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PROPERTIES OF TEMPERATURE DEPENDENCE OF THRESHOLD IN PURE AND IMPURITY-DOPED BLUE BRONZES *

TIAN MING-LIANG(田明亮), MAO ZHI-QIANG (毛志强), and
ZHANG YU-HENG(张裕恒)[1)]
Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, China

ZHANG YI-MIN(张一民)[2)], SHI JING(石 兢), and
TIAN DE-CHENG(田德诚)
Department of Physics, Wuhan University, Wuhan 430072, China.

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Temperature dependence of the threshold of pure and impurity-doped blue bronzes has been studied. It is found that for pure blue bronzes the threshold field near 100K has an anomalous peak, but for impurity-doped samples no anomaly is observed in the range of liquid nitrogen temperature, and the value of the threshold field gradually increases with the decrease of temperature. The results show that in the high-quality pure blue bronzes, there may exist an incommensurate to quasi-commensurate transition near 100K. But for the impurity-doped or "dirty" pure samples, such an incommensurate to quasi-commensurate transition near 100K can be extensively restrained by impurities or defects, which leads to a pure incommensurate CDW in a wide temperature range.

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I. INTRODUCTION

The layered structure compounds blue bronzes, $A_{0.3}MoO_3$(A=K, Rb or Tl), are typical model materials with charge-density-waves(CDW). They belong to quasi-one dimensional conductors[1] at room temperature and undergo a metal-semiconductor(M-S) transition at 180K, which is known to be a Peierls transition and accompanied by the formation of charge-density-wave(CDW) connected with the $2K_F$ periodic lattice distortion[2-4]. In earlier time, the CDW mechanism proposed by Fröhlich[5] was used to explain the one-dimensional superconductivity, but due to its lack of experimental evidences, such a mechanism did not give

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1)Also Chinese Center of Advanced Science and Technology (CCAST)(World Laboratary), Beijing 100080, China.
2)Laboratory of Electron Diffraction, Engineering college of Luoyang, Luoyang 471039, China

rise to attention by then. Since 1976, when Monceau *et al.*[6] first provided the existence of CDWs in the quasi-one dimensional conductor $NbSe_3$, much attention has been attracted. They also proposed that the sliding transport of the CDW is not freely undamping, but is strongly damped due to the pinning effects by defects or other impurities; when the electric field exerted on the sample is less than a critical value E_T, the CDW condensate is still pinned and cannot carry current, so that the DC conductivity has a normal ohmic behavior. At $E > E_T$, the CDW depinned by the applied field can be driven into current-carrying state, and leads to a nonlinear transport. Such a critical field E_T is usually defined as the threshold field. Based on Fukuyama-Lee model[7], the magnitude of the threshold field can reflect the pinning strength of CDW, thus the changes of the threshold behavior with temperature are able to provide some important information on the pinning mechanism of the charge-density-wave. Almost all of the threshold properties of the CDW compounds are sensitive to temperatures and defects[8]. Therefore, the study of the relations between CDW and defects is an effective way in order to have a deep understanding of the CDW dynamical properties. In the past years, although the transport properties[9], NMR[10] and EPR[11,12] microprobe researches on the blue bronzes clearly showed an anomaly in the vicinity of 100K, which seems to indicate an incommensurate to commensurate(I-C) transition at 100K, X-ray diffraction studies[13,14] of the pure and impure crystals did not present a clear evidence that the CDW system reaches a real commensurate modulation ($0.75b^*$ along b-axis), on the contrary, it shows a small deviation from $0.75b^*$. Hence, whether there really exists such an I-C transition at 100K, it still remains controversial. In this paper, by comparison with the temperature dependence of the threshold properties of pure and impurity-doped bronzes, we further investigate the possible I-C transition existing at 100K.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Single crystals of pure $A_{0.3}MoO_3$(A=K, or Tl), impurity-doped $(K_{1-x}Tl_x)_{0.3}MoO_3$($x = 0.2, 0.5$) and $Tl_{0.3}Mo_{1-x}W_xO_3$($x < 0.1$) blue bronzes used in this work were grown by electrolytic reduction method[15]. The structures and components were verified by X-ray photoemission spectroscopy(XPS), X-ray diffraction(XRD) and scanning tunneling microscopy(STM) measurements, the results are in good agreement with those in Ref.[16]. Physical property researches[17,18], photoacoustic spectra[19] and Raman spectroscopic measurements[20] at low temperatures provided the information that the crystals undergo a metal-semiconductor transition at 180K which is accompanied by the formation of charge-density-wave(CDW).

All measurements of the samples were performed by two-probe method. Electrical contacts were made by means of soldering metal indium on the evaporated Au-film at the two ends of the sample. At each contact two Au conducting wires were attached as the current and voltage leads, respectively. The threshold field E_T at various temperatures were determined from the measured DC $I-V$ characteristic curves. In the measurements the current was applied by constant current source. In order to ensure the virgin state of the samples, all of the threshold values were determined from the first DC $I-V$ characteristic curve recorded at each temperature.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Figures 1 and 2 show, respectively, the curves of the threshold field E_T versus temperature for pure $K_{0.3}MoO_3$ and $Tl_{0.3}MoO_3$. It can be clearly seen that, for these two pure blue bronzes, there exists an anomalous peak of the threshold field in the vicinity of 100K. For the pure potassium bronze, at $T < 90$K, the value of the threshold field reduces slightly with the decrease of temperature, while at $T > 90$K, the threshold value increases with the decrease of temperature, and thus leads to a wide and smooth peak at about 90K. For the pure thallium bronze, there also exists a sharp peak at 106K; at $T > 106$K, the threshold value increases with the decrease of temperature, while at $T < 106$K, the value decreases with decreasing temperature.

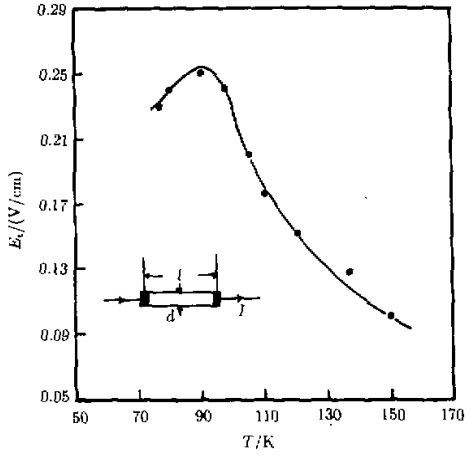

Fig. 1. Threshold field E_T versus temperature T curve for pure $K_{0.3}MoO_3$. $l \times d \approx 2\text{mm} \times 1\text{mm}$.

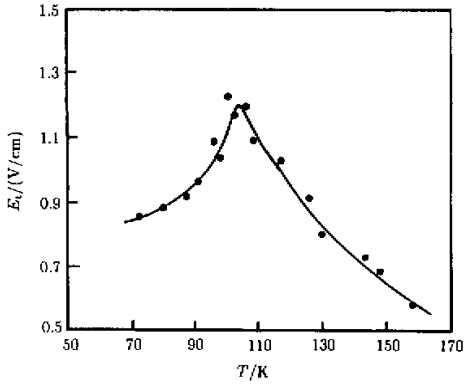

Fig. 2. Threshold field E_T versus temperature T curve for pure $Tl_{0.3}MoO_3$. $l \times d \approx 3mm \times 2mm$.

Figures 3, 4, and 5 show the E_T versus T curves for $(K_{0.8}Tl_{0.2})_{0.3}MoO_3$, $(K_{0.5}Tl_{0.5})_{0.3}MoO_3$ and $Tl_{0.3}Mo_{1-x}W_xO_3$ alloy samples. It is interesting that for three impurity-doped alloy samples, no anomalous behavior was observed in the measured temperature range; in contrast, we found that the threshold field gradually increases with the decrease of temperature. Besides, for the W-doped sample, at T >120K, the threshold field is weakly dependent on temperature, while at temperatures very near the Peierls transition temperature T_p, the threshold field increases slightly.

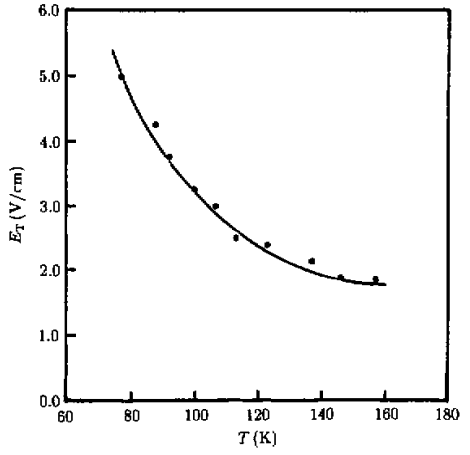

Fig. 3. Threshold field E_T versus temperature T curve for impurity-doped $(K_{0.8}Tl_{0.2})_{0.3}MoO_3$ alloy blue bronze. $l \times d \approx 2mm \times 0.5mm$.

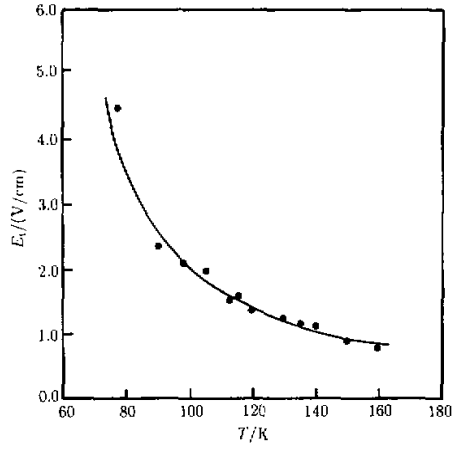

Fig. 4. Threshold field E_T versus temperature T curve for impurity-doped $(K_{0.5}Tl_{0.5})_{0.3}MoO_3$ alloy blue bronze. $l \times d \approx 3.0\text{mm} \times 1.5\text{mm}$.

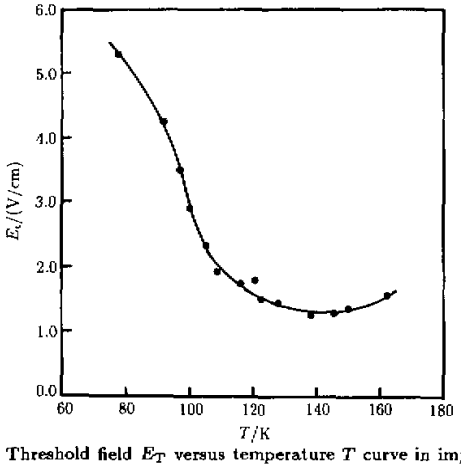

Fig. 5. Threshold field E_T versus temperature T curve in impurity-doped $Tl_{0.3}Mo_{1-x}W_xO_3$ alloy blue bronze. $l \times d \approx 2\text{mm} \times 1\text{mm}$.

According to Fukuyama and Lee model[7], the static CDW states pinned by impurities and other defects have a relatively lower energy. For the strong pinning centers, the threshold field E_T of CDW condensate can be described by the relation $E_T \propto n_i$, where n_i denotes the concentration of the impurities. For the weak pinning centers, $E_T \propto n_i^2$. But in fact, the two kinds of pinning centers (strong and weak) always co-exist in the samples measured. From Figs.1–5, it can be seen that the threshold value of CDW depinned for the pure samples are smaller than that for the impurity-doped alloy samples. They indicate that the threshold E_T of CDW is indeed closely related with the defects and impurities of the samples. With

respect to the threshold behavior of the blue bronzes, some researchers have ever reported different results. Dumas *et al.*[9] showed an anomalous peak of the threshold field at 100K, this result is in good agreement with our measured results. But Fleming *et al.*[21,22] reported different experimental results in the different papers, for example, in Ref.[21] the reported temperature dependence of the threshold field reduced monotonically with the decrease of temperature. In Ref.[22] the threshold field presented a drop at 40K, then increased with the increase of temperature; when the temperature reached 110K, a broadened peak occurred. Up to now, to our knowledge, all reported results did not show the threshold feature of the impurity-doped samples. However, we found in this work that the anomalous behavior of the threshold field at about 100K can only be observed in the pure blue bronzes, as compared with the impurity-doped samples. This indicates that such a difference of the threshold fields in the two kinds of samples is not by accident, it might be closely associated with the internal pinning mechanism. We speculate that a possible origin is due to the existence of the incommensurate to quasi-commensurate transition at about 100K in the high quality pure blue bronzes. But in the impurity-doped alloy samples, the randomly distributed impurities or defects, to some extent, destroy the long range order of the CDW, and therefore greatly restrain the alloy samples from the formation of the commensurate CDW states at 100K, so the CDW system is still incommensurate in whole temperature range considered. In addition, according to the behavior of the temperature dependence of the threshold field in impure samples which increases with the decrease of temperature, it means that the pinning force for CDW condensate increases with the decrease of temperature, i.e. the coupling between the impurities and CDW condensate increases. This corresponds to the increase of the degree of order for the impurities or defects in the incommensurate modulated field. In this model, a small fraction of impurities will become ordered in the field of modulation, and lead to a possible formation of defect-density-wave (DDW)[23] due to the developing of order of the defects with decreasing temperature. Although we have no unambiguous evidence to show whether or not such an ordering is essentially associated with defect-density-wave (DDW), the memory effects due to DDW have been reported in several incommensurate system[24,25]. Hence, in the impurity-doped blue bronzes, concerning whether the observed large memory effect, electric and heat hysteresis phenomena are related with the DDW, a further investigation may be needed.

The reason why X-ray diffraction and neutron scattering experiments on pure blue bronzes did not reveal a completely, commensurately modulated wave vector $0.75b^*$ along b-axis at 100K may be due to the influence of the defects and impurities in the large crystals used, the whole crystal may not undergo a commensurate transition at 100K; a possible case is that the CDW system takes an incommensurate to quasi-commensurate transition at 100K in pure samples, i.e. at $T < 100$K, a lot of commensurate domains of CDWs

form along b-chains, separated by walls (discommensurate of phase soliton etc)[26]. For this case the pinning by walls also can be attributed to the defect mechanism, and therefore the depinning of CDW in the electric field would not need higher energy. When the temperature decreases from 100K, the volume of the commensurate domains will increase, and correspondingly, the walls of domains decrease, which leads to the reducing of the pinning force. This means that the threshold field of CDW depinning will decrease with decreasing temperature. At $T > 100$K, the degree of order in the CDW system for the pure samples gradually increases with the decrease of temperature, and this leads to the increase of the threshold field with reducing temperature. In X-ray diffraction and neutron scattering experiments, the case with commensurate domains structure will not be clearly distinguished from the incommensurate case. They give only an average results of the entire crystal studied. Evidences of the commensurate domains below 100K have been demonstrated by the NMR[10], EPR[11,12] microprobe studies. Raman scattering studies[20] at low temperatures for pure $K_{0.3}MoO_3$ and impure $(K_{0.5}Tl_{0.5})_{0.3}MoO_3$ samples have also found that only in pure samples the strength of the soft mode of the CDW amplitude has an anomaly at 100K, and therefore they provide further the evidence of the existence of such an incommensurate to quasi-commensurate transition at 100K in pure samples. Such a transition can be quenched by impurities or other defects. Our measurements of the threshold are more direct and sensitive to reflect such a transition.

In summary, we have studied the temperature dependence of the threshold field properties of pure and impurity-doped blue bronzes, and qualitatively provided that the incommensurate to commensurate transition of blue bronzes at about 100K are sensitive to the influence of the impurities or defects, only in the high-quality pure samples such an I-C transition can be observed, and in the impure crystals the system remains to be pure incommensurate.

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