Temperature dependence of the structural parameters of the host lattice in blue bronze $K_{0.3}MoO_3$

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Structural parameters of the host lattice in quasi-one-dimensional blue bronze $K_{0.3}MoO_3$ were measured in the range 10–300 K. It is found that the temperature dependence of the unit cell parameters *a*,*b*,*c*, cell volume *V*, and angle β, and parameters $a_{[102]}$ and $d_{[\bar{2}01]}$ all present noticeable unusual changes in the slope near about 178 and 50 K, respectively. The change of the structural parameters near 178 K is in relation to the Peierls phase transition, while the second change near about 50 K may be an indication of some subtle variations in structures at 50 K.

Blue molybdenum bronzes $A_{0.3}MoO_3$ (A=K, Rb, and Tl) are quasi-one-dimensional conductors at room temperature and undergo a Peierls phase transition near about 180 K.[1,2] They have been extensively studied in the past because of their rich variety of dynamical properties with a charge-density wave (CDW) in presence of an applied electric field.[3] Two separate regimes for nonlinear CDW conductivity have been observed in blue bronze. At temperatures above 50 K, the transport of the CDW above a small depinning electric field $E_{T1}\sim 10-100$ mV/cm involves a viscous damping due to Coulomb screening of the CDW fluctuation by normal carriers.[4] At lower temperatures below about 50 K, where the normal carriers become too small to provide screening, a drastic drop of damping for the sliding of the CDW occurs, and the CDW condensate moves almost rigidly above a large second abrupt threshold $E_{T2}\sim 10-150$ V/cm.[5,6] Usually, the change of the two regimes near 50 K is accompanied by a series of anomalies in physical properties, for example, a tiny kink in magnetic susceptibility,[7] a big negative peak in thermoelectric power,[8] and glasslike relaxation in dielectric responses[9] and polarization.[10] Whether these anomalies are, to some extent, related to a phase transition or some change in the host lattice structures is still unclear.

A number of structural studies by x-ray and neutron scattering were made previously,[11,12] and many were focused on the variations of the CDW modulation structures. It was revealed that the periodic distortion of the CDW is characterized by a wave vector $\mathbf{q}=(0,q_b(T),0.5)$, where the component q_b along the b^* direction is incommensurate from 180 K down to 10 K. In contrast, little was reported for the variations of the host lattice as a function of temperature. As suggested by Duggan and Ong[13] and Wang and Ong,[14] a change in host parameters exerts a stress on the CDW if the CDW condensate cannot adjust quickly enough to a change in the host. Actually, the external stress has been shown to have a large effect on the properties of the CDW.[15,16] In order to obtain more structural information about blue bronzes, we pay attention to the variations of the host lattice at low temperatures. The results present some noticeable changes in the host lattice near the phase transition and 50 K. A brief explanation for these subtle changes was presented correspondingly.

Single crystals of blue bronze used in this work were grown by standard electrolytic reduction of a K_2CO_3-MoO_3 melt with a mole ratio of 1:4.35.[17] The starting mixture was melted in alumina crucible at 555 °C by using a vertical tube furnace. A current of 20 mA was maintained through the melt for electrolysis about 4–10 h. Platelet crystals with average dimensions of $5\times3\times1$ mm^3 were obtained on the cathode. The crystals were cleaned in dilute ammonia or HCl solution. Transport[18] and specific heat measurements[19] have shown previously that the Peierls phase transition that is accompanied by the formation of a CDW takes place near about 178 K.

The x-ray experiment was carried out with copper $K\alpha$ x rays from an 18-kW MXP18AHF rotating anode generator (MAC Science Co., Japan). The crystals were powered and pressed into a copper sample chamber, then fixed in a helium closed-cycle refrigerator with an appropriate temperature controller. The whole system was controlled automatically by a computer, and the temperature could be varied in the range 10–300 K. The spectra of powder x-ray diffraction were collected at various temperatures in the range of 2θ angles from 5° to 80°. The diffraction peaks of the host lattice were indexed preliminary on the unit cell proposed by Graham and Wadsley.[20] The refinements of the unit cell parameters were carried out carefully by the least-squares refinement program.

Figures 1(a), 1(b), and 1(c), respectively, show the host lattice parameters *a*, *b*, and *c* as a function of temperature from 10 to 300 K. It is seen that three parameters *a*, *b*, and *c* all decrease with temperature from 300 to 178 K, and then decrease more rapidly down to 50 K. The clear change of the curve slope for three parameters were observed near the Peierls transition 178 K. Below about 50 K, the parameters *a* and *c* become almost temperature independent, while parameter *b* presents an observable upturn kink at 50 K, and then

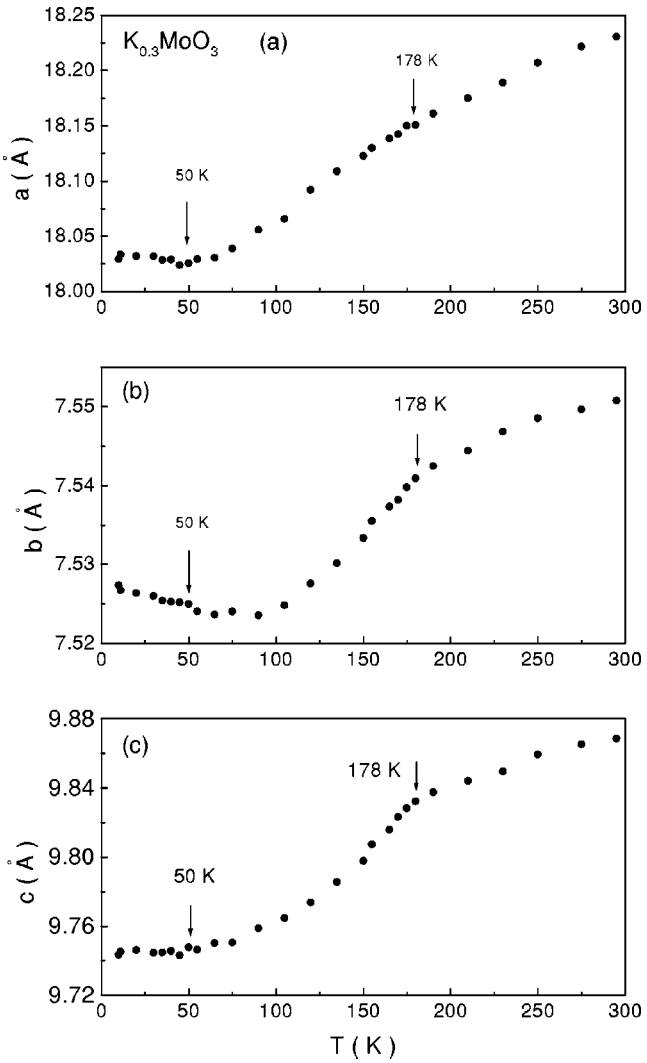

FIG. 1. (a), (b), and (c), respectively, show temperature dependence of the unit cell parameters *a*, *b*, and *c* in the range 10–300 K.

shows slight expansion down to 10 K (the parameter *b* is almost constant from 100 to 50 K). The result for the unit cell parameter *c* near 50 K is in agreement with the preliminary data shown in Ref. 1, but there are no data for the parameter *b* there. Ghedira *et al.*[21] reported the data measured by x-ray diffraction measurements at temperatures above 110 K. They observed a very small discontinuity for the cell parameters at about 220 K, but no data were given below 110 K.

Figures 2(d), 2(e), 3(f), and 3(g), respectively, show the variations of the unit cell volume V, angle β, parameter $a_{[102]}$ along the [102] direction in the slab, and the space distance $d_{[\bar{2}01]}$ between the $(\bar{2}01)$ cleavage surfaces as a function of temperature. The parameters V, $a_{[102]}$, and $d_{[\bar{2}01]}$ all show a very similar behavior with those observed in Fig. 1. The noticeable changes of the slope for three parameters V, $a_{[102]}$, and $d_{[\bar{2}01]}$ are clearly seen at temperatures 50 and 178 K, respectively. But the change of the slope for the space distance $d_{[\bar{2}01]}$ is smoother at 178 K than that for the vector $a_{[102]}$ along the [102] direction in the slab. Below about 50 K, the parameter $a_{[102]}$ shows a similar behavior with the parameter *b*, i.e., a small upturn kink below about 50 K at first, and then expands noticeably down to 10 K. In Fig. 2(e),

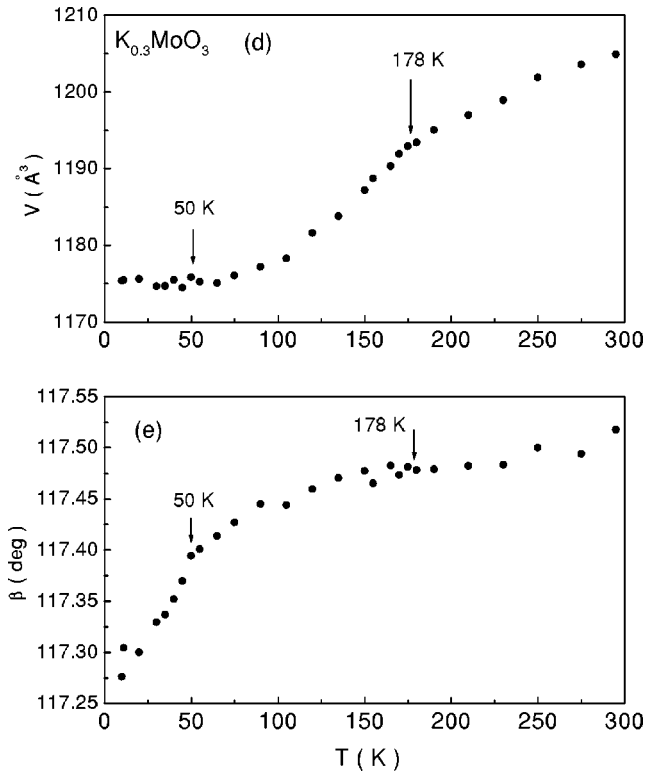

FIG. 2. (d) and (e), respectively, show the temperature dependence of the unit cell volume V and angle β in the range 10–300 K.

the parameter β decreases with the temperature from 300 to 10 K. It is worth noting that a downturn kink at 50 K and a meaningful change near the transition temperature 178 K were distinguished in the precision of the experiment.

Figure 3(h) shows the relative changes, $\Delta\alpha/\alpha_0$, of the host parameters *a*, *b*, *c*, unit cell volume V, parameter $a_{[102]}$, and space distance $d_{[\bar{2}01]}$ as a function of temperature, where α_0 and $\Delta\alpha=\alpha-\alpha_0$, respectively, denote the magnitude of the parameters at room temperature and the variation at different temperatures. It is seen that the relative changes of these parameters *a*, *b*, *c*, V, $a_{[102]}$, and $d_{[\bar{2}01]}$ reach about -1.13%, -0.35%, -1.26%, -2.47%, -1.01%, and -1.19% at 50 K, respectively. The value of $\Delta b/b_0 \sim -0.35\%$ at 50 K is smaller than the values of $\Delta a/a_0$, $\Delta c/c_0$, $\Delta a_{[102]}/a_{0[102]}$, and $\Delta d_{0[\bar{2}01]}/d_{0[\bar{2}01]}$ by about a factor of 3.2, 4.1, 2.9, and 3.8, respectively.

As mentioned above, these results indicate that the thermal linear expansion of the unit cell is strongly anisotropic in the studied temperature range. The extensive variations take place mainly along [102] and $[\bar{2}01]$ directions; a slight change was observed along the *b* chain. These results mean that, with decreasing temperature, the structure contracts mainly along $[\bar{2}01]$ direction perpendicular to the MoO_6 octahedral slabs and the [102] direction transverse to the MoO_6 chain. The large change of $\Delta d_{[\bar{2}01]}/d_{0[\bar{2}01]}=-1.19\%$ along $[\bar{2}01]$ direction does not result from the reduction of Mo-O bonds in the MoO_6 octahedral slabs, but must result from the reduction of the K-O bonds. Such a structural rearrangement around the potassium K atoms at low temperatures is in agreement with expectation, as the K-O bond is weaker than the Mo-O bond in the MoO_6 chains. Except for the large change of $\Delta d_{[\bar{2}01]}/d_{0[\bar{2}01]}$, the change of $\Delta a_{[102]}/a_{0[102]}$

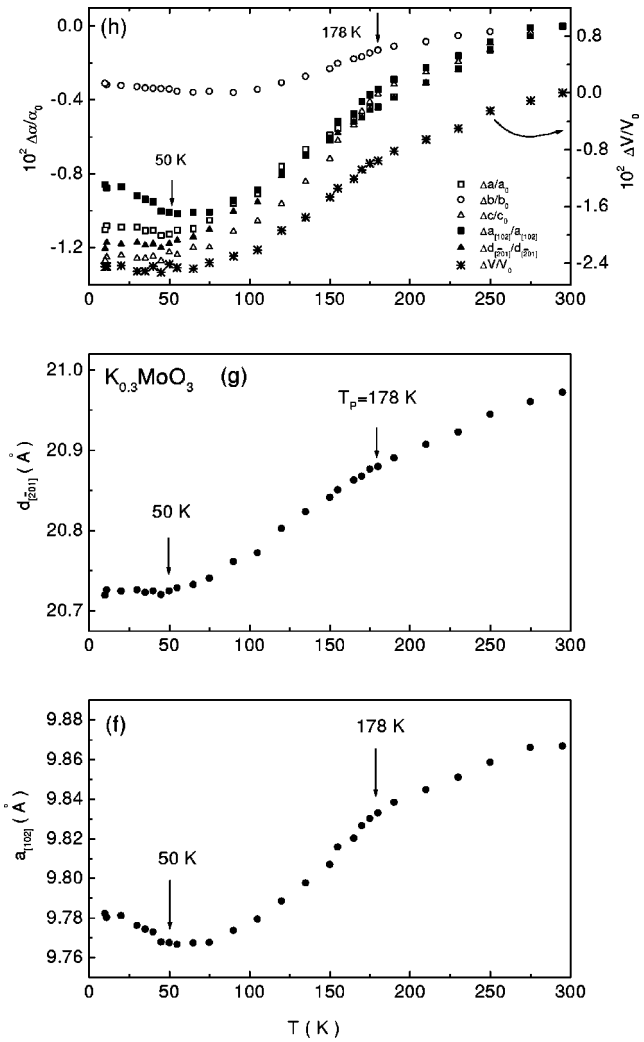

FIG. 3. (f) and (g), respectively, show the temperature dependence of the parameter $a_{[102]}$ and the space distance $d_{[\bar{2}01]}$. (h) shows the relative changes of the host lattice parameters in the range of 10–300 K; the right scale is for cell volume $\Delta V/V_0$.

along the [102] direction in the slab also reaches about -1.01%, which is 2.9 times larger than that for $\Delta b/b_0$. This big change would be independent of the K-O bond, which is related to the contraction of the Mo-O bonds along the [102] direction. That is to say, the distortion of the MoO_6 octahedra or displacements of the Mo atoms takes place mainly along the transverse direction towards the bridge oxygen connected the two MoO_6 octahedra chains. This is in agreement with the previous structural determination by x-ray diffuse scattering measurement;[22] the b direction with one-dimensional MoO_6 chains is more rigid.

Two significant aspects would be noted in this Brief Report: (1) The changes of the slope of the curves for all host parameters were observed near 178 K. The large changes are mainly along the b and [102] directions within the MoO_6 octahedra slab, while perpendicular to MoO_6 octahedra slab, a weak and smooth change in the slope for the space distance $d_{[\bar{2}01]}$ was seen near 178 K. Obviously, the changes in the slope for the host lattice near 178 K are related to the Peierls thermodynamics phase transition concerning the MoO_6 octahedra slab, at which a sharp anomaly of specific heat was observed.[19] (2) The host lattice was frozen below about 50 K along a, c, and $[\bar{2}01]$ directions, where the parameters become almost temperature independent down to 10 K. In contrast, the parameters b and $a_{[102]}$ within the MoO_6 slab exhibit a slight expansion below about 50 K. In addition, the angle β presents a downturn kink at 50 K. Although the freezing phenomenon of the host lattice at lower temperatures is not considered to be an unusual case for some materials (for example, in aluminum), the freezing aspects found in blue bronze seem to be very fascinating in that the decrease or suppression of the space distance $d_{[\bar{2}01]}$ perpendicular to the MoO_6 slab was accompanied by a slight unusual expansion along the [010] and [102] directions within the MoO_6 slab below about 50 K. As is known, the CDW condensate parameters are also mainly within this slab. At present, we cannot yet confirm that the dramatic changes of the host lattice are really related to a possible phase transition near about 50 K, but some anomalies in the physical properties as mentioned in the literature were indeed observed near about 50 K. The slight downturn kink of the angle β at 50 K might be indicative of some subtle structural variations in blue bronze. Since the cessation of the CDW condensate in the blue bronze below about 50 K has also been explored experimentally,[23,24] where the relaxation time is very slower and is of the order of a year, the stress effect on the frozen CDW condensate induced by the unusual expansion of the host lattice along [010] and [102] directions might also be considered as a mechanism for the anomalies of some physical properties below about 50 K.

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