# Low-temperature specific heat of the quasi-two-dimensional charge-density wave compound $KMo_6O_{17}$

Junfeng Wang,[1] Rui Xiong,[1] Di Yin,[1] Changzhen Li,[1] Zheng Tang,[1] Ququan Wang,[1] and Jing Shi[1,2,*]
[1]*Key Lab of Acoustic and Photonic Materials and Devices of Ministry of Education and Department of Physics, Wuhan University, Wuhan 430072, China*
[2]*International Center for Material Physics, Shenyang 110015, China*

Yue Wang and Haihu Wen
*National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijng 100080, China*
(Received 3 December 2005; revised manuscript received 2 February 2006; published 11 May 2006)

Low temperature specific heat ($C_p$) of quasi-two-dimensional charge-density wave (CDW) compound $KMo_6O_{17}$ has been studied by a relaxation method from 2 to 48 K under zero and 12 T magnetic fields. The results show that no specific heat anomaly is found at 16 K under both zero and 12 T magnetic fields, although an anomaly is clearly observed in the resistivity and magnetoresistance measurements. From the data between 2 and 4 K, the density of states at Fermi level is estimated as 0.2 $eV^{-1}$ per molecule and the Debye temperature is extracted to be 418 K. A bump appearing in $C_p/T^3$ is found between 4 and 48 K centered around 12.5–15 K, indicating that the phason excitations contribute to the total specific heat similarly as in quasi-one-dimensional CDW conductors. Using a modified Debye model, a pinning frequency of 0.73 THz for $KMo_6O_{17}$ is estimated from the phason contribution.

DOI: 10.1103/PhysRevB.73.193102 PACS number(s): 71.45.Lr, 65.40.Ba

Quasi-one-dimensional (1D) and quasi-two-dimensional (2D) charge-density wave (CDW) conductors have attracted much attention in past years.[1–4] Below a critical temperature ($T_p$) where the Peierls phase transition takes place, the charge is periodically modulated, associated to an incommensurate modulation of the underlying lattice. This leads to a lot of unusual properties, for instance, 1D blue bronzes $A_{0.3}MoO_3$ ($A$=K, Rb, or Tl) show nonlinear transport properties such as nonohmic conductance above a threshold field, noise, and switch phenomena, etc.;[5] 2D purple bronzes $AMo_6O_{17}$ ($A$=Na, K, or Tl) exhibit a large positive magetoresistance (MR) etc.[6,7]

Extensive studies have been made to investigate the thermodynamic behavior of CDW. For 1D CDW compounds, the early specific heat ($C_p$) studies paid more attention to the behavior near the Peierls phase transition,[8–10] while recent interests focused on the anomalies of low temperature specific heats.[11–20] Low temperature deviation from the Debye law shows two features: (1) a quasilinear-in-$T$ contribution at low-$T$ range ($<1$ K),[13–16] and (2) a bump in $C_p/T^3$ at high-$T$ range ($\sim 10$ K).[16,19,20] The later feature has been attributed to the excitations of the CDW phase (phasons), also observed by other techniques[21,22] and the former to the low energy excitations. For 2D CDW compounds, Buder *et al.*[23] have measured the specific heat of $KMo_6O_{17}$ from 2 to 140 K using a relaxation technique, but focused their presentation and discussion only on 2–5 K range data. Filippini *et al.*[24] reported the data of $KMo_6O_{17}$ around CDW transition temperature $T_p$ and found an enhanced specific heat between 80 and 120 K corresponding to the Peierls phase transition. However, the intermediate temperature range (such as 5–50 K) of the specific heat data has not been considered.

$KMo_6O_{17}$, which is so-called potassium purple bronze, has a layered structure consisting of planes of Mo-O polyhedra separated by K ions.[25] It exhibits 2D transport properties within *ab* cleavage plane, and undergoes a Peierls transition to a CDW state at 110 K. Scanning tunneling microscopy (STM) studies have established that the superstructure in a CDW state is a triple-$q(2a\times 2b)$ hexagonal one.[26,27] High magnetic field study up to 55 T shows that a first order transition takes place above 30 T.[28] Recent MR measurements revealed a second anomaly at 16 K, which was suppressed and moved to higher temperature with increasing magnetic field and disappeared under 12 T.[29] This anomaly was attributed to be either an SDW-like or a second CDW-like transition. The true origin has not been yet completely understood.

In this paper, we studied in detail the specific heat of $KMo_6O_{17}$ in temperature range from 2 to 48 K under zero and 12 T magnetic fields. The results show that although a transition takes place at 16 K in the resistivity measurement, no anomaly of specific heat is found near 16 K under both zero and 12 T magnetic fields. Further more, a bump appearing in $C_p/T^3$ is found for $KMo_6O_{17}$ similar to that of 1D compounds. These findings for a 2D compound $KMo_6O_{17}$ and comparison with that of 1D systems will make a further understanding on the CDW excitations.

$KMo_6O_{17}$ crystals were grown by electrolytic reduction of $K_2CO_3$-$MoO_3$ melts with a molar ratio of 1:6.0.[30] Resulting crystals had a typical size of $2\times 3$ $mm^2$ (*ab* plane) with a thickness of 1 mm (*c* axis). The crystals were characterized by the x-ray powder diffraction and the electrical resistivity measurement, and were found to be of good quality. The sample of No. 1024 showing a clear 16 K transition in the resistivity measurement was selected and cleaned for the specific heat study. The sample weight 6.85 mg (the molar mass is 887 g) and has a rectangular shape of $1.5\times 2.5$ $mm^2$ (*ab* plane) with thickness $\sim 0.6$ mm (*c* axis).

Specific heat data were obtained using a relaxation

 

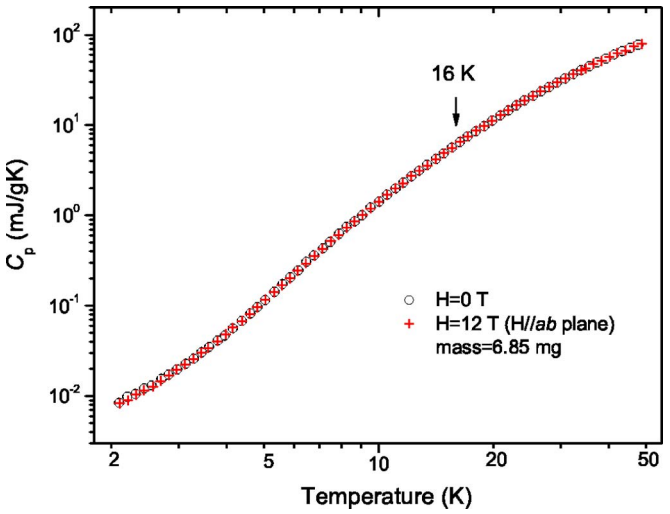


FIG. 1. (Color online) Temperature dependence of the specific heat for $H=0$ and 12 T.

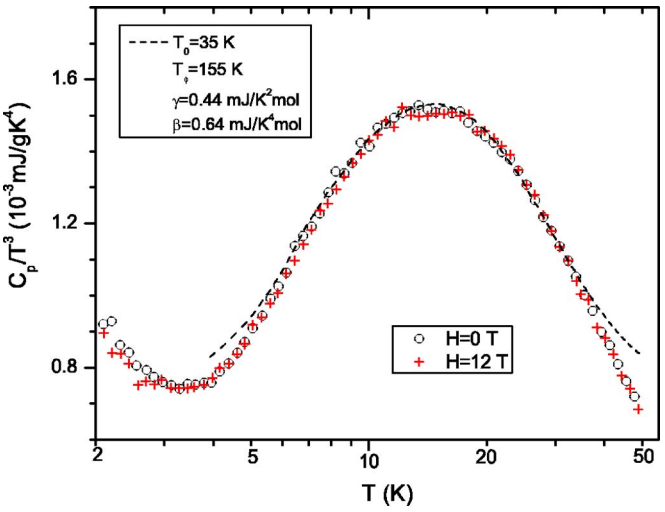


FIG. 2. (Color online) The specific heat data in a plot of $C_p/T^3$ versus $T$ under both $H=0$ T and $H=12$ T. The dashed line represents the best fit using the modified Debye model. Fitting parameters are reported in the inset.

method based on an Oxford cryogenic system MAGLAB. The sample arrangement was similar to that reported recently for the low-temperature electronic specific heats of superconductors $La_{2-x}Sr_xCuO_4$ single crystals,[31] which ensured a good thermal diffusivity. The heat capacity of the addenda was determined in a separate experiment and subtracted from the total heat capacity, thus the $C_p$ value reported here was only from that sample. During the measurements, a stable magnetic field $H$ was applied parallel to the platform (in this work, the $H\|ab$ plane) and the data were collected in the warm-up process from 2 to 48 K. The typical time span of data points varied from 100 s at 2 K to 1000 s at 48 K.

Figure 1 shows the temperature dependence of the specific heat for $H=0$ and 12 T, respectively. It is clear that there is no signature in $C_p$ of the second transition which was observed at 16 K in temperature dependence of resistivity in both $H=0$ and 12 T magnetic fields. Moreover, apart from the lowest $T$ range, there is almost no difference of $C_p$ between $H=0$ and 12 T data. The origin of the 16 K anomaly observed in resistivity measurement needs further investigation and is in progress.

To compare with 1D CDW compounds, we analyze the specific heat data in a plot of $C_p/T^3$ versus $T$ as shown in Fig. 2. It can be found that $C_p/T^3$ of $KMo_6O_{17}$ has a similar $S$ shape to those of 1D compounds.[13–16] In this figure, one can distinguish two features: the increase in $C_p/T^3$ toward lower $T$ below 4 K, and a broad bump centered around 12.5–15 K above 4 K.

In general, a 1D system undergoes the Peierls transition to an insulating CDW state, while a 2D compound maintains metallic in the CDW state due to the opening of partial gaps on the quasicylindrical Fermi surface. In order to separate the normal electronic and acoustic phonon contributions in the low temperature metallic state, we analyze the specific heat data in a plot of $C_p/T$ versus $T^2$. A good linear relation of $C_p/T=\gamma+\beta T^2$ is found between 2 and 4 K with $\gamma=0.44$ mJ/K$^2$ mol and $\beta=0.64$ mJ/K$^4$ mol for the data of zero field as shown in Fig. 3, while the specific heat data fast deviate from this relation above 4 K due to the contribution of CDW excitations. The obtained electronic term is smaller than $\gamma=1.6\pm0.2$ mJ/K$^2$ mol reported by Buder *et al.*[23] In a free electron model, the contribution of normal electrons $C_e$ can be described as

$$C_e=\gamma T=\frac{\pi^2}{3}g(E_F^0)k_B^2T \tag{1}$$

with $k_B$ the Boltzmann's constant and $g(E_F^0)$ the density of states at Fermi surface at zero temperature. From the $\gamma$ value, and taking $g(E_F)\sim g(E_F^0)$, the density of states at Fermi level is estimated as 0.2 eV$^{-1}$ per molecule for $KMo_6O_{17}$, which is only $\sim\frac{1}{6}$ of 1.13 eV$^{-1}$ per molecule given from the thermoelectric power above the Peierls transition temperature.[32]

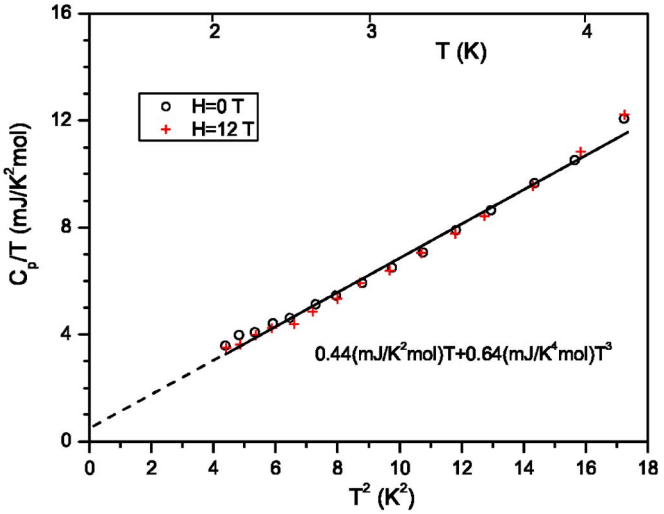


FIG. 3. (Color online) The specific heat data between 2 and 4 K in a plot of $C_p/T$ versus $T^2$ under both $H=0$ T and $H=12$ T. The straight line represents the fit of contributions of normal electrons and phonons.

The Debye temperature can be calculated from the usual formula

$$\theta_D^3 = \frac{12}{5}\pi^4 rR\beta^{-1} \quad (2)$$

with $R$ the gas constant and $r$ the total number of atoms in the formula unit (here $r=24$ for $KMo_6O_{17}$). From the value of $\beta$, we extract a Debye temperature of 418 K, which is higher than $340\pm10$ K reported by Buder *et al.*[23] It is noticed that several groups also gave different Debye temperatures of $K_{0.3}MoO_3$ from the specific heat measurements.[11,16] In Fig. 3, the slight decrease of $C_p/T$ under the 12 T magnetic field which is also reflected in the decrease of $C_p/T^3$ below 4 K in Fig. 2 is supposed due to reduction of the density of states in magnetic field.

In a similar way as developed for 1D CDW materials,[13–16] the bump appearing above 4 K in Fig. 2 is expected to result from the CDW phason excitations. We use a modified Debye spectrum with two cut-off frequencies to describe the phason contribution: the lower one corresponding to the pinning frequency ($\nu_0=k_BT_0/h$, due to the pinning gap) and the upper one analogous to a Debye temperature for phasons ($\nu_\phi=k_BT_\phi/h$). It is known that $KMo_6O_{17}$ shows superlattice reflections below $T_p$ at three equivalent commensurate reduced wave vectors $q_I=(1/2,0,0)$, $q_{II}=(0,1/2,0)$, and $q_{III}=(1/2,1/2,0)$, which undergo the same periodic lattice distortions in the CDW state and are related by a trigonal symmetry.[24,26,27] Each modulation consists of three phason branches (one longitudinal and two transverse), thus the phason contribution $C_\phi$ can be expressed as

$$C_\phi = 27\frac{N_\phi k_B}{\eta^2}\left(\frac{T}{T_\phi}\right)^3 \int_{T_0/T}^{T_\phi/T} (x-x_0)^2 \times \frac{x^2e^x}{(e^x-1)^2}dx,$$

$$\text{and } x = h\nu/k_BT \quad (3)$$

with $N_\phi$ the number of phason excitations, and $\eta$ the anisotropy parameter of phason velocities with $\eta=C_\perp/C_\parallel$ (phase mode velocities parallel and perpendicular to the CDW wave vector $q$). In Fig. 2, we find the best fit for the specific heat data with $T_0=35$ K (3.0 meV energy), $T_\phi=155$ K (13.3 meV energy), and $N_\phi=0.88\eta^2N_A$ ($N_A$ is the Avogadro number). The pinning frequency ($\nu_0=0.73$ THz) obtained for $KMo_6O_{17}$ is as large as 41, 18, 4, and 2 times of those of $NbSe_3$ (17.5 GHz),[13] $(TaSe_4)_2I$ (45 GHz),[14] KCP (0.2 THz),[15] and $K_{0.3}MoO_3$ (0.38 THz),[16] respectively. The value of $T_\phi$ is also significantly larger than those of 1D compounds. Since no investigation in respect to the anisotropy phase velocity has been reported for $KMo_6O_{17}$ in the literature, consequently we cannot evaluate the value of $N_\phi$ from $\eta$. Generally the Debye law fails above $T^*\sim\theta_D/20$;[16] with the obtained value $\theta_D=418$ K for $KMo_6O_{17}$ from Fig. 3, it yields $T^*\sim21$ K, higher beyond the observed bump. In Fig. 2, the deviation of fitting to the data above 32 K reflects that the validity of this kind of modified Debye law for 2D $KMo_6O_{17}$ is similar to that reported in 1D CDW compounds.[15,16]

In conclusion, we have investigated the specific heat of $KMo_6O_{17}$ in a temperature range from 2 to 48 K under zero and 12 T magnetic fields. The results show the absence of the thermodynamical signature of 16 K anomaly of electrical resistivity under both 12 T and zero field. From the data below 4 K, the density of states at Fermi level is estimated as 0.2 $eV^{-1}$ per molecule and the Debye temperature is extracted to be 418 K. Particularly, a bump appearing in $C_p/T^3$ is found above 4 K, indicating the phason excitations contribute to the total specific heat. Using a modified Debye model, a pinning frequency of 0.73 THz for $KMo_6O_{17}$ is estimated from the phason contribution.

This work is supported by the National Natural Science Foundation of China (No. 10474074 and No. 10534030) and the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing (Wuhan University of Technology WUT 2004 M03).

*Corresponding author. Electronic mail: jshi@whu.edu.cn

[1] *Charge Density Waves in Solids, Proceedings*, Budapest, 1984, edited by Gy. Hutiray and J. Solyom (Springer-Verlag, Berlin, 1985).
[2] G. Gruner, *Density Waves in Solids* (Addison-Wesley Company, Reading MA, 1994).
[3] C. Schlenker, ed., *Physics and Chemisry of Low-Dimensional Inorganic Conductor* (Plenum Press, New York, 1996).
[4] M. Greenblatt, Chem. Rev. (Washington, D.C.) **88**, 31 (1988).
[5] J. Dumas, C. Schlenker, J. Marcus, and R. Buder, Phys. Rev. Lett. **50**, 757 (1983).
[6] J. Dumas, E. Bervas, J. Marcus, D. Salomon, C. Schlenker, and G. Fillion, J. Magn. Magn. Mater. **31–34**, 535 (1983).
[7] A. Rotger, C. Schlenker, J. Dumas, J. Marcus, S. Dubois, A. Audouard, L. Brossard, J. P. Ulmet, and S. Askenazy, Synth. Met. **55–57**, 2725 (1993).
[8] R. S. Kwok, G. Gruner, and S. E. Brown, Phys. Rev. Lett. **65**, 365 (1990).
[9] J. W. Brill, M. Chung, Y.-K. Kuo, X. Zhan, E. Figueroa, and G. Mozurkewich, Phys. Rev. Lett. **74**, 1182 (1995).
[10] J. Shi, X. K. Qing, M. L. Tian, H. Chen, X. Wu, and D. C. Tian, J. Phys.: Condens. Matter **6**, 8521 (1994).
[11] K. J. Dahlhauser, A. C. Anderson, and G. Mozurkewich, Phys. Rev. B **34**, 4432 (1986).
[12] J. C. Lasjaunias and P. Monceau, Solid State Commun. **41**, 911 (1982).
[13] K. Biljakovic, J. C. Lasjaunias, and P. Monceau, Phys. Rev. B **43**, 3117 (1991).
[14] K. Biljakovic, J. C. Lasjaunias, F. Zougmore, P. Monceau, F. Levy, L. Bernard, and R. Currat, Phys. Rev. Lett. **57**, 1907 (1986).
[15] J. Odin, J. C. Lasjaunias, A. Berton, P. Monceau, and K. Biljak-

ovic, Phys. Rev. B **46**, 1326 (1992).
[16] J. Odin, J. C. Lasjaunias, K. Biljakovic, K. Hasselbach, and P. Monceau, Eur. Phys. J. B **24**, 315 (2001).
[17] H. Requardt, R. Currat, P. Monceau, J. E. Lorenzo, A. J. Dianoux, J. C. Lasjaunias, and J. Marcus, J. Phys.: Condens. Matter **9**, 8639 (1997).
[18] J. E. Lorenzo and H. Requardt, Eur. Phys. J. B **28**, 185 (2002).
[19] J. C. Lasjaunias, P. Monceau, D. Staresinic, and K. Biljakovic, Eur. Phys. J. B **28**, 187 (2002).
[20] A. Cano and A. P. Levanyuk, Phys. Rev. Lett. **93**, 245902 (2004).
[21] J. P. Pouget, B. Hennion, C. Escribe-Filippini, and M. Sato, Phys. Rev. B **43**, 8421 (1991).
[22] J. Demsar, K. Biljakovic, and D. Mihailovic, Phys. Rev. Lett. **83**, 800 (1999).
[23] R. Buder, J. Devenyi, J. Dumas, J. Marcus, J. Mercier, C. Schlenker, and H. Vincent, J. Phys. (Paris), Lett. **43**, L59 (1982).
[24] C. Escribe Filippini, K. Konate, J. Marcus, C. Schlenker, R. Almairac, R. Ayroles, and C. Roucau, Philos. Mag. B **50**, 321 (1984).
[25] H. Vincent, H. Ghedira, J. Marcus, J. Mercier, and C. Schlenker, J. Solid State Chem. **47**, 113 (1983).
[26] P. Mallet, K. M. Zimmermann, Ph. Chevalier, J. Marcus, J. Y. Veuillen, and J. M. Gomez Rodriguez, Phys. Rev. B **60**, 2122 (1999).
[27] H. Balaska, J. Dumas, H. Guyot, P. Mallet, J. Marcus, C. Schlenker, J. Y. Veuillen, and D. Vignolles, Solid State Sci. **7**, 690 (2005).
[28] J. Dumas, H. Guyot, H. Balaska, J. Marcus, D. Vignolles, I. Sheikin, A. Audouard, L. Brossard, C. Schlenker, Physica B **346–347**, 314 (2004).
[29] M. L. Tian, S. Yue, S. Y. Li, Y. H. Zhang, and J. Shi, J. Appl. Phys. **89**, 3408 (2001).
[30] J. F. Wang, R. Xiong, H. Yu, H. Li, W. F. Tang, Z. X. Yu, J. Shi, D. C. Tian, M. L. Tian, and Y. H. Zhang, Acta Phys. Sin. **3**, 895 (2004).
[31] H. H. Wen, Z. Y. Liu, F. Zhou, J. W. Xiong, W. X. Ti, T. Xiang, S. Komiya, X. F. Sun, and Y. Ando, Phys. Rev. B **70**, 214505 (2004).
[32] 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).