Low-temperature behavior of the annealed molybdenum blue bronzes $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$

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When annealing molybdenum blue bronzes $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$ in the presence of a metal (Ag or Cu), drastic changes of the resistivity are observed below $T \approx 40$ K in the three crystal directions. Nevertheless, dc conductivity and dielectric constant measurements still clearly exhibit the presence of a charge-density wave. Electronic paramagnetic resonance studies of annealed samples revealed a high concentration of Mo^{5+} sites with respect to untreated samples suggesting an additional conduction via orbital overlaps of the Mo^{5+} cations. This could also be responsible for some other anomalies observed in the blue bronzes at this temperature. These results are discussed in comparison with unannealed blue bronzes. [S0163-1829(99)02932-X]

Blue bronzes $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$ were synthesized in 1964 by Wold *et al.*[1] Their crystallographic structures were determined by Graham *et al.*[2] Due to their strong electric anisotropy and nonlinearity in the current-voltage characteristics, they have been intensively studied during the last decades.[3] This nonlinear behavior has been explained by the formation of a charge-density wave (CDW). Blue bronzes exhibit a metal-semiconductor transition at $T = 183$ K. Using diffuse x-ray scattering, Pouget and Kagoshima[4] proved this to be a Peierls transition towards an incommensurate CDW ground state along the *b* axis. Below $T = 183$ K, the resistivity $\rho(T)$ of blue bronzes shows a thermally activated, semi-conducting behavior given by

$$\rho(T) = \rho_0 e^{\Delta(T)/k_B T},$$

where Δ is an activation energy which is becoming constant and equal to $\Delta(0)$ below 100 K. The values of $\Delta(0)$, the ground-state energy gap, vary from crystal to crystal (340 to 470 K). Several anomalies have been observed around $T = 40$ K in the magnetic susceptibility,[5] thermopower,[6] dielectric constant,[7] and the lattice parameter[8] measurements. Despite numerous studies, the understanding of these phenomena are still a challenge for the scientific community. In order to heighten insight into these behaviors, we report the measurements on annealed molybdenum blue bronzes with metallic contacts. After a short description of the experimental configuration, we present a detailed study of the resistivity along three axes for annealed samples. Then, the dc resistivity versus the applied electric field in the $[MoO_6]$ chain along the *b* axis will be reported. The results of measurements of the real part of the dielectric constant ε' will also be presented. Finally, we discuss how the structural evolution is correlated to the appearance of a plateau in the resistivity measurements of annealed samples and how this evolution could contribute to the other anomalies observed in blue bronze.

The $K_{0.3}MoO_3$ crystals used in our studies were grown electrochemically as described in Ref. 1. After cleaving, the samples have typical dimensions of 4 mm along the *b* axis, 1.5 mm along the [102] direction, and 1 mm perpendicular to the (201) planes. In order to obtain a low contact resistance and contacts that are stable in time, high-quality contacts are necessary to perform high-quality dielectric measurements; we have developed another contact process. The crystal edges are polished perpendicularly to the high conduction crystallographic *b* axis using thin abrasive paper and are subsequently covered by a thin silver film (200 nm) using an evaporation process. In a silica tube sealed under vacuum the samples were annealed for six hours at 400 °C. After annealing, the samples were indium soldered to platinum-plated electrode contacts which were evaporated on a sapphire substrate and were mounted in a standard He cryostat. The resistivity measurements have been performed using a programmable current source and a voltmeter. The instrumentation was computer controlled using two, four, or six probe configurations. For each measurement, the electric field at the sample voltage probe was limited to 3 mV/cm in order to stay in the ohmic regime. Resistivity measurements were carried out on many samples of different sizes with good reproducibility.

The dielectric constant measurements were performed in a two-probe configuration, using a lock-in amplifier. The ac voltage from the lock-in is converted into an ac current by a reference resistor (R_I, where $R_I \approx 50*R$ sample) connected in a series with the sample. The sample voltage is detected by a very low noise preamplifier with an amplification factor of 100, and then directed to the lock-in amplifier. Before each measurement, a calibration was performed in order to eliminate the amplitude and phase errors. The capacitance and inductance of the experimental configuration were determined in the entire temperature range by replacing the sample with an open or short end. We ensured that our measurements were in the linear regime by applying a current at least 30 times lower than the dc threshold current. For each temperature the sample voltage was measured in the frequency range between 1 Hz and 100 kHz. Details of the complete experimental configuration will be published elsewhere.
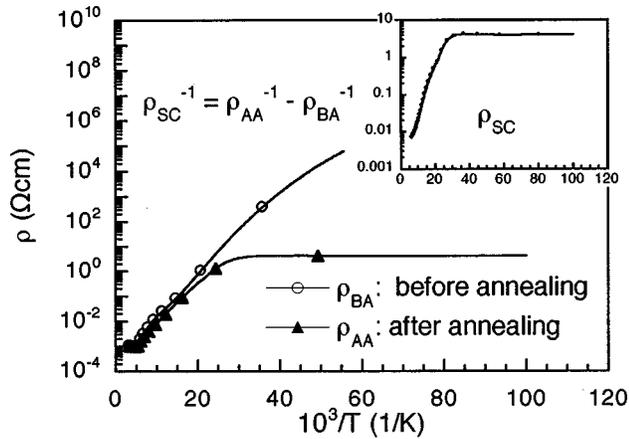
FIG. 1. Resistivity of the potassium blue bronze before and after annealing versus $1000/T$ (K^{-1}). Inset shows a hypothetical short circuit resistivity ρ_{SC}.

FIG. 3. Evolution of the resistivity of an annealed potassium blue bronze sample after successive thermal cycles versus $1000/T$ (K^{-1}).

A surprising feature of the resistivity of annealed blue bronzes (Fig. 1) is the appearance of a plateau at $T \approx 40$ K and a slow decrease in resistivity as the temperature is lowered. The very unusual resistance behavior of the annealed samples has urged us to make some verification. In order to eliminate all experimental errors, we measured our samples with two different experimental settings. To obtain a plateau we need metal (copper or silver) on the ends during the annealing process. In order to exclude a trivial short circuit by metallic diffusion, we analyzed the annealed samples by an inductively coupled plasma mass spectrometer (ICPMS) method. Typically, we found 10-ppm of silver particles that cannot explain the presence of the plateau. These particles probably result from the very weak silver deposit on the external ($\bar{2}$01) planes of the samples. Nevertheless, by comparing the resistivity of a sample before and after annealing (Fig. 1), we calculated the resistivity of an eventual short circuit ρ_{SC} (inset of Fig. 1) showing again the nontrivial resistivity behavior. In the end we took a sample, made the thermal treatment, and cleaved it in two parts: sample 1 and sample 2. Sample 1 is measured and shows a plateau. Sample 2 is recleaved in order to divide cross surface by 10 but its length stays exactly the same in order to reserve the electric contacts already deposed. Then we obtained sample
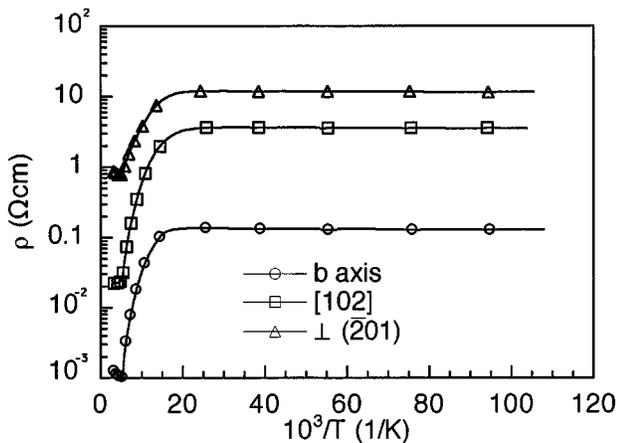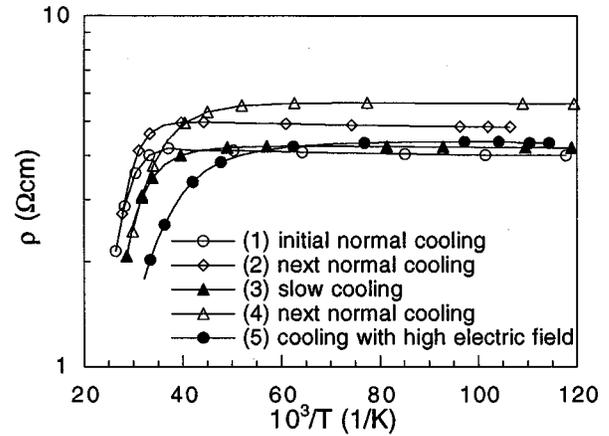
3, which has exactly the same resistivity as sample 1. From these verifications, we can exclude a surface phenomenon. X-ray powder diffraction studies at room temperature on normal and annealed samples showed no clear difference.

The Peierls transition temperature, characterized by a peak in $(1/\rho)[d \ln(\rho)/dT]$, is not modified after annealing. The resistivity for each crystal direction shows a plateau below $T \approx 40$ K. The electrical anisotropy ratios are of the same order of magnitude as in the unannealed samples (Fig. 2). We observed a 5% decrease of the resistivity between 40 K and 35 mK. The absolute level of the plateau increases after a few thermal cycles, whereas the onset temperature for the plateau formation T_{plat}, defined by the peak of derivative $d\rho/dT$, decreases. We can significantly decrease the plateau level by cooling the sample very slowly or by applying a high electric field during the cooling (Fig. 3). However, all these procedures have no effect on the onset temperature of the plateau T_{plat}, which decrease monotonously without correlation to the plateau level (Fig. 4).

In order to explain the presence of this plateau, a better description of the electronic structure of the annealed samples was necessary. Previous electron paramagnetic results (EPR) for nonannealed blue bronzes[9] have provided

FIG. 2. Resistivities of the potassium blue bronze after annealing in three crystalline directions versus $1000/T$ (K^{-1}).
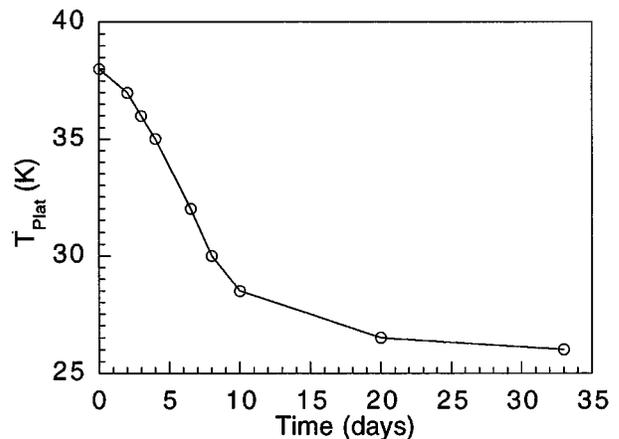
FIG. 4. Evolution of the onset temperature of the plateau T_{plat} versus time (days) obtained after successive cooling.
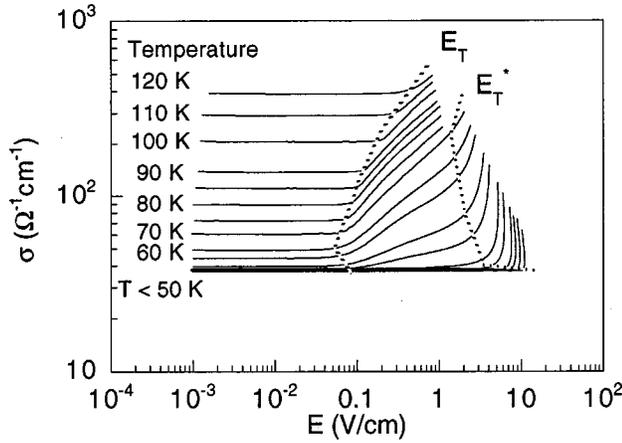
FIG. 5. Conductivity in the annealed potassium blue bronzes versus electric field measured between 10 and 120 K. The threshold fields E_T and E_T^* are marked by dotted lines.

some interesting information about the CDW ground state, we have carried out such an analysis for our annealed samples. We found a very strong EPR signal coming from the unusually high concentration of isolated Mo^{5+} sites with respect to unannealed samples, indicating an electronic transfer inside the annealed samples. By comparing the EPR signal with the untreated blue bronze, we found that the Mo^{5+} concentration, typically 1000 ppm in our annealed blue bronzes, is one order of magnitude larger than untreated samples. In agreement with our resistivity measurements, the Mo^{5+} defects are well distributed over the entire sample volume.

The semiconducting behavior of the untreated blue bronzes results from the Peierls gap opening in the Fermi surface below the CDW formation temperature $T = 183$ K. Nevertheless, the change of resistivity behavior observed below $T \approx 40$ K in the annealed samples does not affect the CDW. Indeed, dc resistivity measurements versus applied electric field yielded both threshold fields E_T and E_T^*. This is observed and defined in other CDW materials such as NbSe$_3$.[10] These measurements are in the same range as those of nonannealed samples (Fig. 5). In the annealed samples it is possible to follow the thermal evolution of E_T^* in the 10 to 70 K temperature range and for some samples we can observe the merging of the E_T curve in the E_T^* curve below 30 K (Fig. 6).

Between 100 and 40 K, the dielectric constant is very similar to the one measured in unannealed samples (Fig. 7), showing a cusp in the vicinity of $T = 50$ K. Below 50 K a rapid drop can be observed but the dielectric constant keeps a significant value of 10^5.

The same qualitative results were observed on annealed rubidium bronzes with silver or copper contacts.

The change in resistivity leads us to suggest structural evolution in the blue bronzes at $T \approx 40$ K, which could be in agreement with Schutte's measurement[8] of the lattice parameters, which suggest strong changes in the lattice properties.[11] This evolution could be related to several anomalies observed in the blue bronzes in this temperature range.[5-7] Our measurements of the threshold field and of the dielectric constant corroborate the presence of a CDW at low
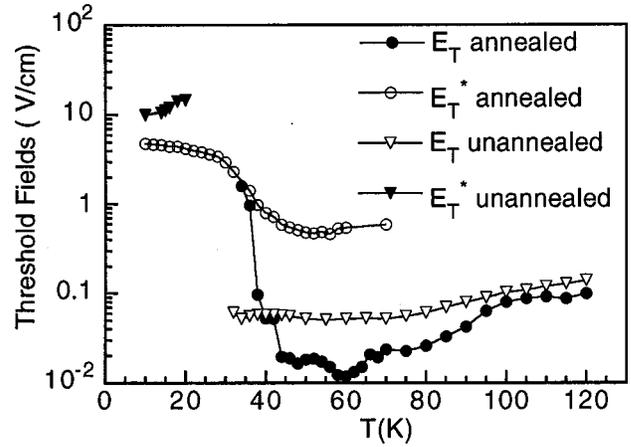

FIG. 6. Thresholds fields E_T and E_T^* in the unannealed and annealed potassium blue bronzes versus temperature.

temperatures in annealed samples but are short circuited by an additional conductivity mechanism. This phenomena could be explained by the existence of Mo^{5+} sites, localized outside of the conducting chains (Mo two sites[2]). These sites do not contribute to the conduction above $T \approx 40$ K. These defects with respect to the perfect structure can be produced by an annealing in the presence of a metal that gives electrons by redox reaction or by catalysis. The additional sites Mo^{5+} can contribute to the conductivity via orbital overlaps only after a structural evolution at low temperature. The resistivity of the annealed samples depends at least on two parameters such as absolute number of the defects in Mo^{5+} and their ordering. Contrary to the plateau level, T_{plat} is totally independent of an applied electric field during cooling. One possible explanation is that a high electric field may order the defects and decrease the plateau level but cannot affect their number. More precisely, the Mo atoms valence increases with time independent of the cooling conditions. This is also observed in hydrated blue bronzes.[12]

The temperature of the plateau formation T_{plat} should only depend on the number of defects, whereas the plateau level should also depend on the disorder of the defects affected by
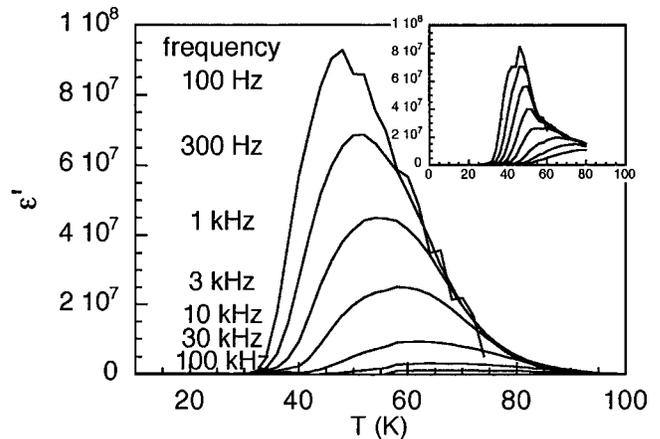

FIG. 7. Real part of the dielectric constant in the annealed potassium blue bronzes versus temperature measured between 100 Hz and 100 kHz. The inset shows the real part of the dielectric constant versus temperature in the unannealed potassium blue bronze for the same frequencies.

the application of the high electric field during the cooling. In the unannealed samples, the defects Mo^{5+} are also present but not numerous enough to significantly lower the total resistivity; however, other anomalies can appear by a local perturbation of the conductivity.

In conclusion, the annealed molybdenum blue bronzes with metal contacts show a plateau in the resistivity below $T \approx 40$ K, increasing after thermal cycling. Our measurements of the dc and ac conductivity corroborate the existence of a CDW at temperatures below 40 K. The structural evolution revealed by additional conduction due to an orbital overlap of defects Mo^{5+} induced by annealing with metallic contacts could explain the plateau. This evolution could also be responsible for the other anomalies observed in the unannealed blue bronzes at $T \approx 40$ K.

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