

## Excess low-temperature specific heat in $K_{0.3}MoO_3$

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The thermal conductivity and specific heat of the charge-density-wave compound  $K_{0.3}MoO_3$  have been measured between 0.1 and 1 K. The thermal conductivity is typical of a good crystal, while the specific-heat measurements show an excess contribution which is linear in temperature and corresponds to approximately  $2 \times 10^{20}$  states/eV  $cm^3$ . This excess specific heat indicates significant randomness, in spite of good stoichiometry and crystal quality. We speculate that the phase distortions of the randomly pinned charge-density wave are responsible for the excess low-lying excitations.

Both structural glasses and spin glasses show a number of low-temperature phenomena directly attributable to their randomness. Among the best known of these are specific heats which are approximately linear in temperature,<sup>1,2</sup> long-time pseudologarithmic relaxations,<sup>3-5</sup> and low-frequency susceptibilities which are nonanalytic in frequency.<sup>6</sup> Similar behaviors have been found recently in the class of quasi-one-dimensional materials which support sliding charge-density waves (CDW). Fleming and Schneemeyer,<sup>7</sup> and Mihály and Mihály,<sup>8</sup> have found pseudologarithmic time decays of the quasiparticle electrical conductivity. Wu, Mihály, Mozurkewich, and Grüner<sup>9</sup> have measured, in several materials, power-law frequency dependences of the conductivity [ $\sigma(\omega) \propto \omega^\alpha$ ,  $\alpha \approx 0.9$ ], which resemble phonon-assisted hopping between metastable states, and Cava *et al.*<sup>10</sup> have demonstrated a nonanalytic cusp in the frequency-dependent dielectric constant as  $\omega \rightarrow 0$  in  $K_{0.3}MoO_3$ . These and other experiments<sup>11</sup> emphasize the importance of randomness in the dynamic response of impurity-pinned CDW's. We were motivated therefore to look for a corresponding linear specific heat  $C$  at low temperature, such as has been found in other disordered systems. Here we report the observation of a linear specific heat in the blue molybdenum bronze  $K_{0.3}MoO_3$ .

Blue bronze shows a metallic temperature dependence of resistance at room temperature but undergoes a complete metal-insulator transition into the charge-density wave state<sup>12</sup> at 180 K. Below this temperature the non-linear electrical transport properties associated with CDW conduction have been observed.<sup>13</sup>

Blue bronze was chosen for this experiment because it is the only member of the class of sliding CDW conductors which can be obtained as high quality crystals of dimensions several millimeters on a side. The samples were grown by Barakat Alavi, using the electrolytic technique,<sup>14</sup> and sample quality was confirmed by x-ray examination and threshold-field measurements.

The specific heat was measured on two samples.<sup>15</sup> Sample 4 consisted of three intergrown twins of total mass 2.05 g, while sample 5 was a single crystal of mass 0.77 g. Each specific-heat specimen was clamped between two sapphire plates, heat pulses were introduced, and the transient tem-

perature responses were digitally averaged<sup>16</sup> to improve the signal-to-noise ratio. The estimated heat capacity of the heater and thermometer addenda was  $\lesssim 15\%$  of the total  $C$ .

The specific-heat results for both samples, corrected for addenda, are shown in Figs. 1 and 2. In Fig. 1 the data are plotted as  $C/T^3$  vs  $T$  and compared with data for an amorphous dielectric, vitreous silica, and for copper. Figure 1 emphasizes the departure at low temperature from the Debye phonon contribution for a good crystal, given by the

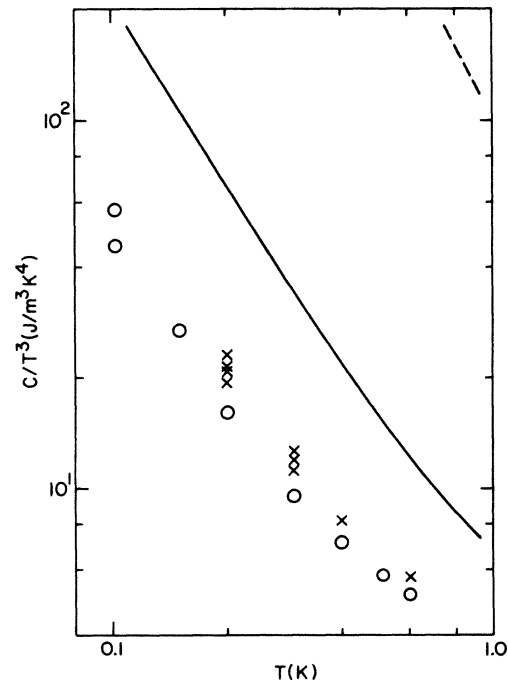


FIG. 1. Log-log plot of total specific heat  $C$ , divided by the cube of the temperature  $T$ , for blue bronze samples 4 ( $\circ$ ) and 5 ( $\times$ ). Also shown for comparison are  $C/T^3$  for vitreous silica (solid line) and copper (dashed line). The phonon contribution to  $C/T^3$  for the blue bronze is represented by the bottom margin of the graph.

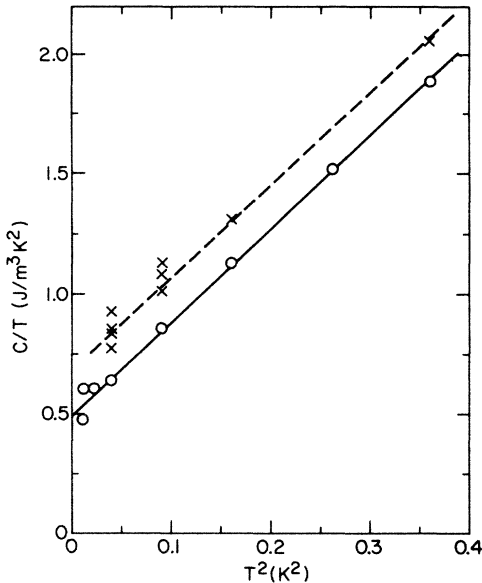


FIG. 2. Total specific heat  $C$ , divided by  $T$ , vs  $T^2$  for blue bronze samples 4 (○) and 5 (×). Here, and in Fig. 1, data for sample 5 below 0.3 K were obtained in three completely independent runs. The lines show the best fit to  $C = \gamma T + \beta T^3$ .

equation

$$C_{\text{Debye}} = (2\pi^2 k_B^4 / 5 \hbar^3 \bar{v}^3) T^3 = \beta T^3, \quad (1)$$

which is constant on such a plot. Here  $\bar{v}$  is an average thermal phonon velocity. The observed increase in  $C/T^3$  towards lower  $T$  reveals an extra specific-heat contribution which, in  $K_{0.3}MoO_3$ , is a factor of 3 smaller than the two-level system contribution in vitreous silica and two orders of magnitude smaller than the degenerate electron gas contribution in copper.

In Fig. 2 the specific-heat data are plotted as  $C/T$  vs  $T^2$ . The best fit to  $C = \gamma T + \beta T^3$  for the larger sample (No. 4, for which we expect smaller uncertainty) requires  $\gamma = 0.49 \text{ J/m}^3 \text{ K}^2$  for the linear coefficient and  $\beta = 3.9 \text{ J/m}^3 \text{ K}^4$  for the phonon contribution. The coefficient  $\beta$ , from Eq. (1), gives  $\bar{v} = 3.1 \times 10^3 \text{ m/sec}$ , assuming that phonons make the only contribution to the cubic term. If the coefficient  $\gamma$  is analyzed within the two-level system model used for glasses,<sup>17</sup> the energy-independent density of states is found to be  $D(\epsilon) \approx 2 \times 10^{20} \text{ states/eV cm}^3$ . From the available data it is not possible to estimate either the number of excitations per unit volume or the width of their energy distribution.

A previous study<sup>18</sup> found  $\beta$  nearly twice as large as the value reported here. We do not know the reason for this discrepancy. The earlier study also found  $\gamma = 0$ , but the measurements were confined to temperatures above 1.6 K.

The measured specific heat became increasingly time dependent with decreasing temperature. This time dependence indicates that at least some of the nonphonon excitations had thermal equilibration times as long as  $\approx 1 \text{ sec}$  near 0.1 K, which may be compared to a sample equilibration time of  $\approx 10^{-3} \text{ sec}$  estimated from  $C$ ,  $\kappa$ , and the sample dimensions. The data shown in Figs. 1 and 2 are the "total" specific heats measured for times  $\geq 10 \text{ sec}$  follow-

ing the applied heat pulse. The time dependence increases the uncertainty in the plotted data at the lowest temperatures.

In a separate experiment, the specific heat of sample 5 was measured at 0.2 K before and after application of an electric field large enough to cause nonlinear conduction. The field of 85 V/cm was applied for several seconds, temporarily heating the sample (which was maintained in vacuum) to 7 K. Transient application of a field above threshold has been shown to polarize  $K_{0.3}MoO_3$  by putting it into a different metastable state.<sup>19</sup> To an accuracy of 1% (determined by direct comparison of the transient temperature responses recorded before and after applying the electric field), the measured specific heat was independent of the state of polarization.

The thermal conductivity  $\kappa$  was measured along the monoclinic  $\mathbf{b}$  axis on a separate sample, No. 8a, which was cleaved into a plate roughly  $12 \times 5.3 \times 1.2 \text{ mm}^3$ . The technique utilized two heaters and one thermometer because of the limited sample length. The data are presented in Fig. 3. The largest uncertainty ( $\pm 20\%$ ) arises in determining the ratio of the cross-sectional area to the distance between heaters, since the cross section of the specimen was not uniform. Included in Fig. 3 for comparison are data from an amorphous solid, vitreous silica, which has a much smaller conductivity. The solid line in Fig. 3 is the conductivity computed from the Debye model,

$$\kappa = (2\pi^2 k_B^4 / 15 \hbar^3) (T^3 \bar{l} / \bar{v}^2), \quad (2)$$

using  $\bar{v} = 3.1 \times 10^3 \text{ m/sec}$  deduced from the specific-heat data and a fitted mean free path  $\bar{l}$  of 1.6 mm for all phonon modes. This mean free path of 1.6 mm is comparable to the sample thickness<sup>20</sup> of 1.2 mm. The indications are that the thermal conductivity of blue bronze is contributed by phonons, and that these phonons have long mean free paths of order of the sample dimensions. Therefore the sample is of good quality, and the extra excitations contri-

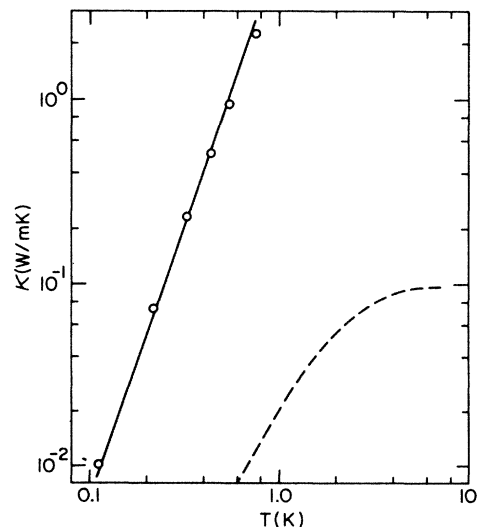


FIG. 3. Thermal conductivity  $\kappa$  of blue bronze. The solid line indicates a  $T^3$  temperature dependence as discussed in the text. The dashed line represents data from vitreous silica, for comparison.

buting to the low-temperature specific heat neither contribute to thermal transport nor interact strongly with the strain fields of phonons.

Two known origins of linear specific heat are a degenerate electron gas and randomness on the microscopic scale. Conduction electrons are responsible for the linear specific heat<sup>21</sup> in NbSe<sub>3</sub> because NbSe<sub>3</sub> remains metallic even below the lower of its Peierls transitions. Conduction electrons cannot account for the data in blue bronze because K<sub>0.3</sub>MoO<sub>3</sub> undergoes a complete metal-insulator transition<sup>12</sup> at 180 K. Its resistance rises by more than ten orders of magnitude by 4 K and, in the temperature range of this experiment, the number of remaining conduction electrons is entirely negligible.

Microscopic randomness can take a number of forms, each contributing an excess low-temperature specific heat: (1) In spin glasses, interacting spins are distributed randomly among the host lattice sites, and the linear specific heat comes from an enhanced density of low-lying excitations somewhat analogous to spin wave modes.<sup>22</sup> This mechanism is inapplicable in blue bronze because of the small concentration of paramagnetic centers.<sup>23</sup> (2) In structural glasses, the atomic sites themselves are disordered. The atoms are believed to tunnel between nearly degenerate arrangements, and the linear specific heat comes from a broad distribution of these "two-level" systems.<sup>17</sup> However, the specimens used in this investigation show sharp x-ray spots, and their crystalline quality is also demonstrated by the long thermal phonon mean free path which is comparable to sample dimensions. (3) In certain superionic conductors at elevated temperatures, small ions hop between vacant sites along well-defined conducting channels or planes, while at low temperature they are like structural glasses,<sup>17</sup> but with the atomic disorder confined to these special channels or planes. Likewise the excess specific heat<sup>24</sup> may be attributed to two-level systems. For blue bronze it is difficult to exclude this possibility with confidence. The potassium ions in blue bronze reside in the van der Waals gap between planes of MoO<sub>6</sub> octahedra,<sup>25</sup> and if some of the equivalent K<sup>+</sup> sites are vacant, the potassium ions might be mobile at high temperature and disordered at low temperature. Yet we believe for the following reasons that blue bronze is not an ionic conductor: First, it is currently believed that the compound is stoichiometric,<sup>26</sup> despite earlier reports<sup>14</sup> of a significant fraction of missing K<sup>+</sup> ions. Second, attempts to produce the known compound Rb<sub>0.3</sub>MoO<sub>3</sub> by ion exchanging Rb for K have failed. Third, appreciable mobility generally is associated with appreciable phonon scattering,<sup>24</sup> yielding  $\kappa \propto T^2$  rather than the observed  $T^3$  behavior.<sup>27</sup>

Based on the above discussion, it seems plausible to attribute the excess heat capacity of blue bronze to excitations of the randomly pinned CDW. We now consider the possible nature of these excitations. The CDW's actual phase configuration must minimize, as well as possible, the competing demands of the CDW stiffness  $K$  (which opposes distortions), and the potentials  $V_i$  of the randomly located impurities.<sup>28</sup> Two limiting cases are recognized. If the  $V_i$  are strong enough, the local CDW phase is forced to have a specified value at every impurity site ("strong pinning"), while, if  $K$  dominates, the phase adjusts to maxim-

ize the net effect of all impurities within regions of characteristic scale  $L$  ("weak pinning").<sup>28</sup> In either case there will, of course, be some lowest-energy configuration  $\phi_0(\mathbf{r})$ . But, because of the random nature of the pinning, there will also be many nearly degenerate, metastable minima corresponding to different phase configurations  $\phi_i(\mathbf{r})$ . In the two limiting cases, explicit descriptions of these configurations can be tentatively given. In strong pinning, some impurities will be located by chance where the local CDW phases  $\phi = \phi_0$  and  $\phi = \phi_0 + 2\pi$  are equally or nearly equally favorable energetically. The metastable states of the whole system can be identified with the set of all such local phase distortions. In weak pinning, the configurations differ from each other by adding  $2\pi$  phase kinks ("solitons") to the ground state, or by displacing a fixed number of kinks between nearly equivalent sites.<sup>29</sup>

Several experimental signatures of the existence of metastable minima were cited in the introduction,<sup>7-11</sup> and they also are found theoretically<sup>30</sup> and in numerical simulations.<sup>29</sup> Given the existence of these metastable minima, at least two mechanisms for the low-lying excitations observed in the heat capacity can be identified.

(1) If the CDW configuration can tunnel between metastable minima, then the existence of multiple minima will be observable in the specific heat. If the density of energy splittings  $D(\epsilon)$  is (roughly) independent of  $\epsilon$  for  $\epsilon < k_B T$ , then a (roughly) linear specific heat would result.<sup>31</sup> This mechanism is directly analogous to the two-level systems model developed for glasses,<sup>17</sup> in which the distribution of splittings is a consequence of the randomness. This mechanism requires that large segments of CDW (of order the volume per impurity, at least) can tunnel through the distance of a CDW wavelength (about four lattice constants). Whether CDW tunneling on a macroscopic scale has appreciable probability is a matter of current controversy<sup>32</sup> which will not be discussed here. However, the time dependence of specific heat observed at our lowest temperatures might be regarded as evidence in favor of interconfigurational tunneling.

(2) If the tunneling probability is insignificant, then at low temperature the CDW phase will be frozen into a particular metastable configuration. The normal modes of vibration of the CDW about that minimum will be modified by the random pinning, and if the resulting density of states is roughly constant, a linear specific heat would result. The randomly pinned CDW problem is analogous to the random-field  $XY$  model.<sup>33</sup> To our knowledge, the low-temperature specific heat of that model has not been calculated. Yet the situation bears a loose similarity to the spin-glass problem where, at low temperature, the spins are frozen into one of many nearly degenerate configurations, and the density of normal modes of the interaction spins produces a nearly linear specific heat over a limited temperature range.<sup>22</sup> It would be worthwhile to perform the analogous calculation for the present problem.

In summary, we have found in the CDW compound K<sub>0.3</sub>MoO<sub>3</sub> a contribution to the low-temperature specific heat which is linear in  $T$  and corresponds to  $2 \times 10^{20}$  states/eV cm<sup>3</sup>. The thermal conductivity is typical of a good crystal. The extra specific heat is time dependent, and it does not appear to be related to known sources of

linear specific heat. Therefore we suggest that the excess specific heat may be due to CDW phase distortions induced by random pinning. For the additional density of states, it is impossible at present to distinguish between a picture of two-level systems and a model of modified normal modes.

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