Thermodynamics of Charge-Density Waves in Quasi One-Dimensional Conductors

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Simple methods are described to evaluate quantitatively the influence of charge-density–wave fluctuations on the thermodynamics of quasi one-dimensional conductors, and are applied to experimental data for $K_{0.3}MoO_3$. These fluctuations are found to affect strongly the magnetic susceptibility and electronic entropy and heat capacity over a large temperature range.

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Strictly one-dimensional (1D) conductors have been shown theoretically to exhibit no long-range charge-density-wave (CDW) ordering transitions above temperature $T=0$, although CDW fluctuations can occur which then determine the temperature depenence of various physical properties.[1] However, even weak coupling between chains can lead to long-range CDW order at a critical temperature T_c which is an appreciable fraction of the mean-field transition temperature T_c^{MF},[1-3] and the CDW fluctuations are then expected to die out below T_c.

Recently, *inorganic* quasi 1D conductors such as $NbSe_3$, TaS_3, $(TaSe_4)_2I$, and $K_{0.3}MoO_3$ have attracted much attention, primarily due to the discovery of CDW transport and other associated phenomena which occur in these materials in the vicinity of and below the respective CDW T_c's.[4] However, the influence of CDW fluctuations on the thermodynamic properties of these compounds has not previously been quantitatively assessed, even though diffuse electron scattering results for orthorhombic TaS_3[5] and x-ray[6] and neutron[7] scattering studies on $K_{0.3}MoO_3$ have proved their presence even at temperatures far above the respective T_c's. In this article, I outline results of a quantitative examination of their effects on the magnetic susceptibility (χ) and electronic contributions to the entropy (S_e) and heat capacity (C_e) of the representative quasi 1D[8,9] inorganic conductor $K_{0.3}MoO_3$.[10] In this compound, the CDW ordering transition at $T_c \approx 180$ K completely removes the Fermi surface, leading to a metal-semiconductor transition at T_c.[6,8,9]

Below T_c, a nonzero average gap $2\langle\Delta\rangle(T)$ opens up in the density of electronic states (D) at the Fermi energy E_F, whereas above T_c, CDW fluctuations may induce a temperature-dependent pseudogap in D near E_F as discussed in Refs. 1 and 2; both effects reduce χ^{spin} from the unperturbed value χ^{Pauli}, where χ^{spin} is the intrinsic conduction electron spin susceptibility. In order to evaluate self-consistently the influence of the fluctuations on $\chi^{spin}(T)$ in both temperature ranges, I adopt the following strategy. I first model the deviation of χ^{spin} at *each* temperature from χ^{Pauli} as arising from a uniform effective semiconducting gap $E_g = 2\Delta_{eff}$ in $D(e)$ at E_F, and I derive $\Delta_{eff}(T)$ from $\chi^{spin}(T)$. In the absence of fluctuations, $\Delta_{eff}(T)$ is presumably the same as $\langle\Delta\rangle(T)$, and this situation should occur from $T=0$ to somewhat below T_c. By comparing $\Delta_{eff}(T)$ with $\langle\Delta\rangle(T)$ found directly from neutron diffraction experiments,[7] I have determined that fluctuations begin to be important to $\chi^{spin}(T)$ by 20 K below T_c. Above T_c, a crossover in $\chi^{spin}(T)$ and $\Delta_{eff}(T)$ to behavior predicted theoretically for isolated 1D chains is found; thus the fluctuations appear to be solely responsible for the strong temperature dependence we find in $\chi^{spin}(T)$ above T_c. Finally, $C_e(T)$ and $S_e(T)$ will be computed from $\Delta_{eff}(T)$ and shown to be consistent with a strong influence of CDW fluctuations.

In order to apply the above model, we assume that a 1D tight-binding band picture is appropriate at all temperatures, and that the conduction electrons are noninteracting. We further assume linearized valence and conduction bands and that $k_BT \ll E_F, W-E_F$, where k_B is Boltzmann's constant and W is the unperturbed bandwidth. The density of states $g(E,\Delta_{eff})$ of a 1D semiconductor with uniform gap $2\Delta_{eff}$ is then $g(E,\Delta_{eff}) = D_0|E|/E(E^2-\Delta_{eff}^2)^{1/2}$ if $|E| \geq \Delta_{eff}$ and 0 otherwise, where D_0 is the unperturbed density states. $\chi^{spin}(T)$ is just $\mu_B^2 g(\Delta_{eff})_T$, where μ_B is the Bohr magneton and $g(\Delta_{eff})_T$ is the thermal average of g at the temperature T[1]: $g(\Delta_{eff})_T \equiv \int g(E,\Delta_{eff}) \times (-\partial f/\partial E)\,dE$, where f is the Fermi function. Thus, defining $A \equiv \Delta_{eff}/k_BT$ and $\chi^{Pauli} = \mu_B^2 D_0$, one obtains

$$\frac{\chi^{spin}}{\chi^{Pauli}} = 2\int_A^\infty \frac{x}{(x^2-A^2)^{1/2}} \frac{e^x}{(e^x+1)^2}\,dx. \qquad (1)$$

From Eq. (1), $\chi^{spin}/\chi^{Pauli} \simeq A^{1/2}\exp(1-A)$ for $A \gtrsim 4$, a temperature dependence in agreement with standard results in the 1D quasi free electron approximation. For $A \lesssim \frac{1}{4}$, $\chi^{spin}/\chi^{Pauli} \simeq 1 - 0.21\,A^2$. The general shape of $\chi^{spin}(T/\Delta_{eff})$ is similar to that of the thin solid curve in Fig. 1(b).

The magnetic susceptibility of single crystal $K_{0.3}MoO_3$ was measured with a Faraday magnetometer[11] between 4 and 720 K in a magnetic field of 6.4 kG; the data presented here have been corrected for small contributions from ferromagnetic and paramagnetic impurities. We write the resulting susceptibility as $\chi(T) \equiv \chi_0 + \chi^{spin}(T)$, where $\chi^{spin}(0) \equiv 0$. The value of the orbital susceptibility $\chi_0 = -(1.0 \pm 0.5) \times 10^{-6}$ cm^3/mole is in good agreement with that computed using available values for MoO_3 and K^{+1}. χ^{spin} is plotted versus T in Fig. 1(a) for $T < 720$ K; an expanded plot of the data below 320 K is shown in Fig. 1(b). The temperature dependence of χ^{spin} is similar to but more precise than the results[9,12] of previous studies. The long-range CDW ordering is manifested in the data in Fig. 1 via a pronounced slope change at $T_c = 183$ K. From Fig. 1, $d\chi^{spin}/dT$ monotonically and smoothly decreases and remains positive above T_c.

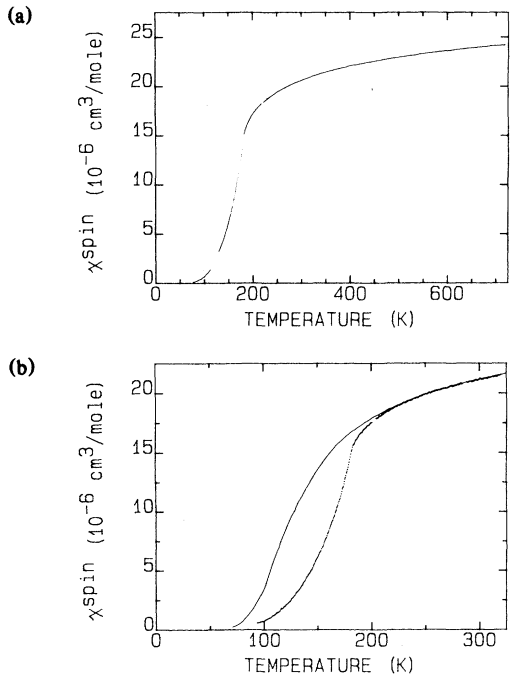

FIG. 1. (a) Conduction electron spin susceptibility χ^{spin} vs temperature for $K_{0.3}MoO_3$ below 720 K. (b) An expanded plot of the data below 320 K where a fit of the theory of Ref. 1 to the data above 225 K is shown as the thin solid curve.

This indicates that χ^{spin} is approaching an asymptotic limit ($\equiv \chi^{Pauli}$) with increasing T. Therefore, Coulomb correlations are not important above T_c, since if they were, one would expect to see a maximum in $\chi^{spin}(T)$.[13] From Fig. 1, we take $\chi^{Pauli} \equiv \chi^{spin}(720\text{ K})$, leading to $D_0 = 0.75$ states/eV-molecule and, via the usual expressions for tight-binding bands, to $W = 3.1$ eV and $E_F = 0.26$ eV. The large values of W and E_F validate the use of Eq. (1) below about 300 K $= E_F/10$.

From the experimental $\chi^{spin}(T)$ data and Eq. (1), $\Delta_{eff}(T)$ was extracted and is plotted in Fig. 2 for $T < 300$ K. $\Delta_{eff}(T)$ rises sharply below $T_c = 183$ K, then bends over at lower temperatures. Since $\langle\Delta\rangle(T > T_c) = 0$ and $\Delta_{eff}(T > T_c) \neq 0$, $2\Delta_{eff}$ evidently includes the contribution of fluctuations and is therefore to be identified with some average over the chain length of the magnitude of the energy gap (see Johnston[14]). I have obtained an extrapolated $\Delta(0)$ by scaling $\langle\Delta\rangle(T)/\Delta(0)$ versus T obtained from the neutron diffraction data[7] to the $\Delta_{eff}(T)$ data below T_c and requiring that the two measurements converge with decreasing T; precise agreement was obtained below 160 K with $\Delta(0) = 565$ K, as shown in Fig. 2. The value of $E_g(0) = 2\Delta(0)$ is comparable with the optical edge at 100 K,[8] and is in agreement with the approximate value of 1200 K obtained from the slope of $\ln\sigma$ vs $1/T$ for $T \sim 100$ K.[9] The latter agreement suggests that intrachain Coulomb correlations are not important below T_c, consistent with the result above for $T > T_c$. The experimental value of $\Delta(0)$ and the mean-field relation $2\Delta(0) = 3.52 k_B T_c^{MF}$ give $T_c^{MF} = 321$ K, about 75% larger than T_c.

From Fig. 2, Δ_{eff} becomes nearly independent of

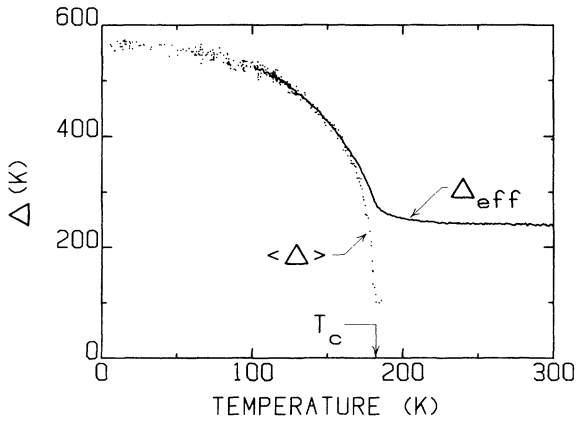

FIG. 2. Effective uniform energy gap/2 (Δ_{eff}) vs temperature for $K_{0.3}MoO_3$ as derived from $\chi^{spin}(T)$ (connected points); isolated points are $\langle\Delta\rangle(T)$ data obtained from the neutron diffraction data of Ref. 7.

temperature above T_c. If our postulate is correct that the temperature variation of χ^{spin} above T_c arises from CDW fluctuations, then their influence on $\chi^{spin}(T)$ near T_c^{MF} is equivalent to that of a nearly temperature-independent uniform semiconducting gap $2\Delta_{eff} \approx \Delta(0)$. Quantitative analysis of the $\chi^{spin}(T)$ data above T_c in terms of the variation predicted for isolated 1D metallic chains exhibiting CDW amplitude fluctuations by Lee, Rice, and Anderson[1] confirms the present interpretations. Scaling their prediction for χ^{spin}/χ^{Pauli} vs T/T_c^{MF} to the data between 225 and 320 K yielded the fit shown as the thin solid curve in Fig. 1(b) with $T_c^{MF} = 330$ K and $\chi^{Pauli} = 23.4 \times 10^{-6}$ cm^3/mole. The remarkable agreement of T_c^{MF} with that found independently above at $T << T_c$ [i.e., from $\Delta(0)$] is strong evidence that the variation of $\chi^{spin}(T)$ above T_c is indeed due to CDW amplitude fluctuations. Analysis of their $\chi^{spin}(T)$ prediction in terms of Eq. (1) also shows that Δ_{eff} becomes nearly independent of temperature above about $T_c^{MF}/2$ and that $\Delta_{eff}(T > T_c^{MF}/2) \approx \Delta(0)/2$ as found experimentally above. To my knowledge, this is the first case where the theory of Lee, Rice, and Anderson[1] has been quantitatively verified for a quasi 1D conductor. From comparison of $\langle\Delta\rangle$ with Δ_{eff} in Fig. 2, fluctuations begin to contribute to χ^{spin} and Δ_{eff} above about 160 K, or 20 K below T_c. From Fig. 1(b), 2D and/or 3D fluctuations begin to be important below about 225 K, as seen in a divergence between the data and 1D theory prediction below this temperature.

In view of the self-consistency of the above analyses, we proceed to calculate the electronic heat capacity C_e and entropy S_e for $K_{0.3}MoO_3$. It was shown above that $\chi^{spin}(T)$ could be modeled as that of a 1D semiconductor with a uniform gap $2\Delta_{eff}(T)$, where $\Delta_{eff}(T)$ was derived from $\chi^{spin}(T)$. We assume here that $C_e(T)$ and $S_e(T)$ can be computed from the same model using the previously determined $\Delta_{eff}(T)$.[15] For a semiconductor with a uniform gap, C_e is given by[16]

$$C_e = \frac{2}{T}\int_0^\infty g(E, \Delta_{eff})\left(-\frac{\partial f}{\partial E}\right)\left(E^2 - \frac{T}{2}\frac{d\Delta_{eff}^2}{dT}\right)dE, \tag{2}$$

where the notation is the same as above Eq. (1). Using $\Delta_{eff}(T)$ from Fig. 2 and Eq. (2), C_e and $S_e = \int_0^T (C_e/T)dT$ were computed and are plotted in Fig. 3, normalized to the values $\gamma_0 T$ in the absence of a gap, where $\gamma_0 = \pi^2 k_B^2 D_0/3$; for $K_{0.3}MoO_3$, $\gamma_0 = 1.76$ mJ/mole·K^2. A discontinuity ΔC_e is seen in C_e at T_c given by $\Delta C_e/C_e(T_c+) = 0.9$; this

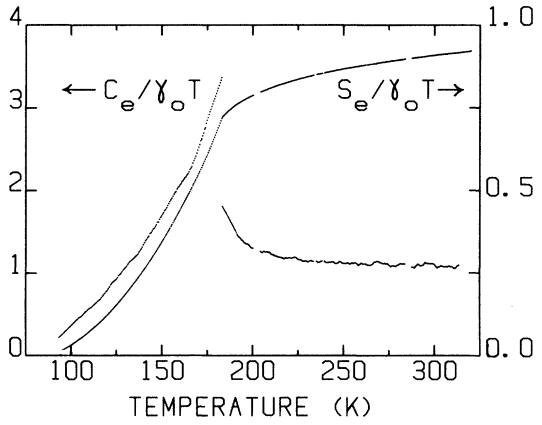

FIG. 3. Electronic heat capacity C_e and entropy S_e vs temperature for $K_{0.3}MoO_3$ as derived from $\chi^{spin}(T)$; each quantity is normalized to the unperturbed value $\gamma_0 T$ (see text).

is significantly smaller than the mean-field value 1.43, consistent with extensive CDW fluctuations above T_c. $S_e(T_c)$ is only 70% of that in the absence of fluctuations, again illustrating the influence of fluctuations on the thermodynamics. $C_e(T)/\gamma_0 T$ as well as $S_e/\gamma_0 T$ approach their asymptotic limit of 1 very slowly with increasing temperature above T_c, as expected for a 1D metal.[14]

In conclusion, the analyses outlined here were carried through for the compound $K_{0.3}MoO_3$ primarily because it was possible to obtain high quality $\chi^{spin}(T)$ data on a single crystal of this material, and because data could be obtained both far above and far below T_c as well as T_c^{MF}. However, the present analyses are more general, since $\chi^{spin}(T)$ data above T_c for TaS_3[17] and $(TaSe_4)_2I$[18] can also be scaled to lie on the universal curve of Lee, Rice, and Anderson[1] with scaling parameters $\Delta(0) = 1.76\, k_B T_c^{MF}$ in reasonable agreement with the $\Delta(0)$ values extracted below T_c from conductivity data, indicating the importance of CDW fluctuations in determining the physical properties of these compounds and in depressing T_c from T_c^{MF}. Interesting challenges remain to quantitatively establish experimentally and theoretically how the CDW fluctuations influence the temperature dependences of other properties such as the thermoelectric power in this class of materials in the vicinity of T_c and above.

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