Shubnikov–de Haas effect and magnetic breakdown in the low-temperature charge-density-wave state for the thallium purple bronze $TlMo_6O_{17}$

Xiaokui Qin
Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China

Jing Shi
Physics Department, Wuhan University, Wuhan 430072, People's Republic of China

Huayang Gong
Institute of Physics, Academia Sinica, Beijing 100080, People's Republic of China

Mingliang Tian
Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China

Junyin Wei and Hong Chen
Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China

Decheng Tian
Physics Department, Wuhan University, Wuhan 430072, People's Republic of China
and International Center for Material Physics, Shenyang 110015, People's Republic of China
(Received 15 January 1996)

Magnetoresistance has been studied for quasi-two-dimensional thallium purple bronze $TlMo_6O_{17}$ at a temperature of 4.2 K in fields up to 12 T. Shubnikov–de Haas oscillations are observed. The calculated Fermi surface size is about 5×10^{-4} in the high-temperature Brillouin zone and consistent with hidden Fermi surface nesting theory. The field dependence of magnetoresistance is studied in the vicinity of magnetic breakdown. The characteristic field of breakdown is around 0.08 T corresponding to an energy gap of about 2 meV. The effective mobility and cyclotron mass are about 0.025 $m^2\ V^{-1}\ s^{-1}$ and $0.3m_e$, respectively. [S0163-1829(96)07223-2]

I. INTRODUCTION

The purple molybdenum bronzes AMo_6O_{17} (A=Na, K, Tl) are quasi-two-dimensional metals due to a trigonal layered structure including MoO_6 octahedra separated by A^+ ions and MoO_4 tetrahedra.[1] They undergo a metal-metal transition at around 120 K due to a partial opening of gaps on the quasicylindrical Fermi surface. Band-structure calculations using a tight-binding method in a two-dimensional (2D) approximation lead to three partially filled bands crossing the Fermi level.[2] They can be decomposed into three sets of nested 1D Fermi surfaces, which are perpendicular to the a, b, or $(a+b)$ direction of the trigonal lattice.[3] The nesting from such Fermi surfaces causes a charge-density-wave (CDW) formation that removes the nested portions of the combined Fermi surfaces. The nesting in the real Fermi surfaces is not so complete as in the hidden Fermi surfaces, so that some pieces of the Fermi surfaces may remain after the CDW phase transition. Due to the existence of electron and hole pockets on the remaining Fermi surfaces in the CDW state, one may expect positive magnetoresistance and the Shubnikov–de Haas effect to appear in the low-temperature CDW state.

For KMo_6O_{17} very large magnetoresistance is found in the CDW state for the field both perpendicular and parallel to the layer with the current always parallel to the layer.[4,5] Effective mobility $\mu_{\rm eff}$ is found to be extremely large at low temperature with values, for example, of 7×10^3 $cm^2\ V^{-1}\ s^{-1}$ at 25 K for the field perpendicular to the layer. The oscillatory behavior in the magnetoresistance is ascribed to the Shubnikov–de Haas effect. The period of 13 T at 1.9 K corresponds to a very small orbit area, approximately 10^{-3} the high-temperature Brillouin area.[4]

However, there are still some unsolved questions about the magnetic-field-dependent properties for AMo_6O_{17}. First, the field dependence of the magnetoresistance in KMo_6O_{17} was found puzzling, some samples showing an elbow at low temperature around 2 T.[6] Whether it could be due to a magnetic breakdown effect or to spin rotation in a weakly antiferromagnetic spin-density-wave state is not clear at the moment. In addition, Whangbo, Canadell, and Schlenker point out that the size of the hole and electron pockets are not so small (about 1/18 to 1/6 of the Brillouin zone) as suggested by the Shubnikov–de Haas study on KMo_6O_{17} (about 10^{-3} in the high-temperature Brillouin zone).[2] Though the hidden Fermi surface model[3] raised by them later is able to explain the result of the Shubnikov–de Haas study on KMo_6O_{17}, a further experimental check of the Fermi surfaces in AMo_6O_{17} is necessary. Finally, to our knowledge, until now, the field-dependent study has not been extended to other kinds of purple bronzes, such as $TlMo_6O_{17}$.[7,8] The effect

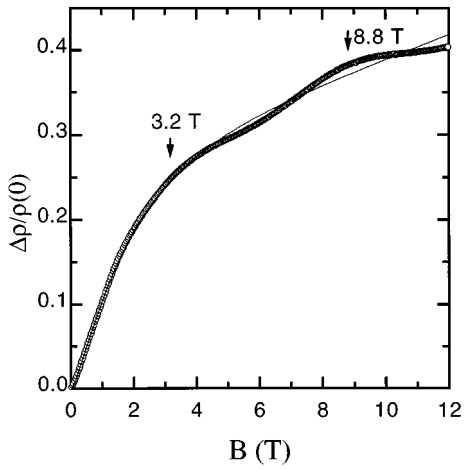

FIG. 1. The field dependence of the magnetoresistance. The solid line is the fitting curve based on Eq. (4).

thallium atoms substituted for potassium atoms in AMo_6O_{17} will have on the magnetic-field-dependent properties is not clear.

In this context, we measured the magnetoresistance for $TlMo_6O_{17}$ at a temperature of 4.2 K in fields up to 12 T. We attempt to clarify the question of whether the magnetic breakdown effect is able to explain the observed field dependence of magnetoresistance or not. At the same time, we can get some information about the remaining Fermi surface in the CDW state through the Shubnikov–de Haas effect in this compound.

II. EXPERIMENTS AND RESULTS

The single crystals were grown from the melt of Tl_2CO_3 and MoO_3 in the molar ratio 1 to 6.5 by an electrolytic reduction method. The samples were identified by x-ray diffraction and electrical resistivity measurement. The crystals are purple elongated platelets of typical size $2\times2\times0.1$ mm^3. Gold contacts were deposited on the crystal surface by evaporation. The current, provided by a Knick J152 dc calibrator, is always parallel to the (a,b) plane. The voltage is measured by a Keithley 182 voltmeter. The sample is put in a commercial ^{3}He cryostat with a magnetic field up to 12 T perpendicular to the (a,b) plane, provided by a superconducting coil.

Figure 1 shows the field dependence of the magnetoresistance at 4.2 K for magnetic fields perpendicular to the layer. The specific resistivity without magnetic field is 20.7 $m\Omega$ cm. Superimposed on a small positive magnetoresistance, two broad oscillations at fields of 3.2 and 8.8 T are observed in Fig. 1. This curve exhibits a downwards curvature. We use a power law,

$$\Delta\rho/\rho(0)=AB^{\alpha}, \tag{1}$$

with

$$\Delta\rho=\rho(B)-\rho(0)$$

to fit the magnetoresistance below 1 T. The fitting results give

$$A=0.103\pm0.005,$$

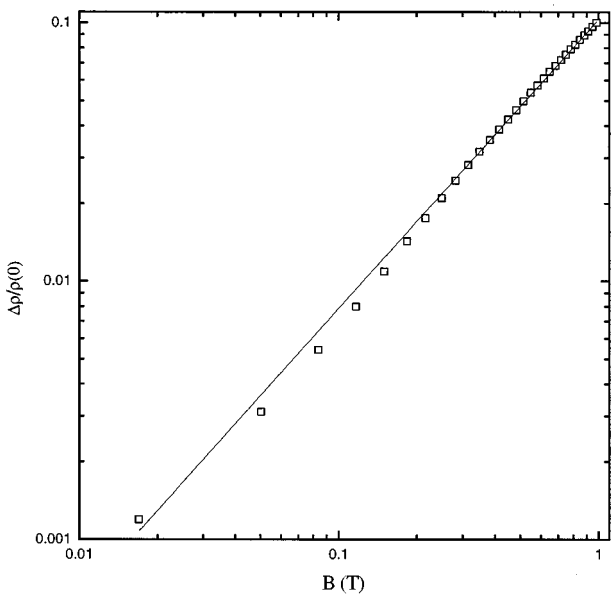

FIG. 2. Log-log plot of the magnetoresistance below 1 T. The solid line is the fitting curve based on Eq. (1).

$$\alpha=1.1\pm0.1.$$

The fitting curve is shown in Fig. 2. α far from 2 means that the semiclassical formula $\Delta\rho/\rho(0)=\mu_{\rm eff}B^2$ is not able to describe the field dependence of magnetoresistance in this compound.

III. DISCUSSION

A. Shubnikov–de Haas effect

In Fig. 1, one can observe two broad oscillations at fields 3.2 and 8.8 T, which are superimposed on a positive magnetoresistance. The oscillatory behavior of the magnetoresistance is usually ascribed to the Shubnikov–de Haas effect, due to oscillations of the density of states at the Fermi level, caused by quantization of electron energy in the presence of the magnetic field. According to this model, the oscillations obey the formula

$$\frac{1}{B_n}=(n+\gamma)\frac{1}{B_F},$$

where $B_F=\hbar A_F/2\pi e$ with A_F the extremal cross-sectional area of the Fermi surface perpendicular to B and $0<\gamma<1$. One may calculate A_F through the formula. From the above observed oscillations at 3.2 and 8.8 T we get

$$B_F=5.0\ \text{T}.$$

This period corresponds to very small extremal orbit areas of $A_F=5.7\times10^{-4}$ $Å^{-2}$. The area of the Brillouin zone at room temperature is about 1.1 $Å^{-2}$ calculated from the unit-cell parameters,[7] so that A_F is approximately 5×10^{-4} in the high-temperature two-dimensional Brillouin zone, which is comparable to that in KMo_6O_{17} (Ref. 4) and η-Mo_4O_{11} (Ref. 9).

Whangbo, Canadell, and Schlenker calculated the electronic band structure of the purple bronze.[2] Their calculations show the presence of the three partially filled d-block

bands. At first, they think that the charge-density-wave transition of $A\mathrm{Mo_6O_{17}}$, which sets in at 120 K, is caused by the nesting of the second d-block band, and the remaining two provide electron and hole carriers below 120 K.[2] Thus the CDW transition does not affect the Fermi surfaces associated with the first and third d-block bands. So the size of the hole and electron pockets of the first and the third Fermi surfaces should be about 1/18 and 1/6 of the Brillouin zone, respectively. However, the Shubnikov–de Haas studies on $\mathrm{KMo_6O_{17}}$, η-$\mathrm{Mo_4O_{11}}$, and $\mathrm{TlMo_6O_{17}}$ suggest the sizes of the carrier pockets are about 1×10^{-3}, $(2–4)\times10^{-3}$, and 0.5×10^{-3} in the high-temperature Brillouin zones, respectively.[4] The failure of the theory is indicated by the experimental results. Later, Whangbo, Canadell, and Schlenker use a hidden Fermi surface nesting model to explain the CDW transition in $A\mathrm{Mo_6O_{17}}$ once more.[3] The essence of this model is that the combination of the three Fermi surfaces, which are associated with the three partially filled d-block bands, can be decomposed into three sets of ideal 1D Fermi surfaces. The nesting of these three sets 1D Fermi surfaces removes almost all the Fermi surfaces. The nesting in the real Fermi surfaces is not so complete, so that some pieces of the Fermi surface may remain after the CDW phase transition. This model explains why A_F observed in the experiment is so small successfully.

The ratio of the size of the carrier pocket to the high-temperature Brillouin zone of potassium purple bronze $\mathrm{KMo_6O_{17}}$ is about 10^{-3}.[4] In $\mathrm{TlMo_6O_{17}}$, this ratio is about 5×10^{-4}. So the size of the carrier pockets is thus much smaller in $\mathrm{TlMo_6O_{17}}$ than in $\mathrm{KMo_6O_{17}}$. This is a clue as to why the specific resistivity in $\mathrm{TlMo_6O_{17}}$ (20.7 mΩ cm) is much larger than that in $\mathrm{KMo_6O_{17}}$ (0.6 mΩ cm).[4] The smaller size of the carrier pockets in $\mathrm{TlMo_6O_{17}}$ may indicate a better Fermi surface nesting in it. One should note the unit-cell parameter c for $\mathrm{TlMo_6O_{17}}$ is longer than that for $\mathrm{KMo_6O_{17}}$.[7] So $\mathrm{TlMo_6O_{17}}$ may have a more pronounced 2D character than $\mathrm{KMo_6O_{17}}$. This is also consistent with the experimentally observed higher Peierls transition temperature in $\mathrm{TlMo_6O_{17}}$. Le Touze *et al.* get similar results in their magnetoresistance measurement for $(\mathrm{PO_2})_4(\mathrm{WO_3})_{2m}$ $(m=4,6)$.[10] They find that the size of the carrier pocket in $m=6$ is only 1/5 the size of the carrier pocket in $m=4$.

B. Magnetic breakdown

In the CDW state, the new periodicity defines the new Brillouin zones in reciprocal space. The energy gaps appear at the boundaries of the new Brillouin zones. The magnitude of the energy gaps, which depends on the CDW strength, is generally small. Therefore the magnetic breakdown through the energy gaps is expected to occur easily in relatively low fields. Thus the possibility of the magnetic breakdown in these compounds is considered. Naito, Tanaka, and Miura have used the magnetic breakdown model to explain the magnetic resistance for $\mathrm{NbSe_2}$ and $\mathrm{TaSe_2}$ successfully.[11] By analogy with the analysis by Naito, Tanaka, and Miura, we fit the magnetoresistance as follows.

According to the semiclassical magnetic breakdown model proposed by Falicov and co-workers, at a finite number of points, which give rise to magnetic breakdown in the orbit of electrons, there may exist a finite probability of transition to (and from) another point in other orbits and the electron undergoes an additional scattering.[12,13] These are points where the energy gaps are small enough to permit an interband transition; they can also be considered the points at which the orbits become coupled to one another, giving rise to a network of possible trajectories. By including this scattering process, the effective relaxation time τ_{eff} of the electron is given as

$$\frac{1}{\tau_{\mathrm{eff}}}=\frac{1}{\tau_0}+\frac{1}{\tau_m},$$

$$\frac{1}{\tau_m}=\omega_c f(P),$$

where τ_0 is the intrinsic relaxation time and τ_m is due to magnetic breakdown. $\omega_c=eB/m_c$ is the cyclotron frequency. m_c is the effective mass of the cyclotron. τ_m is proportional to ω_c^{-1}, because the electron passes through the breakdown points as many times as proportional to ω_c per unit time. P is the breakdown probability, i.e.,

$$P=\exp(-B_0/B)$$

and

$$B_0=K\Delta^2 m/\varepsilon_F\hbar. \tag{2}$$

B_0 is the characteristic field of breakdown, ε_F is the Fermi energy, Δ is the gap between two bands involved in the breakdown, and K is a numerical factor of order 1. The function f depends on the individual case.

If one subtracts the Shubnikov–de Haas oscillation-type magnetoresistance, using the above effective relaxation time, the resistivity in a field is expressed by

$$\rho(B)=\frac{m}{ne^2\tau_{\mathrm{eff}}}[1+(\omega_c\tau_{\mathrm{eff}})^2],$$

$$\frac{\Delta\rho}{\rho(0)}=\frac{\rho(B)-\rho(0)}{\rho(0)}=\frac{\tau_0}{\tau_{\mathrm{eff}}}+\frac{\tau_{\mathrm{eff}}}{\tau_0}(\omega_c\tau_0)^2. \tag{3}$$

As Falicov and Sievert pointed out, in the process of magnetic breakdown when $B\to\infty$ the orbits are decoupled.[12] In other words, in the case $B\to\infty$, the electron will not undergo additional scattering. We can understand this point in the following way. In the presence of the magnetic field B, the electrons run in a circular orbit. The diameter of the orbit is propotional to $1/B$. The strength of the coupling among orbits is mainly decided by the diameters of the orbits. The larger the orbit, the stronger the strength of the coupling. When $B\to\infty$ the orbit is condensed into a point and there exists no coupling among orbits. Consequently, there should exist two characteristic fields in the magnetic breakdown: the onset field B_0 and the termination field B_1. While the onset fields shown in Eq. (2) is determined by the gap between two bands involved in the breakdown, the termination field is the characteristic field at which the orbits begin to decouple. When the fields exceed the onset field, the magnetic breakdown effect will become significant as the consequence of the increase in the probability of breakdown. However, when the fields increase further and exceed the termination field of

breakdown, the magnetic breakdown effect will become insignificant gradually because the coupling of orbits becomes weaker and weaker. In order to compare the experiments with the semiquantitative formula (3), following Naito, Tanaka, and Miura we assume[11]

$$f = c\ \exp(-B_0/B)[1-\exp(-B_1/B)].$$

Here c is a positive constant and B_0 and B_1 are the onset and termination fields of breakdown, respectively. Therefore, Eq. (3) is rewritten as

$$\frac{\Delta\rho}{\rho(0)} = c\mu_{\rm eff}B\exp(-B_0/B)[1-\exp(-B_1/B)] + (\mu_{\rm eff}B)^2/\{1+c\mu_{\rm eff}B\exp(-B_0/B) \times[1-\exp(-B_1/B)]\}, \quad (4)$$

with

$$\mu_{\rm eff} = e\tau_0/m_c. \quad (5)$$

$\mu_{\rm eff}$ is the effective mobility. If c is equal to 0, i.e., the breakdown probability is always zero, Eq. (4) falls to the semiclassical formula

$$\frac{\Delta\rho}{\rho(0)} = (\mu_{\rm eff}B)^2.$$

However, for $TlMo_6O_{17}$, according to the initial analysis in Sec. II, $\Delta\rho/\rho(0) \sim B^{1.1}$. The characteristic parameters of magnetic breakdown of $TlMo_6O_{17}$, i.e., $\mu_{\rm eff}$, c, B_0, and B_1, are determined from the best-fitting procedure according to Eq. (4). They are

$$\mu_{\rm eff} = 0.025 \pm 0.002\ \ {\rm m^2\ V^{-1}\ s^{-1}},$$

$$c = 4.6 \pm 0.4,$$

$$B_0 = 0.08 \pm 0.04\ \ {\rm T},$$

$$B_1 = 3.6 \pm 0.5\ \ {\rm T}.$$

The fitting curves are shown in Fig. 1 by the solid line. Though the fitting curve deviates from the experimental data in the high-field region due to the oscillation of the magnetoresistance, the overall agreement is good. This agreement indicates clearly that the magnetic breakdown model used here is able to explain the experimental results.

The onset field of the magnetic breakdown B_0 is about 0.08 T. If we take $m = m_e$ (free electron mass), $K = 1$, and $\varepsilon_F = 0.3$ eV,[2] the corresponding energy gap Δ is about 2 meV. This value is comparable to that in $TaSe_2$ (4 meV) and $NbSe_2$ (18 meV) estimated from the breakdown fields.[11]

The effective mobility $\mu_{\rm eff} = 0.025\ \ {\rm m^2\ V^{-1}\ s^{-1}}$ of $TlMo_6O_{17}$ at 4.2 K is much smaller than that of KMo_6O_{17}, which is $0.95\ \ {\rm m^2\ V^{-1}\ s^{-1}}$ at 20 K.[4] This means a larger intrinsic relaxation time τ_0 or a smaller effective cyclotron mass m_c in KMo_6O_{17}. We can calculate the ratio of relaxation time through Eq. (3). Using the subscripts K and Tl to stand for the parameters of KMo_6O_{17} and $TlMo_6O_{17}$, respectively, we can derive from (3)

$$\frac{\tau_{0\rm K}}{\tau_{0\rm Tl}} = \frac{\rho_{\rm Tl}(0)n_{\rm K}}{\rho_{\rm K}(0)n_{\rm Tl}}. \quad (6)$$

If we assume that concentration of carriers in the sample is proportional to the remaining carrier pocket size A_F, then we arrive at

$$\frac{\tau_{0\rm K}}{\tau_{0\rm Tl}} = \frac{\rho_{\rm Tl}(0)A_{F\rm Tl}}{\rho_{\rm K}(0)A_{F\rm K}} = \frac{\rho_{\rm Tl}B_{F\rm Tl}}{\rho_{\rm K}B_{F\rm K}}. \quad (7)$$

Substituting the experimental results $\rho_{\rm K} = 0.6\ \ {\rm m\Omega\ cm}$,[4] $\rho_{\rm Tl} = 20.7\ {\rm m\Omega\ cm}$, $B_{F\rm K} = 13$ T (at 1.9 K), and $B_{F\rm Tl} = 5.0$ T to Eq. (7), then we get

$$\tau_{0\rm K}/\tau_{0\rm Tl} = 13.$$

We can further estimate effective cyclotron mass. From Eq. (5), we get

$$\frac{m_{c\rm Tl}}{m_{c\rm K}} = \frac{\mu_{\rm effK}\tau_{0\rm Tl}}{\mu_{\rm effTl}\tau_{0\rm K}}.$$

We substitute the experimental results $\mu_{\rm effTl} = 0.025\ {\rm m^2\ V^{-1}\ s^{-1}}$, and $\mu_{\rm effK} = 0.95\ {\rm m^2\ V^{-1}\ s^{-1}}$ (at 20 K) (Ref. 4) to Eq. (7), then we get a crude estimation:

$$m_{c\rm Tl} \approx 3m_{c\rm K}. \quad (8)$$

One should note that the effective mobility used in the calculation for KMo_6O_{17} is taken at temperature of 20 K. Usually, the lower the temperature, the higher the mobility. So the actual effective cyclotron mass for $TlMo_6O_{17}$ should be greater than that in Eq. (8). The effective cyclotron mass for KMo_6O_{17} is about $0.1m_e$.[4] Here m_e is the mass of electron. So the effective cyclotron mass for $TlMo_6O_{17}$ is about 0.3 times of the free-electron mass. This indicates that the carriers are rather light.

IV. CONCLUSION

The magnetoresistance of thallium purple bronze has been measured at 4.2 K in magnetic field up to 12 T. The Fermi surface calculated from the Shubnikov–de Haas effect is consistent with the hidden Fermi surface theory. The field dependence of $\Delta\rho/\rho(0)$ can be well described by the magnetic breakdown model.

ACKNOWLEDGMENTS

This work was supported by the National Foundation of Science of China and Stiftung Volkswagenwerk.

[1] *Low Dimensional Properties of Molybdenum Bronzes and Oxides*, edited by C. Schlenker (Kluwer Academic, Dordrecht, 1989).
[2] M.H. Whangbo, E. Canadell, and C. Schlenker, J. Am. Chem. Soc. **109**, 6308 (1987).
[3] M.H. Whangbo, E. Canadell, P. Foury, and J.P. Pouget, Science **252**, 96 (1991).
[4] A. Rotger *et al.*, Synth. Met. **55-57**, 2725 (1993).
[5] A. Rotger *et al.*, Physica B **177**, 318 (1992).
[6] J. Dumas and C. Schlenker, Int. J. Mod. Phys. B **7**, 4045 (1993).
[7] M. Ganne, M. Dion, A. Boumaza, and M. Tournoux, Solid State Commun. **59,** 137 (1986).
[8] K.V. Ramanujachary, B.T. Collins, M. Greenblatt, and J.V. Waszczak, Solid State Commun. **59**, 647 (1986).
[9] C. Schlenker, J. Dumas, C. Escribe-Filippini, H. Guyot, J. Marcus, and G. Fourcaudot, Philos. Mag. B **52**, 643 (1985).
[10] C. Le Touze *et al.*, J. Phys. I (France) **5**, 437 (1995).
[11] M. Naito, S. Tanaka, and N. Miura, in *Physics in High Magnetic Fields*, edited by S. Chikazumi and M. Miura, Springer Series in Solid State Science Vol. 24 (Springer-Verlag, Berlin, 1981), p. 320.
[12] L.M. Falicov and P.R. Sievert, Phys. Rev. **138**, A88 (1965).
[13] L.M. Falicov and M.J. Zuckermann, Phys. Rev. **160**, 372 (1967).