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Optical investigation of quasi-one- and two-dimensional systems $A_{0.9}Mo_6O_{17}$ (A = Li, K, and Na)

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Reflectivity measurements of the ternary molybdenum oxide purple bronzes $A_{0.9}Mo_6O_{17}$ (A=Li, Na, and K) are presented at 300 and 6 K. The optical properties show different dependence of light polarization and temperature for the two-dimensional K and Na compounds compared to the one-dimensional Li compound. The possibility of a charge-density-wave onset is investigated, and a discussion in connection with recent transport-property investigations and new theoretical models is presented.

INTRODUCTION

The so-called "purple bronzes" $A_{0.9}Mo_6O_{17}$ (with A = Li, K, Na) belong to the family of ternary molybdenum oxides $A_xMo_zO_y$. In this class of materials the alkali metal (A) usually donates its outer electron to the transition metal (Mo). These electrons can partially fill the π^* conduction band, formed by the overlap of t_{2g} $4d$ orbitals of molybdenum and p_π orbitals of oxygen in the extended lattice, and the material will exhibit metallic behavior. If the electrons donated by the alkali metals are localized in the band-gap region of the usually insulating Mo_zO_y oxide, then the bronze $A_xMo_zO_y$ will be semiconducting.

Generally speaking, the molybdenum bronzes are near the boundary between the metallic and the semiconducting region: In the case of the tungsten bronzes M_xWO_3, the $5d$ electrons with large radial extension of their orbitals form good conduction bands, whereas the vanadium bronzes $M_xV_2O_5$ with localized $3d$ electrons have phase transitions to the insulating state. The electrical conductivity of these materials is correlated to the crystal structure.

$Na_{0.9}Mo_6O_{17}$ and $K_{0.9}Mo_6O_{17}$ are essentially isostructural. The crystal structure is built up of stacked layers of corner-sharing MoO_6 octahedra and MoO_4 tetrahedra. For the K and Na compounds each stack consists of four layers of MoO_6 octahedra, sharing corners with MoO_4 tetrahedra at the edges. These stacks are arranged perpendicular to the c axis and are held together by a layer of alkali ions in an icosahedral environment of oxygens. $Li_{0.9}Mo_6O_{17}$ has a similar structure, however, the stacks consist of three *distorted* layers of MoO_6 octahedra sharing corners with MoO_4 tetrahedra. However, the polyhedra corner share in the c direction as well, so that the two-dimensional (2D) layer structure is not preserved. Most of the d electron density is located on molybdenum atoms forming Mo—O—Mo zig-zag chains along the b crystallographic direction in such a way that quasi one-dimensional behavior might be expected. (For a more detailed description of the $A_{0.9}Mo_6O_{17}$ phases with A = Li, Na, and K, we refer to the literature[1-3] and in particular to Figs. 1 and 2 of Ref. 3.)

Anisotropic electrical conductivity is expected in these bronzes, because of the layer structure of the Na and K compounds where the Mo—O—Mo bonding is infinite only in the planes and disrupted along the c direction, and because of the location of the charge density primarily on Mo atoms along the b direction in $Li_{0.9}Mo_6O_{17}$. This is confirmed by the transport properties, which reveal low-dimensional behavior.

The resistivity $\rho(T)$ measurements demonstrate quite similar behavior along the so-called easy direction (in the ab plane of the platelets) and the c direction perpendicular to these planes. However, the magnitude of $\rho(T)$ is orders of magnitude larger along c. With decreasing temperature an upturn in $\rho(T)$ is found. The upturn occurs at $T_c \approx 24$, 120 and 88 K for the Li, K, and Na compounds, respectively. For the Li compound it is thought to be a metal-semiconductor transition, since the resistivity increases exponentially only below 24 K down to 2 K, followed at $T_s \approx 1.9$ K by a transition to the superconducting state. The K and Na compounds show a sigma-shaped metal-metal transition at T_c which has been confirmed by diffraction techniques to be due to a transition associated with a charge-density-wave (CDW) state.[4-7]

The "blue" $K_{0.3}MoO_3$ and "red" $K_{0.33}MoO_3$ bronzes also belong to the class of these ternary molybdenum oxides, with similar structural and transport properties. The optical spectroscopy of the blue and red bronzes were investigated in our laboratory.[8] Polarized optical reflectivity measurements revealed for the first time that the blue bronze $K_{0.3}MoO_3$ may be considered a quasi-one-dimensional (1D) metal and that the phase transition at 180 K is of Peierls type. Furthermore the CDW onset, associated with the Peierls transition, was confirmed by the optical detection of the ir-active phase mode.[8]

Optical spectroscopy is then an ideal technique to investigate the microscopic consequences of the Peierls transition. In this paper we present our reflectivity measurements on the $A_{0.9}Mo_6O_{17}$ (A =Li, Na, and K) purple bronzes. We then discuss our results, in an attempt to find a consistent physical picture between the optical and the transport properties, in terms of the transitions seen in the $\rho(T)$ data.

EXPERIMENT AND RESULTS

The optical reflectivity of large single crystals of $Li_{0.9}Mo_6O_{17}$, $K_{0.9}Mo_6O_{17}$, and $Na_{0.9}Mo_6O_{17}$, which have been grown by a temperature gradient flux technique[9] or by an electrolytic reduction,[1] has been measured in an extended photon energy range from 12 eV down to 1 meV using linearly polarized light, in the temperature range between 6 and 300 K.

We have made use of four spectrometers. In the far-infrared (FIR) region a Fourier spectrometer was employed using a He-cooled Ge bolometer as detector. Furthermore it is well known that all other optical properties can be obtained through conventional Kramers-Kronig transformation of the reflectivity data.[10]

The reflectivity spectra (Fig. 1) in the planes of the platelets of the K and Na crystals at 300 and 6 K are quite similar and are metal-like, i.e. the reflectivity tends to 100% towards the lowest photon energy of 1 meV. We have not found any polarization dependence in the plane sheets of the samples and the measurements presented were made with unpolarized light. Besides the plasma edge at about 2 eV, we find at 300 K broad structures at about 0.07 eV for both K and Na compounds. At 6 K, well below the transition temperatures, the 0.07-eV structure becomes more pronounced and a small second peak is now detected at about 0.015 eV (structures C and D in the inset of Fig. 1).

In contrast to the Na and K purple bronzes, the Li compound presents a polarization dependence. We have in fact found two main axes in the plane sheets of the sample which are orthogonal to each other. One direction is metal-like and the other one is semiconducting, where below 0.1 eV typical phonon lines appear, particularly the well known phonon modes of MoO_3.[11] This behavior remains the same down to even 6 K (Figs. 2 and 3).

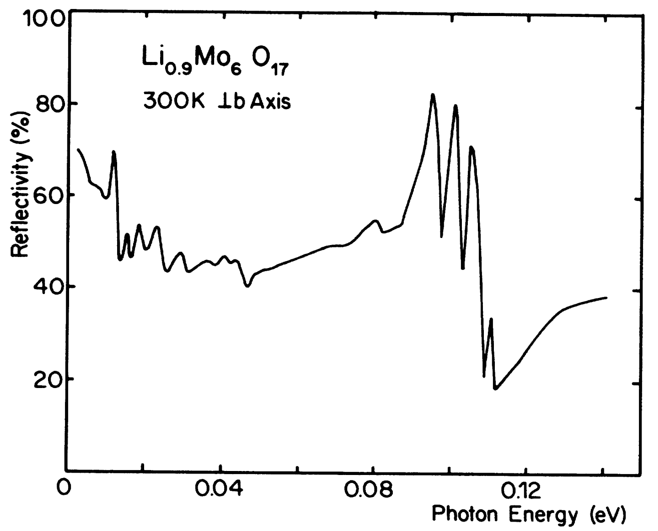

FIG. 2. Reflectivity spectrum of $Li_{0.9}Mo_6O_{17}$ at 300 K between 1 meV and 0.14 eV for linearly polarized light perpendicular to the easy axis b.

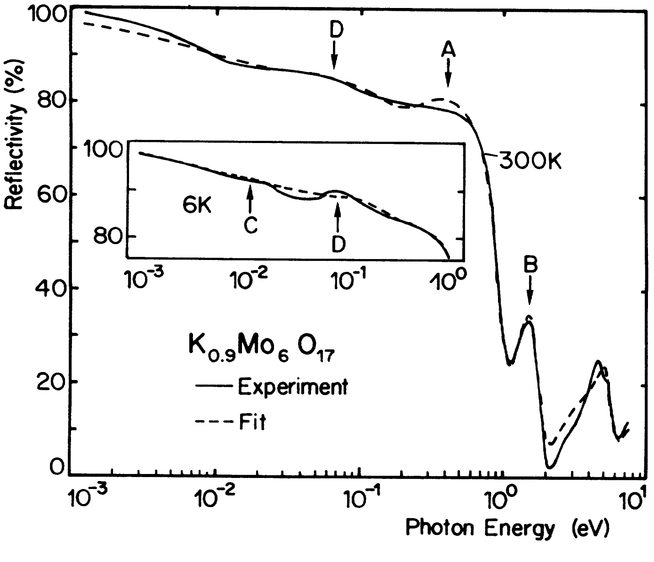

FIG. 1. Reflectivity spectrum of $K_{0.9}Mo_6O_{17}$ at 300 K between 1 meV and 12 eV. The inset shows the spectrum at 6 K in the energy range where a temperature dependence is found. The fit is explained in the text.

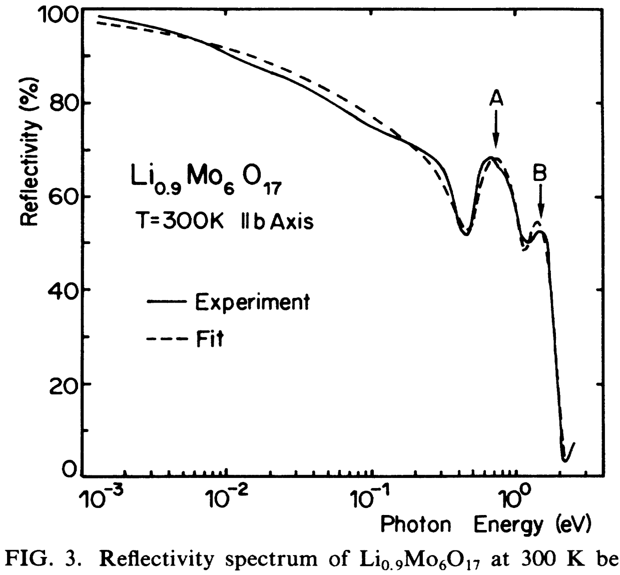

FIG. 3. Reflectivity spectrum of $Li_{0.9}Mo_6O_{17}$ at 300 K between 1 meV and 3 eV for light polarized along the b axis, with the fit explained in the text.

TABLE I. Structures below the plasma edge, considered in the phenomenological fit (taken from experimental spectra at 300 and 6 K). All values are in eV.

	A	B	C only at 6 K	D
Li	0.65	1.45		
K	0.5	1.5	0.014	0.75
Na	0.6	1.6	0.014	0.75

The three bronzes also show two structures at approximately 0.4 and 1.9 eV which are superimposed on the plasma behavior. (They are noted with the letters A and B in Figs. 1 and 3). The main features (peaks or bump structures) below the plasma edge for the three compounds investigated are summarized in Table I.

Finally, the reflectivity spectra above the optical plasma edge are very similar for all bronzes in the energy range where electronic transitions are expected. The dependence on linearly polarized light in the uv region is negligible [i.e., this permits a $R(\omega)$ measurement above 4 eV for the Li compound without polarized light]. We will examine these structures in more detail in the discussion.

DISCUSSION

First of all, let us sketch some general considerations about the phenomenological fit that will be used as partial support of our discussion. We will compare the reflectivity spectra with a fit, based on the classical dispersion theory of Lorentz. It consists of treating all transitions (e.g., electronic, quasiparticle transitions or phonon modes) as oscillators with Lorentzian curves and the free charge carrier contribution with the Drude law.

We consider

$$\hat{\varepsilon}=\varepsilon_1+i\varepsilon_2=\epsilon_\infty-\frac{\omega_p^2\tau_p^2}{1+\omega^2\tau_p^2}+\frac{4\pi e^2}{\mu}\sum_j\frac{Nf_j}{(\omega_j^2-\omega^2)-i\Gamma_j\omega} \quad (1)$$

(the sum is over all j oscillators), and

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \quad (2)$$

where n is the index of diffraction and k the absorption coefficient.

Combining the relations $\varepsilon_1=n^2-k^2$ and $\varepsilon_2=2nk$ with the above formulas (1) and (2) we obtain a fit of $R(\omega)$. The fitted parameters then are the high frequency background dielectric constant ϵ_∞, the energy ω_j, the damping Γ_j, the oscillator strength f_j of the jth oscillator and, for the Drude law the relaxation time τ_p and plasma frequency ω_p.

The reflectivity measurements of the Li compound support the anisotropic behavior of the resistivity $\rho(T)$ in the plane sheets (i.e., about 1 order of magnitude[5]) and are a clear evidence of the one-dimensionality of this bronze, similarly to that found at 300 K for the blue bronze.[8]

In contrast to the Li purple bronze, the K and Na compounds do not have any polarization dependence in the ab plane, confirming the two-dimensionality of these samples, even though an anisotropy of about 1 order of magnitude in $\rho(T)$ is observed in the plane sheets.[6,7] This means that the anisotropy in $\rho(T)$ in the plane sheets of the Li compound should be much more pronounced than observed,[5] based upon our observation of an optical anisotropy of at least 6 orders of magnitude. This is directly obtained from the $R(\omega)$ spectra for light polarized parallel and perpendicular to the b axis. In the conducting direction (Fig. 3) we find a plasma edge of about 2 eV and in the semiconducting direction (Fig. 2) a plasma edge, if any, smaller than 1 meV. Since the square of the plasma energy is proportional to the charge concentration, we can immediately evaluate the magnitude of the anisotropy in $\rho(T)$. The mentioned disagreement between the optical and dc resistivity measurements is quite typical in such systems; in fact, also in the blue bronzes,[8] the optical measurements were more suitable to observe the anisotropy in $\rho(T)$, since with perpendicularly incident polarized light we can select the direction in the ab plane to be investigated, without any interference from the other ones, which is not always the case with dc measurements (see below). Thus the optical data indicate 2D behavior in the Na and K purple bronzes, while the Li analog shows evidence of 1D properties. In addition to differences in dimensionality, these systems also differ in the temperature dependence of their $R(\omega)$ spectra.

We now move to the Drude part of our discussion, dealing first with the K and Na bronzes. For the sake of brevity we will concentrate on the K compound and note that the two compounds have similar properties; which can be seen by an examination of Tables I–III.

For the phenomenological fit we consider the Drude law for the plasma behavior and three oscillators for the structures at 0.07, 0.5, and 1.4 eV in $R(\omega)$ at 300 K and a fourth one for the little bump at 0.014 eV at 6 K. Furthermore, in order to calculate the *unscreened* square of the plasma frequency (ω_p^2), we consider also an oscillator at ≈ 3 eV for both temperatures, which should represent the first electronic transition above the optical plasma edge.

We recall the well-known formula

$$\sigma_0=\frac{\omega_p^2\tau_p}{4\pi}, \quad (3)$$

which relates the static resistivity σ_0, the square of the unscreened plasma frequency, ω_p^2, and the relaxation time τ_p. In the fit we can couple ω_p^2 to τ_p, taking σ_0 from $\rho(T)$ measurements or as limit of the optical conductivity $\sigma(\omega)$ for $\omega\rightarrow 0$ as a fixed value (i.e., we reduced the number of the fitted parameters), even though a full consistency is always difficult to reach between the two possibilities [e.g., see the discrepancy in $K_{0.3}MoO_3$ (Ref. 8)].

In order to maintain at least the consistency between the reflectivity measurement and the Kramers-Kronig-derived $\sigma(\omega)$, we take σ_0 from the limit for $\omega\rightarrow 0$ of the optical conductivity. The fitted parameters are summarized in Table II.

As shown in Fig. 1, the agreement between model fit

TABLE II. Fitting parameters for the (a) K and (b) Na purple bronze.

	ε (eV)		γ (eV)		f (eV^2)		ω_p^2 (eV^2)	
Structure	6 K	300 K	6 K	300 K	6 K	300 K	6 K	300 K
			(a) K purple bronze					
A	0.3	0.3	0.393	0.265	4.93	4.66	1.9	3.23
B	1.5	1.46	0.54	0.53	5.09	4.98		
C	0.014		0.01		0.03			
D	0.075	0.08	0.14	0.179	3.79	2.86		
			(b) Na purple bronze					
A	0.27	0.28	0.52	0.57	3.96	3.24	2.06	3.98
B	1.5	1.46	0.54	0.52	4.39	4.18		
C	0.014		0.024		1.2			
D	0.075	0.083	0.093	0.0967	3.41	3.4		

and experiment is very good, indicating that the main physical features are contained in such an approach. We believe that the optical experiments strengthen the idea of a partial opening of a gap at the Fermi surface as a consequence of a Peierls transition, caused by the onset of a charge-density wave (CDW). We assign the structure at 0.08 eV to the electronic transition across the Peierls gap (at 300 K it is a pseudogap as precursor of the transition) and the one at 0.015 eV (detected only at 6 K) as a possible evidence of the phason mode.

This point of view is supported by the numerical values of ω_p^2. The best fitted ω_p^2 parameter at 6 K is approximately 60% of the value at 300 K. This means that about 40% of the free charge carriers condense in the CDW below the transition at T_c. Of course the remaining free charge carriers provide for the metallic conduction, i.e., plasma behavior in $R(\omega)$, below T_c.

In a very crude model which assumes that the mobility is the same for both types of carriers and does not change at the transition, we can also estimate from the electrical resistivity data the decrease of the carrier concentration at low temperature. From the $\rho(T)$ behavior between the value at 80 K [i.e., by the maximum in $\rho(T)$], and the one extrapolated from the linear high-temperature curve, this corresponds to a decrease of roughly 50% of the carrier concentration at the transition.[6,12] This is in full agreement with the conclusions inferred from our fit of $R(\omega)$. Furthermore, the partial opening of a gap at the Fermi surface at T_c is predicted by recent band-structure calculations, based on a tight-binding method, performed on these systems by Whangbo *et al.*[13] Their results show that the Fermi surfaces of the three partially filled *d*-block bands are typical of a two-dimensional metal and that the CDW transition results from the nesting of one of these Fermi surfaces, and the remaining two provide electron and hole carriers below T_c, where consequently the Na and K compounds remain a 2D metal.

The nesting vectors $\mathbf{q}$ of one of the three *d*-block Fermi surfaces are $\mathbf{q}_a=(a^*/2,0,0)$, $\mathbf{q}_b=(0,b^*/2,0)$, and $\mathbf{q}_{a+b}=(a^*/2,b^*/2,0)$ (a^*,b^* are reciprocal vectors), as also found experimentally by electron diffraction studies.[12] The former considerations support the polarization independence of our $R(\omega)$ measurements also in the CDW state (i.e., below T_c).

We conclude the discussion about the 2D Na and K purple bronzes, dealing with the two structures at 0.7 and 1.4 eV superimposed on the plasma behavior. The relative breadth of the peak at 0.7 eV as compared to that at 1.4 eV raises some doubt as to the origin of the former. However, since in the isostructural one-dimensional Li compound, the two structures appear clearly, and since the phenomenological fit was unsuccessful without the oscillator corresponding to the "bump" at 0.7 eV, we conclude that the poorly structured reflectivity around 0.7 eV is consistant with an optical transition.

We claim that these are electroniclike transitions (which are also confirmed by the order of magnitude of the fitted parameters). Based upon the tight-binding calculation of Whangbo *et al.*,[13] who considered only the *d* states, and of Mattheiss, who has performed similar calculations on ReO_3,[14] we can ascribe the transition at 0.7 eV to an *intraband d* transition and the one at 1.4 eV to an *interband p*-oxygen to *d*-molybdenum transition.

Comparison with ReO_3 is instructive and pertinent, since in the purple bronzes the octahedral layers are of the ReO_3 type (see also discussion below). The model calculation of Mattheiss allows interband transitions down to very low energies (i.e., below 2 eV, the plasma edge). However, the calculated joint density of states (Fig. 9, Ref. 4) suggests that these low-energy transitions will be weak from a density-of-states point of view. This explains the negative results of Feinleib *et al.*,[15] who did not find any evidence of these transitions below 2 eV in ReO_3, i.e., superimposed on the plasma behavior. We believe that the low dimensionality of our systems effects the density of states in such a way as to favor such optical transitions in this energy range.

We now discuss the reflectivity spectra of the Li compound (Figs. 2 and 3), which indeed show a polarization dependence. Along the direction perpendicular to the easy *b* axis, the typical features of a semiconducting behavior with many phonon modes are seen. A realistic phonon analysis is very difficult because of the large number of atoms in the unit cell. In the following, we will not discuss further the semiconducting direction but, since our main purpose is to build a bridge between the transport properties [e.g., the upturn of $\rho(T)$ along the b axis] and our optical investigations, we will pay attention only to the spectra along the b axis. The $R(\omega)$ spectra for the Li compound, contrary to the K and Na compounds, do not present any temperature dependence.

Furthermore, superimposed on the plasma behavior (Fig. 3), two peaks at ≈ 0.6 and 1.4 eV are clearly evident. Regarding our previous discussion on the two-dimensional bronzes, we assign these two structures as well to the intra and interband electronic transitions; again the lower dimensionality of the Li compound favors the resolution of the lowest energy transition.

The phenomenological fit, performed at 300 K, is presented in Fig. 3 and the fitted parameters are summarized in Table III. As expected, the unscreened ω_p^2 has the same value as in the Na and K compounds, since the conductivity at 300 K for the three bronzes (i.e., for the Li one only along the b axis) are of the same order of magnitude.

The similarity at 300 K between the spectra of the blue bronze[8] and our Li purple bronze might suggest that the transition seen at 24 K is due to the onset of a CDW as originally proposed by Greenblatt *et al.*[5] However, our $R(\omega)$ data at 6 K do not show any temperature dependence and, since no evidence of a Peierls transition is detected, this seems to argue against the presence of a CDW at 24 K. Furthermore, as pointed out by Greenblatt *et al.*[5] and more precisely by Matsuda *et al.*,[16] the temperature-independent Pauli paramagnetism down to 4 K in the Li compound lacks evidence for an opening of a gap at the Fermi surface associated with a CDW.

Another possible instability could be caused by a spin density wave (SDW). However, since a pinned SDW can be recognized by the same optical feature as a CDW (i.e., optical gap), it seems quite improbable that the upturn in $\rho(T)$ could be explained by this kind of instability.

Another interesting system of restricted dimensionality, to be compared to the Li one, is $NbSe_3$, a metal with two giant resistivity anomalies at 145 and 59 K, indicative of phase transitions.[17] It is now well accepted that the two anomalies are associated with the presence of a CDW. Besides, $NbSe_3$ becomes a superconductor under pressure (and the CDW transitions are completely suppressed). This is a further indication that the CDW and the superconducting states are mutually exclusive. But this is precisely not the case for the Li compound, where the superconducting transition is evident also at ambient pressure. It is possible that if the 24-K transition is associated with a CDW in $Li_{0.9}Mo_6O_{17}$, at lower temperature it disappears in favor of superconductivity. In $NbSe_3$, it is high pressure, in $Li_{0.9}Mo_6O_{17}$ it is low temperature that stabilize superconductivity.

TABLE III. Fit parameters for the Li purple bronze at 300 K.

	ε (eV)	γ (eV)	f (eV^2)	ω_p^2 (eV^2)
A	0.54	0.21	1.31	3.76
B	1.2	0.34	0.43	

At this point neither the transport nor the optical-property investigations support the physical picture of a partial opening of a gap at the Fermi surface due to a CDW onset as cause for the upturn of $\rho(T)$ at 24 K, even though a preliminary band-structure calculation[18] does not seem to exclude the existence of a nesting Fermi surface.

Thus the 24-K transition in the Li purple bronze still remains a puzzling problem. There is the conviction that the upturn in $\rho(T)$ at 24 K and the superconducting transition at ≈ 2 K are related to each other. According to Sato *et al.*[19] the compound can be considered to be a microscopically random material, which exhibits two conflicting phenomena, superconductivity and electron localization. The superconductivity is found to be an intrinsic phenomenon with almost the Bardeen-Cooper-Schrieffer (BCS) value of the energy gap. Furthermore, the shape of the tunneling density of states confirms the idea that the same electron system exhibits the superconductivity and the resistivity upturn.[20] Of course, it is well known that the enhancement of the Coulomb repulsion due to the localization effect is expected to be very large, suppressing the superconducting transition temperature T_s (see Fig. 4, Ref. 21).

An indication that a localization effect is operating is given by the $\rho(T)$ measurements of $Li_{0.9}(Mo_{1-x}W_x)_6O_{17}$ (Fig. 4 of Ref. 15), where 1% substitution of the Mo atoms by W suppresses almost completely the superconducting transition.[20-22] In fact the W substitution introduces a randomness in the path of the conductivity electrons (in contrast to the alkali-metal-atom substitution, because the role of the alkali metals is just to donate the outer electrons to the conduction band of the Mo and O atoms.[16]

If a localization effect is present, it would show itself by a reduced mobility of the charge carriers. This would imply a smaller plasma frequency due to a larger effective mass, since the carrier concentration does not change, and a larger relaxation time τ_p. Then from formula (3) a reduced conductivity σ_0 is expected.

Optically we would expect some changes in the plasma edge behavior. However, the temperature independence of the spectra seems to show very little, if any, localization effect, which even at 6 K (i.e., well below the transition temperature T_c) cannot effect the $R(\omega)$ measurements. Furthermore the ratio $\tilde{\gamma}$ of $\rho(T)$, for T below 24 K, and ρ(300 K) is always less than a factor of 3 and it is just equal to 1 at 6 K. This is really a critical situation from an optical point of view (i.e., such factors are quite usual between optical and static measurements) and it is not surprising that one can fit the reflectivity at 6 K by nearly the same parameters as those at 300 K.

Finally, we remark that some uncertainities should be considered also for the static measurements. It is well known that the electric contacts for the $\rho(T)$ measurements are not always on the *same* layers. This would mean that on the *ab* plane a certain contribution of the large resistivity in the c direction could be important, especially for the Li compound, with a distorted quasi-layer structure. Thus $\rho(T)$ in the c direction shows the same upturn at 24 K but with values two orders of magnitude larger than in the *ab* plane. In order to avoid this problem, a $\rho(T)$ measurement with a socalled free contact method is necessary. However, for reflectivity measurements by perpendicular incident light there is no interference from the semiconducting gap in the *c* direction, and relative to the resistivity measurement the optical investigation may be more powerful. However, as pointed out before, the lowest temperature that we can reach is about 6 K, which may not be low enough in view of the possible competition between superconductivity and localization effects.

Lastly, a few observations regarding the energy range above 2 eV (i.e., the plasma edge energy) where the three purple bronzes have the same polarization- and temperature-independent reflectivity spectra. As expected, the similarity with the corresponding spectra of the blue bronze is evident; but even more evident is the similarity with the optical reflectivity of ReO_3.[15] As pointed out before, this is a consequence of the same octahedral building blocks in these structures.

Referring to the band-structure calculation of Mattheiss[14] on ReO_3 and more precisely the corresponding joint density of states (Fig. 9, Ref. 14), we can easily assign the interband transitions in the purple bronzes to the corresponding ones in ReO_3, involving *p* oxygen and Re *d* states.

CONCLUSION

A systematic and thorough optical investigation of the purple bronzes $A_{0.9}Mo_6O_{17}$ with $A =$ Li, Na, and K are consistent with previous structural and physicochemical results. The optical data confirm that the Na and K purple bronzes have quasi-2D electronic properties; the metal-metal transitions observed in the $\rho(T)$ data and ascribed to a Peierls-like transition, manifest themselves in the optical data by a significantly lower value of ω_p^2 below T_c than at 300 K. This is attributed to the loss of charge carriers which have condensed into the CDW state.

The optical data confirm unambiguously the quasi-1D electronic behavior of $Li_{0.9}Mo_6O_{17}$. The nature of the upturn in the $\rho(T)$ data at 24 K could not be resolved by the optical investigation. Thus for the Li bronze, a definitive understanding of the transition in $\rho(T)$ remains far from final. Low-temperature x-ray and neutron diffraction measurements are essential for an unambiguous resolution of the upturn in the $\rho(T)$ data at 24 K. In addition it would be of importance to investigate the charge carrier type below 24 K by Hall effect measurement. However, once again the optical measurements seem to be a powerful method in order to complement the investigation of the transport properties.

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