composition. (The dash-dot line shows their extrapolation of the reflectance below a frequency of 20 cm^{-1}). The two curves have shapes that are qualitatively similar. However, our reflectance data are about 3% lower below $\omega = 50$ cm^{-1}. Our estimated uncertainty in the magnitude of R is 0.5%. At lower ω, we have found a minimum in R at 8 cm^{-1}. From this point to our lowest frequency (4 cm^{-1}), the reflectance rises toward unity.

The complex conductivity was calculated using the standard Kramers-Kronig transformation,[6] incorporating data from Travaglini and Wachter up to a frequency of ~ 6 eV.

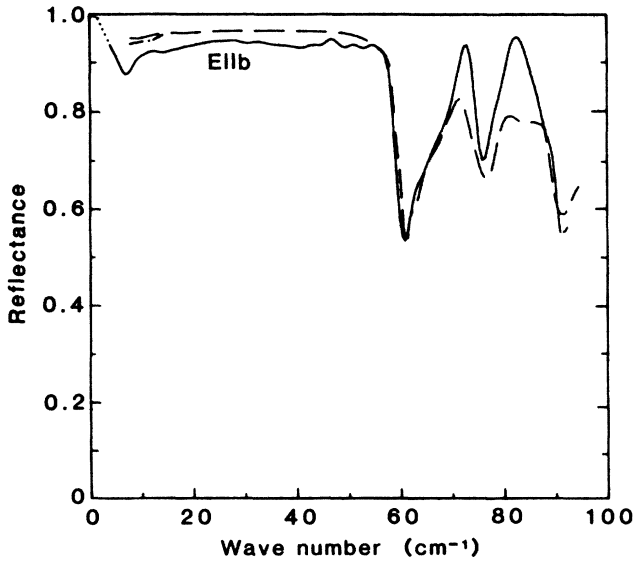

FIG. 1. Reflectance data for **E** $\|$ **b**: Solid line is this work at 2 K, dashed line from Ref. 4 at 5 K. Dotted line shows our extrapolation to $\omega = 0$.

Above this frequency a ω^{-4} tail was added analytically. Below our lowest frequencies, various extrapolations only changed the magnitude and not the profile of the conductivity above 4 cm^{-1}. Our choice was to extrapolate so as to reproduce roughly the microwave measurements.[2,3] These data are shown as triangular points in Fig. 2, along with the results of our analysis.

In Fig. 2 (solid line), we show a plot of $\sigma_1(\omega)/\sigma_{max}$ where σ_{max} is the maximum conductivity in this frequency region (below 8 cm^{-1}). In our case $\sigma_{max} \simeq 130$ $(\Omega\,cm)^{-1}$ and occurs at $\simeq 2.8$ cm^{-1}. The maximum conductivity is strongly affected by the magnitude of R and can be a factor of 2 higher. The rise in conductivity above 8 cm^{-1} forms the lower-frequency tail of the higher-frequency mode observed by Travaglini and Wachter[4] at 15 cm^{-1}, although we find its peak at 22 cm^{-1}. Raman scattering experiments[7,8] show a CDW amplitude mode $A+$ at higher frequency (50 cm^{-1}).

We have, for comparison, plotted the data taken at $T=160$ K (measured using microwaves) for TaS_3 by Shridhar, Reagor, and Gruner.[9] This compound undergoes a Peierls transition[10] at 225 K into a CDW state. The pinned frequency is at 0.3 cm^{-1} (10 GHz). At 40 K, the peak moves up in frequency to 1.7 cm^{-1} (50 GHz).

A simple phenomenological theory to describe the observed conductivity is the single-oscillator model

$$\sigma(\omega)=\frac{ne^2\tau}{m^*}\frac{i\omega}{(\omega_0^2-\omega^2)\tau+i\omega}, \tag{1}$$

where n, e, τ, and m^* are the electronic density, charge, relaxation time, and effective mass, respectively. In this model, ω_0 can be thought of as the pinning frequency. The dash-dot line shows a fit to the experimental data using $\omega_0=2.8$ cm^{-1}, $1/2\pi\tau=5.5$ cm^{-1}, and $\sigma_{max}=ne^2\tau/m^*=130$ $(\Omega\,cm)^{-1}$. The overall fit is reasonable although there probably is a distribution of pinning frequencies as found by Cava *et al.*[1] If another model is used for the frequency region below which we have data, we estimate that the pinning frequency and the peak conductivity might vary by as much as a factor of 2. However, the single-oscillator model works well in the two other materials referenced above, and we have no reason to expect that it will not work here.

Assuming that all the electrons entering the dc conductivity at room temperature participate in the sliding CDW, then the effective mass $m^*=ne^2\tau/\sigma_{max}\simeq 10^4 m_e$. (Due to the uncertainty in R alone, m^* could be a factor of 2 lower.) This assumption is not unreasonable since the dc conductivity at 2 K is practically zero, indicating that all the spectral weight has been transferred up into the infrared modes. In this calculation we use the electronic density[4] of 5.4×10^{21} cm^{-3}. Compared with other inorganic materials (at much higher temperatures), this effective mass is an order of magnitude larger. The larger mass may be due, in part, to increased interchain coupling in the CDW at the low temperature of our experiment, in addition to the growth of the order parameter.

A point to note when comparing our data with lower-frequency measurements is that all the lower-frequency measurements were done at higher temperatures (>40 K) than ours (2 K). In the higher-temperature regime, the real part of the conductivity shows a rise as a function of increasing frequency,[2] which is close to being proportional to $\sqrt{\omega}$. After rising to 26 $(\Omega\,cm)^{-1}$, it appears to saturate at a frequency of 0.3 cm^{-1} (9 GHz) when $T=40$ K. Our fits to the conductivity indicate that at low temperature the rise continues up to a peak of about 130 $(\Omega\,cm)^{-1}$ at 2.8 cm^{-1} (84 GHz). These two experiments are consistent provided that the temperature difference is taken into account. The studies below 9 GHz show a significant decrease in the conductivity as the temperature decreases, consistent with the shift in spectral weight discussed above.

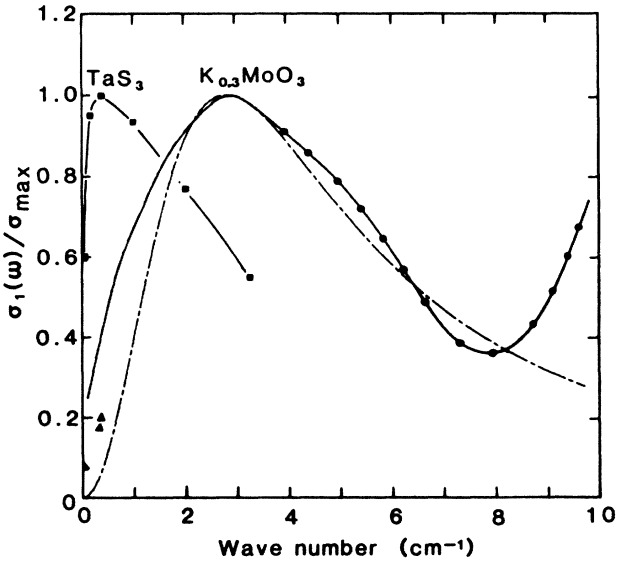

FIG. 2. Normalized conductivity (to σ_{max}) at $T=2$ K: Solid line is a guide to the eye above 4 cm^{-1} and the result of our extrapolations to low frequency. The dash-dot line is a fit using the single-oscillator model. Triangular points are microwave data at $T=40$ K (Refs. 2 and 3). For comparison the data for TaS_3 (squares, Ref. 7) at $T=160$ K are also plotted.

Our value of the pinned frequency 2.8 cm^{-1} (84 GHz) is roughly in the same frequency range as other inorganic CDW materials. For example, in TaS_3 the pinned frequency is at 0.3 cm^{-1} at 160 K and 1.7 cm^{-1} at 40 K. The mode observed at 15 cm^{-1} by Travaglini and Wachter is, however, about five times higher in ω and also temperature independent in its peak position. Intuitively one would expect the pinned mode to increase in frequency as the temperature decreases. A phonon that is strongly coupled to the CDW would not, however, be affected in frequency but decrease in oscillator strength as the temperature goes up.

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