Magnetoresistance of quasi-two-dimensional purple bronzes $A\mathrm{Mo_6O_{17}}$ (A=Na, K, and Tl)

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Magnetoresistances (MR's) of quasi-two-dimensional purple bronzes $A\mathrm{Mo_6O_{17}}$ (A=K, Tl, Na) are comparatively studied at 2 K for magnetic fields of $H\|c$ and $H\perp c$, respectively, where c is the direction normal to the two-dimensional plane of the sample. Unusually huge positive MR's for $H\|c$ are analyzed quantitatively by a two-band carriers galvanomagnetic effect on the ungapped residual Fermi surfaces, in which the concentration of the carriers is modified by an applied magnetic field. The modified two-band model can explain the MR's well, and the resulting parameters suggest that the purple bronzes belong to an uncompensated metal.

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Unusual huge positive magnetoresistance (MR) properties in charge-density-wave (CDW) states of quasi-one- or two-dimensional (Q1D or Q2D) conductors, such as $\mathrm{NbSe_3}$,[1–3] $\mathrm{KMo_6O_{17}}$,[4] and $(\mathrm{PO_2})_4(\mathrm{WO_3})_{2m}$,[5,6] have received considerable attention. Balseiro and Falicov[7] proposed a theory in which the magnetic field can remarkably improve the nesting of the FS, and results in an enhancement of the CDW gap. Thus the huge positive MR was attributed to an enhanced gap or a decrease of the normal carriers induced progressively by applied magnetic fields parallel to the FS. A similar model was regarded as a standard model for a formation mechanism of the field-induced spin-density wave observed in Q1D organic conductors.[8]

Using $\mathrm{NbSe_3}$, Parilla *et al.*[9] and Hundley *et al.*[10] gave evidence of magnetic-field-induced enhanced gaps by transport measurements. They observed a 30% increase of the CDW carriers at 30 K under a field of 7.5 T. However, Tritt *et al.*[11] presented negative results; they found that even at $H=10$ T the effect of the magnetic field on the MR was less than 5%. In addition, recent studies of the pressure effect on large MR,[12] and for x-ray scattering[13] in magnetic fields up to 10 T in $\mathrm{NbSe_3}$, further suggested that the large MR might not result from the change in the CDW order parameter with magnetic field but rather from light carriers in small ungapped pockets of the Fermi surface (FS) generated by an imperfect nesting of the FS. Until now, the nature of the huge positive MR effect in the CDW state is still ambiguous.

Compared with $\mathrm{NbSe_3}$, molybdenum purple bronzes $A\mathrm{Mo_6O_{17}}$ (A=Na, K, and Tl) are Q2D CDW materials, but they exhibit very similar transport and a huge positive MR effect below the Peierls transition temperature T_P.[4] Generally, FS's in these compounds reveal very similar features directly related to the so-called ''hidden'' nesting, for which the FS's can be viewed as a combination of Q1D structures with distinct 1D nesting vectors parallel to the 2D plane.[14] For $A\mathrm{Mo_6O_{17}}$ (A=Na, K, and Tl), although they are considered to be pseudoisostructures,[15–17] the physical properties in sodium purple bronze, to some extent, show subtle differences from those in both K/Tl purple bronzes. For example, the Peierls transition temperature T_P in sodium purple bronze is about 80 K,[18–20] and about 110 K in both K/Tl purple bronzes.[18,21] The comparative study among three purple bronzes may be a good candidate to test the present theories or to clarify the related controversies.

In our previous work,[22] we reported the in-plane resistivity as a function of temperature for three purple bronzes $\mathrm{KMo_6O_{17}}$, $\mathrm{TlMo_6O_{17}}$, and $\mathrm{NaMo_6O_{17}}$, respectively, at various magnetic fields H parallel to or normal to the c axis. Comparative studies suggested that the huge positive MR effect in purple bronzes is closely related to the large modification of the third FS along the [100] direction induced by the magnetic field, and to the normal galvanomagnetic effect on the ungapped residual FS. The different MR behaviors between Na and K/Tl purple bronzes originate from their different FS structures. Moreover, a simple one-band semiclassical galvanomagnetic model, $\Delta\rho(H)/\rho_0 \sim H^2$, cannot describe the positive MR effect in purple bronze. In a low-magnetic-field range, we found that the MR follows an empirical power-law relation, $\Delta\rho(H)/\rho_0 \sim H^{\zeta}$, with $\zeta \sim 1.26$, far less than 2[23]. Up to date, the quantitative discussion for the unusual MR effect is still absent. In this paper, we try to analyze the unusual huge MR data for $H\|c$ in terms of a two-band-carrier galvanomagnetic effect on the small ungapped electron and hole pockets; the carrier concentrations are considered to be modified by an applied magnetic field.

Figures 1, 2, and 3, respectively, show the relative variation of the MR, defined as $\Delta\rho(H)/\rho(0)=[\rho(H)-\rho(0)]/\rho(0)$, for three purple bronzes at 2 K as a function of magnetic field $H\|c$ (left-hand axis) and $H\perp c$ (right-hand axis). The magnitude of the MR increases greatly with increasing applied magnetic field. The curves show a concave shape for $H\|c$, a slight convex shape for $H\perp c$ in the low-field range, and then an almost linear dependence in the high-field range. All the curves do not show saturation behavior in the measured magnetic field range. At $H=14$ T, $\Delta\rho(14T)/\rho(0)$ reaches about an order of $\sim$750% in both K/Tl purple bronzes and 40% in Na purple bronze for $H\|c$, and 50–90 % in K/Tl bronzes and 10% in the sodium bronze for $H\perp c$.

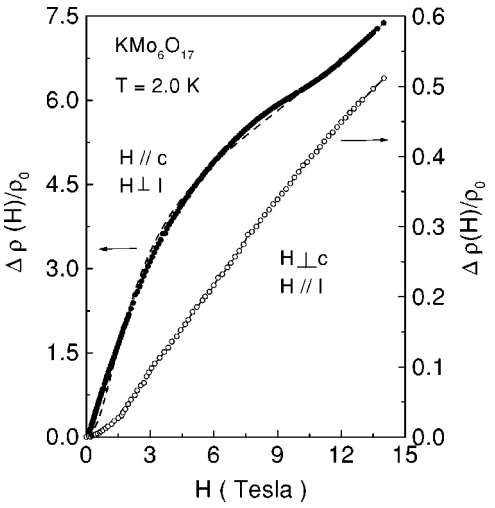

FIG. 1. Magnetoresistance $\Delta\rho/\rho_0$ vs H at 2 K for $H\|c$ (left axis) and $H\perp c$ (right axis).

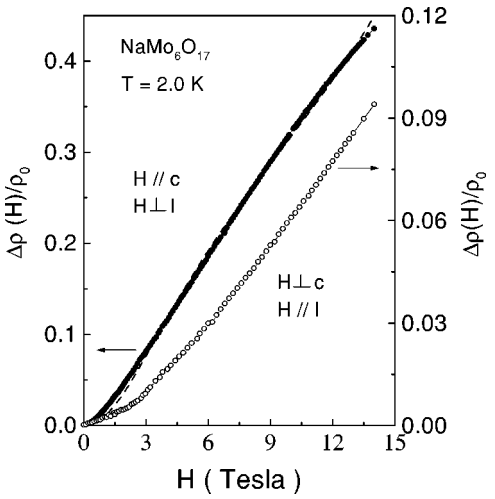

FIG. 3. Magnetoresistance $\Delta\rho/\rho_0$ vs H at 2 K for $H\|c$ (left axis) and $H\perp c$ (right axis).

According to the qualitative model developed by Balseiro and Falicov,[7] the huge positive magnetoresistance is associated with the improvement of the imperfect nesting of the FS induced by the magnetic field. The small pieces of the electron and hole pockets left by the opening of the Peierls gap can be destroyed progressively by the applied magnetic field. This results in an enhanced gap. From this model, it is expected that the relative change of the normal carriers induced by the magnetic field, $\Delta n/n_0=[n(H)-n(0)]/n(0)=1/[\Delta\rho(H)/\rho_0+1]-1$ [$n(0)$ and $n(H)$ denote the total normal carriers concentration at $H=0$ and $H\neq 0$, respectively], will exceed -80% for both K/Tl purple bronzes at a field of $H\geqslant 4.5$ T. However, Parilla *et al.*[9] and Hundley *et al.*[10] only observed a -30% increase of the CDW carrier concentration in $NbSe_3$ at 37 K under a field of $H=7.5$ T. Furthermore, Tritt *et al.*[11] observed a slighter change of the CDW concentration less than 5%. These data are far less than those estimated from the BF scenario. In this way, the huge MR effect cannot be completely attributed to the single mechanism concerning the field-induced enhanced gap. The small electron and hole pockets on the ungapped FS may play an important role, and should be also considered. Therefore, a mechanism concerning the two-band galvanomagnetic effect due to the ungapped small electron and hole pockets and the magnetic-field-induced decrease of the normal carriers due to the enhanced gap must be considered simultaneously for an explanation of $\Delta\rho(H)/\rho_0$.

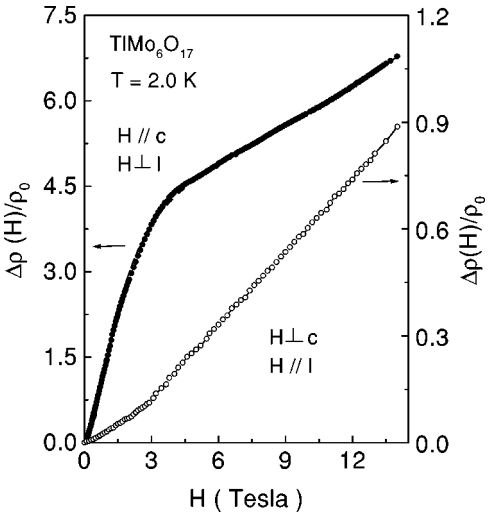

FIG. 2. Magnetoresistance $\Delta\rho/\rho_0$ vs H at 2 K for $H\|c$ (left axis) and $H\perp c$ (right axis).

According to the two-band galvanomagnetic effect model of Noto and Tsuzuku,[24] the MR can be described by a formula of

$$\frac{\Delta\rho}{\rho_0}=\frac{\sigma_1\sigma_2(\mu_1+\mu_2)^2H^2\cos^2\theta}{(\sigma_1+\sigma_2)^2+(\sigma_1\mu_2-\sigma_2\mu_1)^2H^2\cos^2\theta}, \qquad (1)$$

where σ is the conductivity, μ is the mobility, and the subscripts 1 and 2 refer to the two types of carriers (electronlike and holelike in the bands), respectively; θ is the angle between the magnetic field, and the c axis normal to the ab plane. In our case for $H\|c$, $\cos^2\theta=1$ with $\theta=0$. Assuming that both the carriers have the same relaxation time and mass, we obtain $\overline{\mu}=\mu_1\approx\mu_2$, and $\alpha=\sigma_2/\sigma_1\simeq n_2/n_1$, and then Eq. (1) can be simplified to

$$\frac{\Delta\rho}{\rho_0}=\frac{4\alpha\overline{\mu}^2H^2}{(1+\alpha)^2+(1-\alpha)^2\overline{\mu}^2H^2}. \qquad (2)$$

If the effect of a field-induced decrease of the normal carriers is considered, the ratio of both the carrier concentrations α must be a function of the applied magnetic field H but not a constant. Parilla *et al.*[9] found that the concentration of the carriers condensed into the CDW is linearly dependent on H, $n_c(H)\propto H$; then the concentration of the normal carriers at H, $n(H)=n_1+n_2$, can be expressed as: $n(H)=n_0-n_c(H)$, where n_0 is the total carrier concentration at $H=0$. Since the above equation is symmetrical for $\alpha\rightarrow 1/\alpha$, we assume that the magnetic field reacts much differently on both types of the carriers, i.e., H just modifies n_2 but not n_1, or vice versa; we obtain $n_2/n_1=\beta-\gamma H$, where β is the ratio of both types

TABLE I. Fitting parameters estimated from the model for three purple bronzes. $n_1(0)$, $n_2(0)$, and n_0, respectively, represent the concentrations of the minority carriers, the majority carriers and the total normal carriers at $H=0$ T.

Formula	$\beta=\frac{n_2(0)}{n_1(0)}$	γ	$\bar{\mu}=\bar{\mu}_2=\bar{\mu}_1$ ($m^2\,V^{-1}\,s^{-1}$)	n_0 ($\times 10^{17}/cm^3$)	$n_2(0)$ ($\times 10^{17}/cm^3$)	$n_1(0)$ ($\times 10^{17}/cm^3$)
KMo_6O_{17}	2.47	0.032	1.13	5.0	3.55	1.45
$TlMo_6O_{17}$	2.52	0.029	1.6	2.7	1.94	0.76
$NaMo_6O_{17}$	17.2	0.54	0.22	8.3	7.9	0.42

of the carriers at $H=0$, $n_2(0)/n_1(0)$, and γ is a constant. Therefore, the total MR for $H\|c$ can be expressed as

$$\frac{\Delta\rho}{\rho_0}=\frac{4(\beta-\gamma H)\bar{\mu}^2H^2}{(1+\beta-\gamma H)^2+(1-\beta+\gamma H)^2\bar{\mu}^2H^2}. \qquad (3)$$

According to Eq. (3), the measured MR data for $H\|c$ as shown in Figs. 1, 2, and 3 can be fitted with a least-squares optimization procedure. The theoretical curves are presented as dashed lines. The resulting parameters $\bar{\mu}$, β, and γ, determined from the best fit, are shown in Table I, respectively, for three compounds. It can be found that the model fits the experimental data well.

The estimated parameter $\beta=n_2(0)/n_1(0)\geqslant 1$ in three purple bronzes means that n_2 is one of the majority carriers, and n_1 one of the minority carriers. From our earlier thermopower measurements,[18] it was proven that holelike carriers are dominant in both *K*/Tl purple bronzes below T_p, and electronlike carriers are dominant in Na purple bronze. Thus, at $H=0$, the concentration of the holes in both K/Tl purple bronzes would be about 2.5 times of that of the electrons, while in the Na purple bronze the concentration of the electrons would be nearly 17 times of that of the holes. Therefore, the concentrations of both types of the carriers in three purple bronzes at 2 K and 0 T [$n_1(0)=n_0/(1+\beta)$, $n_2(0)=\beta n_0/(1+\beta)$, with a total carriers concentration at $H=0$, $n_0=1/\rho_0 e\bar{\mu}$] can be estimated to be about $n_e=1.45\times 10^{17}/cm^3$ and $n_p=3.55\times 10^{17}/cm^3$ for KMo_6O_{17}; $n_e=0.76\times 10^{17}/cm^3$ and $n_p=1.94\times 10^{17}/cm^3$ for $TlMo_6O_{17}$; and $n_e=7.9\times 10^{17}/cm^3$ and $n_p=0.42\times 10^{17}/cm^3$ for $NaMo_6O_{17}$. These results indicate that the purple bronzes belong to uncompensated compounds below T_p. The higher concentration of normal carriers in Na purple bronze is consistent with the expectation that the weak nesting of the FS in sodium purple bronze leaves more ungapped FS's due to the lack of the third underlying FS along the a^* direction.

The estimated mobility of both types of carriers, $\bar{\mu}$, are about 1.13 $m^2\,V^{-1}\,s^{-1}$ for potassium purple bronze; 1.59 $m^2\,V^{-1}\,s^{-1}$ for thallium purple bronze, and 0.22 $m^2\,V^{-1}\,s^{-1}$ for sodium purple bronze, respectively, as showm in Table I. These values are comparable to that of 0.7 $m^2\,V^{-1}\,s^{-1}$, estimated previously at 20 K for KMo_6O_{17}.[4,25]

At $H\neq 0$, since the magnetic field just modifies the majority carriers n_2 but not minority carriers n_1, the relative change of the normal carriers induced by the magnetic field H, $\Delta n/n_0=-\gamma H/1+\beta$, reaches about -9.2% and -8.3% for potassium and thallium purple bronzes at 10 T, respectively, less than those estimated just from the scenario of field-induced decrease of the normal carriers due to the enhanced gap. However, it is surprising that for sodium purple bronze at 10 T, $\Delta n/n_0$ reaches about -29.6%, much larger than those for K and Tl purple bronzes. This unexpected result may be strongly associated with the greatly different CDW states in Na purple bronze. For example, the investigated MR effect in K/Tl bronzes occurs for the second CDW state below $T_m=16$ K, while in Na purple bronze it occurs for the upper CDW state where the gap opening below T_p (80 K) is progressive, and does not stop till 2 K.[22] Although we cannot exclude another possibility that the model mentioned above is not suitable for the Na purple bronze due to its bad nesting FS, the combined model, at least, is more suitable for explaining the MR data in both K/Tl purple bronzes. This model is also expected to be suitable for $NbSe_3$ and monophosphate tungsten bronzes because of their very similar Q1D FS's.

In the case of $H\perp c$ and $H\|I$, the field dependence of the magnetoresistance should be zero as predicted; the observed weak magnetoresistance indicates that the flow of the current is not exactly in the ab plane. The interlayer transport of the carriers would be responsible for the almost linear field dependence of the MR behavior, but a quantitative explanation is difficult at present.

In conclusion, the mechanism for the MR effect concerning the field-induced enhanced gap survives, but the effect on the normal carriers below 10 T is significantly smaller than that expected by the BF theory.[7] The two-band-carrier galvanomagnetic effect on the surviving FS, in which the concentration of the majority carriers was modified by the applied magnetic field due to the field-induced enhanced gap, seems to be more suitable for explaining the huge MR effect in purple bronzes.

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[1] R. V. Coleman, G. Eiserman, M. P. Everson, A. Johnson, and L. M. Falicov, Phys. Rev. Lett. **55**, 863 (1985).
[2] M. P. Everson, G. Eiserman, A. Johnson, and R. V. Coleman, Phys. Rev. Lett. **52**, 1721 (1984); Phys. Rev. B **30**, 3582 (1984).
[3] P. Monceau and A. Briggs, J. Phys. C **11**, L465 (1978).
[4] C. Schlenker, J. Dumas, C. Escribe-Filippini, H. Guyot, J. Marcus, and G. Fourcaudot, Philos. Mag. B **52**, 643 (1985).
[5] C. Schlenker, C. Hess, C. Le Touze, and J. Dumas, J. Phys. I **6**, 2061 (1996).
[6] C. Hess, C. Schlenker, J. Dumas, M. Greenblatt, and Z. S. Teweldemedhin, Phys. Rev. B **54**, 4581 (1996).
[7] C. A. Balseiro and L. M. Falicov, Phys. Rev. Lett. **55**, 2336 (1985); Phys. Rev. B **34**, 863 (1986).
[8] For a review, see T. Ishiguro and K. Yamaji, *Organic Superconductors* (Springer, Berlin, 1990).
[9] P. Parilla, M. F. Hundley, and A. Zettl, Phys. Rev. Lett. **57**, 619 (1986).
[10] M. F. Hundley, P. Parilla, and A. Zettle, Phys. Rev. B **34**, 5970 (1986); Solid State Commun. **61**, 587 (1987).
[11] T. M. Tritt, A. C. Ehrlich, D. J. Gillespie, and G. X. Tessema, Phys. Rev. B **43**, 7254 (1991); T. M. Tritt, D. J. Gillespie, A. C. Ehrlich, and G. X. Tessema, Phys. Rev. Lett. **61**, 1776 (1988).
[12] S. Yasuzuka, Y. Okajima, S. Tanda, K. Yamaya, N. Takeshita, and N. Mori, Phys. Rev. B **60**, 4406 (1999); S. Yasuzuka, Y. Okajima, S. Tanda, N. Takeshita, N. Mori, and K. Yamaya, J. Phys. Soc. Jpn. **69**, 3470 (2000).
[13] V. Kiryukhin, D. Casa, B. Keimer, J. P. Hill, M. J. Higgins, and S. Bhattacharya, Phys. Rev. B **57**, 1332 (1998).
[14] M. H. Whangbo, E. Canadell, P. Foury, and J. P. Pouget, Science **252**, 96 (1991).
[15] H. Vincent, M. Ghedira, J. Marcus, J. Mercier, and C. Schlenker, J. Solid State Chem. **47**, 113 (1983).
[16] M. Onada, Y. Matsuda, and M. Sato, J. Solid State Chem. **69**, 67 (1987).
[17] M. Ganne, M. Dion, A. Boumaza, and M. Tournoux, Solid State Commun. **59**, 137 (1986).
[18] M. L. Tian, L. Chen, H. Sekine, J. Shi, R. P. Wang, Z. Q. Mao, and Y. H. Zhang, Phys. Lett. A **234**, 477 (1997).
[19] M. Greenblatt, K. V. Ramanujachary, W. H. McCarroll, R. Neifeld, and J. V. Waszczak, J. Solid State Chem. **59**, 149 (1985).
[20] H. Fujishita, C. Murayama, N. Mori, and M. Sato, J. Phys.: Condens. Matter **2**, 8751 (1990).
[21] K. V. Ramanujachary, B. T. Collins, M. Greenblatt, and J. V. Waszczak, Solid State Commun. **59**, 647 (1986).
[22] M. L. Tian, S. Yue, S. Y. Li, Y. H. Zhang, and J. Shi, J. Appl. Phys. **89**, 3408 (2001).
[23] M. L. Tian, S. Yue, J. Shi, S. Y. Li, and Y. H. Zhang, J. Phys.: Condens. Matter **13**, 311 (2001).
[24] K. Noto and T. Tsuzuku, Jpn. J. Appl. Phys. **14**, 46 (1975).
[25] J. Dumas and C. Schlenker, Int. J. Mod. Phys. B **7**, 4050 (1993).