# Magneto-optical properties of $Li_{0.9}Mo_6O_{17}$: Color change in applied magnetic field

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(Received 31 March 2004; published 23 August 2004)

The polarized magneto-optical response of $Li_{0.9}Mo_6O_{17}$ was measured in order to investigate the effect of a high magnetic field on the optical properties of a quasi-one-dimensional conductor. The observed magnetochromic effect is attributed to field-induced changes in the density of states near the Fermi level and is manifest in both Mo $d \rightarrow d$ on-site and O $p \rightarrow$ Mo $d$ charge transfer excitations. The observed polarization dependence of the field-induced color change is consistent with the low energy scale of this effect.

DOI: 10.1103/PhysRevB.70.085107 PACS number(s): 71.30.+h, 71.45.Lr, 78.30.−j, 78.40.−q

## I. INTRODUCTION

Investigations in high magnetic fields are critical to the understanding of various physical phenomemena such as semiclassical Landau level quantization, cyclotron resonance, field-induced confinement, and superconductivity. Work in this area has been dominated by magneto-transport experiments, employed to probe the bulk physical properties of various low-dimensional materials. Examples include the metal-semimetal transition in $(TMTSF)_2ClO_4$ attributed to high field confinement effects,[1] the field-induced carrier conversion observed in $NbSe_3$,[2–4] quantum limiting behavior and the unusual high field insulating state discovered in $\eta$ -$Mo_4o_{11}$,[6] field-induced superconductivity in $\lambda$ -$(BETS)_2FeCl_4$,[7] and the cyclotron resonance features observed in a variety of semiconductor heterostructures.[8,9] The recent report by Tian *et al.* on the dramatic field-induced metal-insulator transitions in the two-dimensional purple bronzes [$A_{0.9}Mo_6O_{17}$ (A=Na, K, and Tl)], has also attracted attention.[10,11] In this work, the substantial magnetoresistance effects were attributed to the destruction of Fermi surface pockets and the subsequent modification of the electronic structure around the Fermi level ($E_F$). The magnetically driven metal-insulator transition was taken as evidence of a gap opening at $E_F$. Nearly two decades ago, Balseiro and Falicov predicted that charge density wave materials may undergo field-induced metal-insulator transitions, with subsequent gap opening (and concomitant drop in carrier concentration) in the high-field, insulating state.[12,13] The magnetotransport work of Tian *et al.* thus provides a testing ground for these ideas, at least from a bulk properties point of view. Despite the aforementioned theoretical predictions[12,13] and magnetotransports measurements,[10,11] there has been no attempt to probe the field-induced modification of the density of states around the Fermi level by a more direct and microscopic technique such as optical spectroscopy.

In the present work, we investigate the magneto-optical response of Li purple bronze, $Li_{0.9}Mo_6O_{17}$. The field-induced color change observed in $Li_{0.9}Mo_6O_{17}$ is particularly unusual considering the diamagnetic nature of this material and the other purple bronzes. The title compound is a member of the molybdenum purple bronze family with chemical formula $A_{0.9}Mo_6O_{17}$ (A=Li, Na, K, and Tl). The Li compound displays a quasi-one-dimensional metallic response at high temperature, a localization-induced upturn in the resistivity at 25 K, and a superconducting transition at 1.9 K.[14–18] The low-temperature resistivity increases in an applied field to at least 8 T.[19] The Na, K, and Tl analogs are all well-known two-dimensional charge density wave materials.[16,20–22] In contrast, quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ seems to be dominated by localization effects,[23] which allows the density of states near the Fermi level to remain stable in spite of the metal-nonmetal transition.[23,24] Li purple bronze was selected for this work because of its quasi-one-dimensional transport properties, well-studied electronic structure, and finite low-temperature density of states at the Fermi level. The strong low-temperature magnetoresistance of $Li_{0.9}Mo_6O_{17}$ and the rich magnetotransport behavior of the more two-dimensional purple bronzes $Li_{0.9}Mo_6O_{17}$ (A=Na, K, and Tl) were additional incentives.[10,11,19]

## II. EXPERIMENT

Single crystals of $Li_{0.9}Mo_6O_{17}$ were grown using the temperature gradient flux method, as described previously.[15,23] Both x-ray powder diffraction and electrical resistivity measurements confirmed that the crystals have single phase and exhibit metallic character down to 25 K. Li content was de-

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termined by the inductively coupled plasma technique and is within ±5% (relative deviation) for all crystals studied. Variable-temperature polarized reflectance measurements were carried out over a wide energy range (from 6 meV to 5.6 eV) with a series of Fourier transform and scanning grating spectrometers and the optical conductivity obtained by Kramers-Kronig analysis.[23] The magneto-optical response of $Li_{0.9}Mo_6O_{17}$ was measured at the National High Magnetic Field Laboratory in Tallahassee, FL, using a grating spectrometer equipped with a change-coupled device detector and a 33 T resistive magnet. Here, we concentrated on the visible optics regime, 1.5–3.5 eV, investigating both the $\|b$ and $\perp b$ polarized response, with $H\|c$. Although the majority of our experiments were done at 4.2 K, selected measurements were carried out at elevated temperatures. In order to capture small magnetic field-induced changes in the electronic structure of Li purple bronze, reflectance at each field was divided by the zero field reflectance to yield reflectance ratios: $[R(H)/R(H=0\mathrm{T})]$. This normalized response provides additional sensitivity to field-induced color changes. We quantified the field-induced spectral changes with standard peak-fitting techniques, using Gaussian oscillators, as appropriate.

### III. RESULTS AND DISCUSSION

Figure 1 displays the 10 K polarized reflectance and optical conductivity of $Li_{0.9}Mo_6O_{17}$.[23] Along the highly-conducting *b*-axis, the compound displays an unusual (non-Drude-type) mobile carrier response at low energy, with partially screened vibrational features. Despite clear carrier localization and the decrease in $\sigma_1$ below 0.1 eV, there is no evidence for optical-gap opening. The 25 K metal-non-metal transition seems to be driven by the localization effects rather than density wave formation.[23] At higher energies, we observe Mo $d\rightarrow d$ transitions near 0.42, 0.57, and 1.3 eV, and an O $p\rightarrow$Mo *d* charge transfer band near 4 eV.[23] These excitations are indicated in Fig. 1(b). The optical spectrum of $Li_{0.9}Mo_6O_{17}$ in the $\perp b$ direction displays semiconducting behavior with an optical gap of ~0.4 eV, rich vibrational structure, and a series of electronic excitations that are similar to those along *b*. Within the sensitivity of our measurements, we find no obvious change in the vibrational response through the 25 K metal-non-metal transition.[23] This result suggests that if the 25 K transition is driven by a charge density wave mechanism, the lattice distortion is quite small. This finding also supported our supposition that localization effects dominate the bulk and microscopic properties of Li purple bronze. It is the visible optics regime (1.5–3.5 eV) that is of interest here.

Figure 2(a) shows the *b*-polarized reflectance ratio of Li purple bronze at 4.2 K as a function of applied magnetic field between 0 and 30 T. With increasing field, the reflectance of $Li_{0.9}Mo_6O_{17}$ decreases by ~2% in the visible spectral range. The overall shape of the reflectance ratio feature changes as well, showing additional complexity and an overall red-shift with increasing field. From a bulk properties point of view, this effect can be considered to be a field-induced color change or "magnetochromism," as a change in

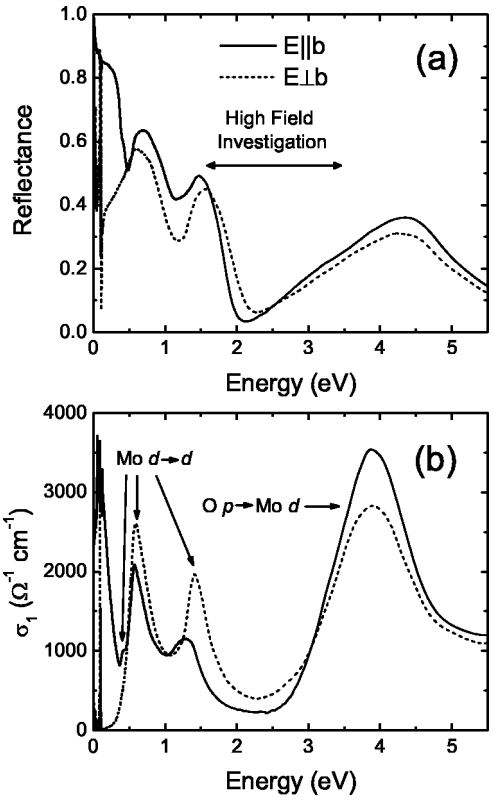


FIG. 1. Reflectance (a) and optical conductivity (b) of $Li_{0.9}Mo_6O_{17}$ along *b* (solid line) and $\perp b$ (dashed line) at 10 K. The arrow in panel (a) indicates the energy range of our magneto-optics investigation, and the text in panel (b) denotes our assignment of optical excitations.

reflectance ratio corresponds to a modication of the absorption spectrum. From the microscopic point of view, excitations in this spectral range correspond to the trailing edge of the ~1.3 eV Mo $d\rightarrow d$ band and the leading edge of the ~4 eV O $p\rightarrow$Mo *d* charge transfer excitation, as indicated in Fig. 1.[23] The surprisingly different energy scale of these excitations compared with that of the applied magnetic field provides an important clue to the mechanism of the magnetochromic effect, as discussed below. The spectrum of $Li_{0.9}Mo_6O_{17}$ does not display any field dependence when measured in the $\perp b$ direction.

To quantify this effect, we fit each magneto-optical reflectance ratio spectrum with several Gaussian model oscillators and calculated the absolute value of their integrated areas [Fig. 2(b)]. Perturbations in position, width, and intensity of each oscillator are observed with applied field. At low fields, the lineshape is relatively symmetric, and the modest magnetochromic effect can be fit with a single oscillator. With increasing field, the reflectance ratio spectrum becomes asymmetric, requiring two or more oscillators to obtain an acceptable fit. At 18 T, the character of the magneto-optical effect changes substantially [bold line, Fig. 2(a)], and the absolute value of the integrated intensity displays an inflection point [Fig. 2(b)]. Using the energy scale of $1\mathrm{T}\sim1.4$ K (for $g=2$), it is interesting to note that 18 T is roughly equal to 25 K, the energy scale of the metal-nonmetal transition in Li purple bronze.[14,16] Despite this coincidence of energy

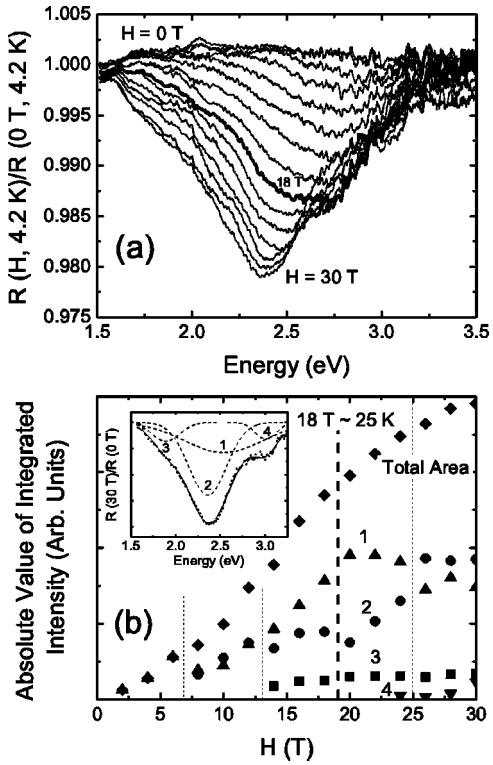


FIG. 2. (a) Reflectance ratio of $Li_{0.9}Mo_6O_{17}$ at 4.2 K along the *b*-axis from 0 to 30 T, with 2 T steps. The 0 T/0 T reflectance ratio is nearly flat, the 18 T/0 T reflectance ratio is denoted with a bold line, and the 30 T/0 T reflectance ratio displays maximum deviation from unity. (b) Absolute value of the integrated oscillator strength of the magneto-optics feature as a function of applied magnetic field (solid diamonds). Solid triangles, circles, squares, and inverted triangles give the field dependence of each oscillator in the fit. Vertical dashed lines indicate magnetic fields at which the integrated areas show inflection points. The inset displays the 30 T reflectance ratio of $Li_{0.9}Mo_6O_{17}$ (dotted line), the four model oscillators (dashed lines), and the resultant fit (solid line).

scales, the magneto-optical effect persists even at elevated temperatures (not shown) without a significant change in shape, which implies that it is mechanistically unrelated but is sensitive to localization effects in $Li_{0.9}Mo_6O_{17}$. A total of four Gaussian oscillators are needed to obtain an acceptable fit to the reflectance ratio data at 30 T [inset, Fig. 2(b)].

The energy scale of the applied magnetic field ($1T \sim 1.4\,K \sim 1\,cm^{-1}$) suggests that the observed magneto-optical effect is a consequence of low-energy modifications to the Fermi surface landscape in the *b* direction. We propose that a part of the Mo *d* block levels that make up the density of states near $E_F$ is altered by magnetic field and that, as a consequence, excitations involving this portion of the electronic structure display small but observable field-induced effects. Such a change arises most probably from the Zeeman interaction between the orbital angular momentum and the magnetic field. The maximization of this interaction would require a rotation of the Mo *d* orbitals, which can be achieved by an orbital mixing between the occupied and unoccupied Mo *d* orbitals, i.e., by mixing occupied and unoccupied $t_{2g}$ orbitals in the vicinity of the Fermi level. The latter will change the transition dipole moments for optical excitations, thereby leading to the observed color change in $Li_{0.9}Mo_6O_{17}$ under magnetic field. The field-induced modifications to the electronic structure of near the Fermi level should alter both Mo $d \rightarrow d$ on-site and O $p \rightarrow$ Mo *d* charge transfer excitations [Figs. 1(b) and 2(a)].[25] This scenario is supported by the observation that the magnetochromic effect appears only along the highly conducting ($E \| b$) direction, where there is a finite density of states at $E_F$ even below the 25 K metal-nonmetal transition.[23,24] We note that both electronic structure calculations and photoemission results indicate that two well-dispersed *d*-block bands cross the Fermi surface along *b* and are therefore susceptible to modification.[26–29] We anticipate that other physical properties sensitive to the dispersion and occupation of these *d*-block bands will be modified in a magnetic field as well. In contrast, optical properties investigations show that there is no density of states near the Fermi level in the $\perp b$ direction due to the $\sim$0.4 eV semiconducting gap,[23] a result that is consistent with both electronic structure and photoemission results. [26–32] The absence of a magneto-optical effect in this direction is therefore a natural consequence of the anisotropic electronic structure and the low energy scale of the mechanism. Essentially, there are no states (within the energy scale of the applied field) to mix in the $\perp b$ direction. That the magneto-optical response along *b* persists at temperatures above 25 K suggests that this effect may be a general phenomenon in highly anisotropic materials, where the character of mobile carriers is easily manipulated by a magnetic field.

Although the theoretical work of Balseiro and Falicov on field-induced metal-insulator transitions in charge density wave materials cannot be directly mapped on to the case of $Li_{0.9}Mo_6O_{17}$,[12,13,23] the broad outlines of their predictions are useful. The concept that an applied magnetic field can modify the density of states of a quasi-one-dimensional conductor near the Fermi level, induce a metal-insulator transition, and open a gap is evidenced by transport results on various quasi-one- and two-dimensional purple bronzes.[10,11,33] The magnetochromic effect in Li purple bronze, reported here, is important as a microscopic confirmation of the field-induced modification of the electronic structure near the Fermi level, which is due most likely to the Zeeman interaction between the orbital angular momentum and the magnetic field.

In closing, we note that magnetochromism has recently been discovered in several other materials including $(CPA)_2CuBr_4$ and $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$.[34,35] Rather than a field-induced modification of the low-energy Fermi surface landscape consisting of the Mo *d* block in the highly conducting direction as proposed for Li purple bronze, these field-induced color changes seem to occur by chromophore rotation and modifications to the $e_g$ orbital occupancy in magnetic field, respectively. That different mechanisms can activate the magnetochromic effect suggests that field-induced color changes may appear in other compounds as well. Analogs of magnetochromism include thermochromism, piezochromism, electrochromism, and photochromism, each of which gives rise to a color change as a result of physical tuning.

## IV. CONCLUSION

We investigated the polarized magneto-optical response of $Li_{0.9}Mo_6O_{17}$ and demonstrated that an applied magnetic field changes the color of this quasi-one-dimensional material. We attribute the magnetochromic effect to a field-induced modification of the electronic structure near the Fermi level, and the resulting changes in both Mo $d \rightarrow d$ on-site and O $p \rightarrow$ Mo $d$ charge transfer excitations. In this picture, the magneto-optical effect is observed along $b$ (the highly conducting direction) because the material has occupied and unoccupied energy levels within the energy scale of the field, whereas in the $\perp b$ direction, the 0.4 eV energy gap eliminates any states within "reach" of the field. We suspect that this small, tunable part of the Fermi surface along $b$ may condense below 1.9 K to form the superconducting condensate Li purple bronze.

## ACKNOWLEDGMENTS

Financial support from the Materials Science Division, Basic Energy Sciences at the U.S. Department of Energy for the work in the Chemistry Departments at the University of Tennessee (DE-FG02-01ER45885) and at North Carolina State University (DE-FG02-86ER45259) is gratefully acknowledged. The Division of Materials Research at the National Science Foundation (0072998) supports work in the Physics Department at the University of Tennessee. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperation Agreement No. DMR-0084173 and by the State of Florida.

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