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Reply to the Comment on

Low temperature specific heat of blue bronze $K_{0.30}MoO_3$

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Abstract. In our Reply to the Comment [1] we refute the "straightforward" interpretation of the excess low-temperature specific heat, C_p, contribution we have measured in our study of CDW systems $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ [2] as originating *solely* from normal phonon modes. The specific sensitivity of the bump in C_p/T^3 at low temperatures to the impurity content is consistent with the increased value of the phason pinning gap while the dispersion of normal phonons remains unaffected. We ascribe at least this part of the anomaly to the phason contribution. As stated in reference [3] that the phonon density of states extracted from neutron scattering measurements is the least reliable in this energy range (<0.5 meV), we conclude that C_p measurements are more accurate for detecting the phason contribution.

PACS. 71.45.Lr Charge density wave systems – 65.40.Ba Heat capacity – 63.50.+x Vibrational states in disordered systems

Incommensurate (IC) modulated structures are currently the object of theoretical and experimental studies. In addition to the conventional Bragg reflections corresponding to the main structure, satellites are detected in diffraction experiments. Incommensurate systems can be ranged in two classes: insulating compounds for which the phase transition is of a structural origin (3D) [4] and quasi one-dimensional systems exhibiting a metal-insulator charge density wave (CDW) phase transition at T_P below which a modulated lattice modulation is associated to a charge modulation [5]. For displacive transitions, a phonon mode softens at the transition temperature, T_P. Below T_P, excitations of the superstructure are of two types: amplitudons and phasons. Similarly to phonons, the dispersion of phasons is linear, but with a gap at zero frequency due to pinning of the phase of the modulation. Phasons are a key feature governing the physical properties of CDW systems in relation to the sliding mode. Moreover at low temperature when the drastic reduction of free carriers has suppressed the screening of the CDW deformations, the dispersion of the longitudinal phason is expected to become optical while those of the transverse phason are not affected [5]. On the other side, fluctuations of the CDW order parameter in the chain direction persists also above T_P in a wide T-range, up to the mean-field temperature T_{MF} [6]; for $T_P < T < T_{MF}$ there are clear evidences of features such as paraconductivity and a "quasi-pinned" response [7]. Amplitudon and phason dispersions have been measured using inelastic neutron scattering techniques in the modulated IC dielectric $(ClC_6H_4)_2SO_2$ [8], in $ThBr_4$ [9] as well as in the CDW compound $K_{0.3}MoO_3$ [10].

As vibrations of a superstructure, phason modes should contribute to the specific heat at low temperature. In a general way, at very low T, these modes are not distinguishable from the normal phonon modes and their contribution should follow a T^3 law. However, as shown by Boriack and Overhauser [11], a cut-off in the dispersion should be taken into account corresponding to the value at which the phason mode frequency reaches the normal acoustic branch; in this condition, the phason contribution is significant only below this cutt-off and appears as a jump in C_p/T^3. In addition, if the acoustic phonon branches do not extrapolate to zero at $q = k_F$ due to the pinning of the CDW phase, the calculation of C_p shows a depression of C_p/T^3 in the low T limit. It is this bump in the temperature variation of C_p/T^3, which is the object of the comment and of our reply.

In the case of the modulated IC dielectric $(ClC_6H_4)_2SO_2$ compound, we have reported [12] that the temperature variation of C_p/T^3 shows a bump at low T. We have successfully interpreted this excess in the low-T

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C_p contribution originating from the incommensurate excitations, consistent with the phason gap and the phason and amplitudon dispersions obtained from low-energy inelastic neutron scattering measurements [8]. This is as much significant as the phonon dispersions are quite regular in this 3D organic IC structure up to 500 GHz what should result with an exact T^3 contribution to C_p, without any peculiar feature inherent to 1D systems. These points give a strong support to our interpretation of the C_p/T^3 bump of this insulating compound in terms of phason and amplitudon excitations.

In the case of CDW compounds, such as $(TaSe_4)_2I$, $K_{0.3}MoO_3$ and KCP [13], very reliable fits of C_p were obtained from the phason contribution. However, specific phonon features result from their strongly anisotropic structural character: flat dispersion of the transverse acoustic modes in a large part of the Brillouin zone, optical modes at low energy ...; features which, when used for calculating the specific heat, yield also a bump in the T variation of C_p/T^3. Thus, taking argument of neutron data, the authors of Comment are led to claim that the excess low T specific heat we measured in CDW compounds is *strictly* of phononic origin.

Neutron scattering is a very powerful method: it gives the dispersions of excitations and the neutron density of states (PDOS) can be extracted from time of flight (TOF) measurements. However "conventional wisdom" on the interpretation of neutron scattering data for calculating C_p implies to be very cautious, following references [3] and [14]:

(i) usually the neutron PDOS yields a much bigger C_p/T^3 anomaly (even 2 times larger);

(ii) the weighted DOS can be 90% due to only one constituent;

(iii) there is a considerable uncertainty for small energies due to multiple scattering processes.

Further information on the very sophisticated weighting, normalizing and adjusting procedure can be found in the original papers [3,14].

To support their argument that phason excitations could not be detected in the low-T specific heat, the authors present in their Comment (Fig. 1) a comparison between our experimental C_p/T^3 data on $(TaSe_4)_2I$ and their calculations obtained from different neutron techniques (phonon dispersion curves and/or phonon DOS from TOF experiment) in such a way that the reader, if not reading carefully the original reference [3], is convinced by the excellent agreement with no adjustable parameters. This assumption is voluntary erroneous as shown below.

We show in Figure 1 two different estimations of C_p/T^3 of $(TaSe_4)_2I$ from the neutron DOS data $G(\omega)$ reported in the inset (from Fig. 4 in Ref. [3]). The first attempt – continuous line in Figure 1 – is obtained by introducing a cutt-off at $E = 0.2$ meV (the lowest energy at which data were recorded). The maximum in C_p/T^3 is rather well reproduced in position, but C_p decreases much very rapidly at low T in comparison to the experiment. The second curve – dashed line – is obtained by the same manner as in reference [3], *i.e.* by extrapolating the PDOS below 0.2 meV down to 0.01 meV by using a ω^2 law. As stated in reference [3], "the specific heat anomaly is reproduced although with a distorted shape and shift in T (peak at 1.5 K instead of 1.8 K)". These estimations show *the great sensitivity of the deduced specific heat* to the extrapolation of $G(\omega)$ below 0.2 meV, *i.e.* in the energy range "below 0.5 meV where the neutron curve is the least reliable" as stated in reference [3].

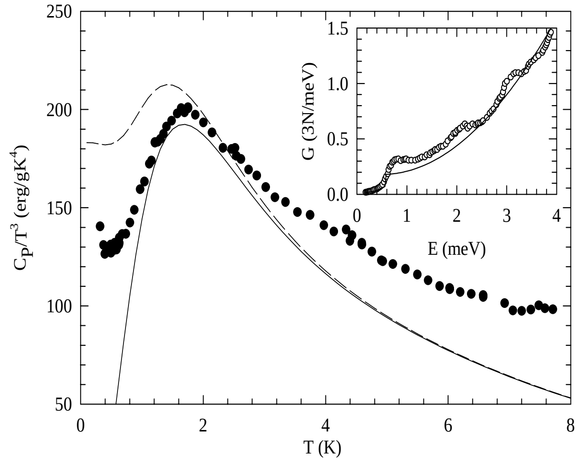

Fig. 1. Temperature variation of C/T^3 of $(TaSe_4)_2I$. Solid circles: experimental data from reference [2]; continuous line: specific heat calculated from the generalized PDOS, with a cut-off for energies lower than 0.2 meV; dashed line, specific heat calculated with a ω^2 law extrapolation down to 0.01 meV. Inset shows the experimental density of states, $G(\omega)$, measured [3] from neutron scattering in $(TaSe_4)_2I$ and used for calculation of C_p/T^3 in the main frame. The $g(\omega)$ curve (solid line in the inset) used in reference [1] and [3] for perfect fitting of the specific heat data is also shown.

These two attempts confirm the impossibility to reach a good agreement between C_p calculated from the PDOS data and experimentally measured without any adjustable parameter, as claimed by the authors of reference [1]. In fact, the excellent agreement presented in Figure 8 of reference [3] as well as in Figure 1 in reference [1] is obtained from a "trial g(ω) PDOS" – it corresponds to the solid line in the inset of the present Figure 1 – which largely differs from the experimental G(ω); in particular, a step is artificially introduced at 0.6 meV and the amplitude of the *ad hoc* DOS $g(\omega)$ is only 50–70% of that of the experimental $G(\omega)$ between 0.75 and 1 meV, the energy range covering C_p/T^3 bump (1.7 to 2.3 K). In addition, the ω^2 law has been adjusted to obtain the agreement with the specific data near 0.5 K. Surprisingly, in such a fit the lower DOS in the entire energy range yields a higher value of C_p/T^3 at temperatures above the maximum!

Similar discrepancies and "adjustments" occur in the case of $K_{0.3}MoO_3$ [1,14]. If no "adjustment" is done, the PDOS directly obtained from TOF neutron scattering yields a discrepancy in the amplitude of C_p/T^3 by a factor ∼1.8–2.5 in the T-range of the bump, although with a shape in a qualitative agreement with the experimental C_p data [14]. However, from the PDOS estimated from the dispersion curves measured by neutron scattering [10], and *normalized* to the limit low-T cubic regime of C_p, the bump in C/T^3 was well reproduced [14] up to a temperature of 15 K; the inclusion of higher energy optic modes in the calculation may improve the fit at higher energies.

In addition, the conclusion on "the absence of a noticeable phason contribution" deduced from the fact that the weighted PDOS is almost the same at 300 K and 150 K, *i.e.* above and below the Peierls transition temperature [3,14] is at least forced, as it is known that "during the data treatment the Debye-Waller factor was taken to be isotropic", and "this leads to an artificial enhancement or depression of phonon branches depending on their polarization" [14]. This point is of a great importance for $(TaSe_4)_2I$ and for blue bronze: the former compound is very anisotropic and 1D fluctuations exist far above T_p [7], up to the mean field temperature $T_{MF} \sim 800$ K ($T_{MF} \sim 400$ K in blue bronze). Far-infrared measurements have revealed pseudo-CDW gap at least up to 450 K [15]. Therefore, for comparison with low T data, PDOS measurements are clearly needed at high enough temperature for suppressing CDW fluctuations and in the critical energy range (<1 meV).

From our original paper [2] it is obvious that we did not ignore the phononic interpretation, as we even estimated the fraction of the bump that can be attributed to this origin. However, the *influence of impurities* on the shape of the anomaly in C_p/T^3, which has been reported in [2], *does not support the straightforward interpretation through normal phonons.* Indeed, no measurable effect on doping was found in neutron scattering [3]. On the other side, acoustic measurements indicate the increase of the transverse sound velocities on doping (Ref. [38] in [2]) in agreement with the slightly depressed acoustic βT^3 background measured from specific heat [2]. Therefore we were led to include the phason contribution in order to account for this effect. In Figure 2, we show the T dependence of C_p/T^3 as resulting from the phason contribution by varying two parameters: θ_φ, the equivalent of the Debye cut-off frequency for phasons and T_0, the lower cut-off frequency due to the pinning gap as: $T_0 = h\nu_0/k_B$. It appears clearly that the low-T part of the C_p/T^3 bump is strongly suppressed when the pinning frequency, that is to say, the impurity content is increased. This result is in perfect agreement with our specific heat data on doped $(TaSe_4)_2I$ and blue bronze as reported in [2]. So, the effect of doping is essentially present at very low energy where neutron measurements are less reliable. It is interesting to note that the fit of the C_p/T^3 bump with the inclusion of the Einstein mode contribution from the amplitudon observed at 1.7 THz in neutron scattering [6] in our fit renders the phason cut-off frequencies ($\nu_0 = 290$ GHz, $\theta_\varphi = 1.4$ THz) closer to the experimentally determined values [6].

In conclusion, we claim that the origin of the peak in the temperature variation of C_p/T^3 that we have measured in several CDW systems cannot be derived from a "straightforward phonon" interpretation. The sensitivity of the shape of the C_p/T^3 bump to doping which can be well accounted for by the increase of the pinning frequency, is a strong indication of the role of phasons in this anomaly. In reference [14], it is admitted that the neutron technique is "the least reliable in the lowest energy: 1 or 2 meV", which corresponds to $T \sim 2.3$–5 K for the specific heat. We insist on the fact that this T-range (corresponding to $E < 0.5$ meV, or $T \leq 1.3$ K in the case of $(TaSe_4)_2I$ – Ref. [3]) is very crucial to test our model of phason excitations and the role of impurities on the pinning frequency. In that T-range, contrary to the neutron TOF technique, the specific heat technique remains very sensitive. Clearly new and more reliable density of states measurements in the crucial low frequency range (<0.5 meV) are needed at low temperature, and at high enough temperature for suppressing the CDW fluctuations and any pseudo-gap effects. It would be also important to perform measurements of the longitudinal and transverse phason dispersion in the low temperature limit. If some evidence of the stiffening of the longitudinal phason mode has been brought [10], the cross-over to an optical character is still missing. More important, these measurements would allow determination of the exact phason density of states beyond the general claim that those are vanishingly small and cannot give any contribution to the specific heat.

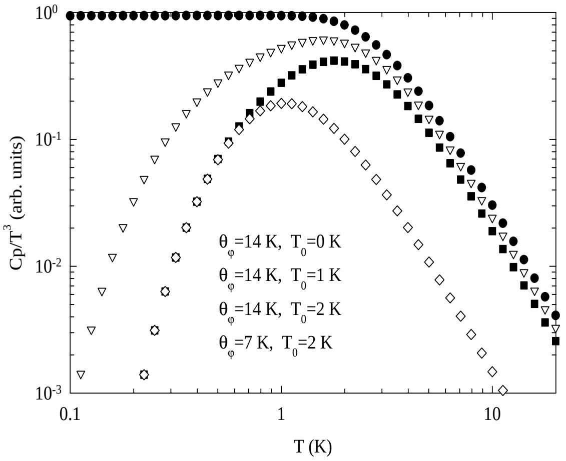

Fig. 2. Schematic presentation of the phason contribution to the specific heat: T_0 represents the lower cut-off defined by the value of the phason gap ν_0, $T_0 = h\nu_0/k_B$, which dominates the low-T wing, θ_φ is the equivalent of the Debye cut-off frequency for phasons, which influences the maximum position. The choice of parameters is comparable to the case of $(TaSe_4)_2I$ ($T_0 = 1.84$ K, $\theta_\varphi = 13.8$ K) [2].

We are thankful to E. Lorenzo and H. Requardt for their stimulating criticism. We hope that these mutual and constructive argumentations will bring new improvements in the understanding of the excitations in incommensurate systems, and specifically in the class of quasi one-dimensional systems [5] for which screening effects play an important role.

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