Incommensurate Systems as Model Compounds for Disorder Revealing Low-Temperature Glasslike Behavior

G. Reményi,[1,2] S. Sahling,[1,2,3] K. Biljaković,[1,2,4] D. Starešinić,[4] J.-C. Lasjaunias,[1,2] J. E. Lorenzo,[1,2] P. Monceau,[1,2] and A. Cano[5,6]
[1]Université Grenoble Alpes, Institut Néel F-38042 Grenoble, France
[2]CNRS, Institut Néel, F-38042 Grenoble, France
[3]TU Dresden, Institut für Festkörperphysik, D-01062, Germany
[4]Institute of Physics, Bijenička cesta 46, HR-10000 Zagreb, Croatia
[5]European Synchrotron Radiation Facility, 6 rue Jules Horowitz, B.P. 220, 38043 Grenoble, France
[6]CNRS, Université Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

(Received 25 April 2014; revised manuscript received 28 November 2014; published 14 May 2015)

We show that the specific heat of incommensurately modulated crystals with broken translational periodicity presents similar features at low temperatures to those of amorphous and glass materials. Here we demonstrate that the excess to the constant $C_p(T)/T^3$ law (or Debye limit) is made up of an upturn below 1 K and of a broad bump at $T \approx 10$ K that directly originates from the gapped phase and amplitude modes of the incommensurate structure. We argue that the low-energy dynamics of incommensurate systems constitute a plausible simplification of the landscape of interactions present in glasses, giving rise to their low-temperature anomalies.

DOI: 10.1103/PhysRevLett.114.195502 PACS numbers: 61.44.Fw, 63.50.Lm, 65.40.−b

In spite of long and continuous efforts during the past century, the physics of glasses, noncrystalline materials, still stands as one of the most challenging topics in condensed matter physics. One of the reasons lies in the difficulty to apply concepts successfully developed for solid state physics of crystalline materials to noncrystalline counterparts. On the other side, glasses share many features with liquids, in particular, the disorder or, better, the lack of long-range order. Glasses exhibit an atomic structure close to that observed in the supercooled liquid phase but display all the mechanical properties of a solid.

A universal feature of glasses and undercooled liquids is the occurrence of an excess of vibrational modes that leads to a deviation of the Debye law dependence of the phonon density of states at low energies, $g(\omega)/\omega^2$. The thermodynamic properties are thus affected by this excess, and the low-temperature specific heat displays a bump in the $C_P(T)/T^3$ vs T plot, the so-called boson peak (BP) at $\sim$10 K [1,2]. The origin and properties of this excess have been long discussed on the basis of the phenomenological properties of glasses. A second ubiquitous component observed in the $C_P(T)/T^3$ vs T plot is an upturn below 1 K. These two features are generally considered as independent. Models aiming at a description of the BP are numerous [2,3], although it seems that there is a consensus that the BP is caused by disorder. Very recently, this consensus has been questioned: The phonon density of states of crystals and related glasses suggests that the BP is caused by the same mechanism, an excess of low-energy phonons [4–7]. The role of disorder is thus challenged, and, whereas the anomalous thermal conductivity may be due to disorder, the BP in the specific heat experiments is due to a lower density of states [7].

The upturn is frequently interpreted in terms of localized, random two-level systems (TLS). The occurrence of atoms or small groups of atoms which can perform quantum tunneling between two or several configurations of approximately the same energy is postulated [8,9]. In a seminal work, Yu and Leggett [10] pointed out that it is very unlikely that this mechanism produces the very same universal constant for the thermal conductivity or the ultrasonic attenuation in any form of glass. Very recently, the suppression of tunneling TLS in ultrastable glasses of indomethacin has been reported [11], thus lending support to Yu and Leggett's criticism.

As the precise origin of these features is still unknown, one question that straightforwardly emerges in this debate is, can one address these topical problems by studying one of the simplest (if not the simplest) systems that systematically show both these features at low temperature?

Like amorphous solids and glasses, incommensurate (IC) systems lack translational symmetry (TS) that gives way to a *weak disorder* in the lattice position [12]. The use of IC structures to introduce and study the effect of disorder in a controlled way has become a current practice in many disciplines. For instance, recent work on IC disorder induced in a 2D vortex lattice has served to explore the effect of symmetry-breaking disorder [13]. Disorder induced by TS breaking is another field of interest in optical Bose-Einstein condensates [14]. Specifically, in this Letter, we study the excitations arising from TS breaking in IC compounds and calculate their contribution to the low-temperature specific heat. Two distinct low-energy phonons associated with changes in the amplitude and in the phase of the IC modulation (the so-called amplitudon and phason modes) appear as relevant [15]. Here we show that, although these excitations pertain to IC structures alone, disorder is rooted in the ground state and manifests on reducing the lifetime of the phason mode. We will show that this mechanism is at the origin of the upturn in the $C_p(T)/T^3$ plot.

IC superstructures have been largely studied in low-dimensional metals, where they can emerge due to the instability of the Fermi surface associated to the Kohn anomaly [16–18]. This is the case of charge-density-wave (CDW) compounds like $NbSe_3$, TaS_3, $(TaSe_4)_2I$, and $K_{0.3}MoO_3$. These systems show unexpected glasslike features in their low-temperature properties as shown in Fig. 1, where we also show the specific heat of vitreous silica [19] for comparison. The bump in the $C_p(T)/T^3$ plot of these CDW systems has been described as the contribution from the modified Debye spectrum with two cutoffs: a lower frequency corresponding to the pinned CDW state and an upper frequency corresponding to the effective Debye temperature for the collective modes (modified Boriack-Overhauser model) [20,21].

As shown in Fig. 1, the bump is accompanied at low temperatures by an extra contribution scaling roughly as T^{-2} in the $C_p(T)/T^3$ plot. As in glasses, it has been explained by invoking the presence of TLS and described as the tail of the corresponding Schottky anomaly. This glassy dynamics is supposed to originate from the pinned CDW, and several models have been proposed to account for this behavior [26,27]. These metastable states, found also sensitive to the magnetic field [28], are attributed to the bisolitons generated at strong pinning centers in the CDW ground state [29,30]. They are decoupled from phonon modes, so that the specific heat exhibits nonexponential relaxation with aging effects [31]. As we see, the interpretation of this glasslike behavior is, however, challenged by the *quasimetallic* character of these systems.

In order to further study the role of disorder, we have turned our attention to IC insulators. The work on IC dielectrics was initiated some years ago on $(ClC_6D_4)_2SO_2$ (BCPS) [24] and on byphenil [25]. Important for low-temperature heat transport is the possibility that the phase mode is gapped and, thus, contributing to the specific heat as a deviation from the T^3 law [21]. A second feature that is acknowledged to be present in many (if not all) IC compounds is that the phason mode is damped [32] or even overdamped as in K_2SeO_4 [33]. The physical origin of this damping results from the disorder in the lattice positions created by the IC structure. More generally, many IC compounds do not have a soft mode, as pretransitional dynamics is rather of the relaxational type. In this case, the decoupling soft phonon → phason + amplitudon is not observed in the inelastic neutron scattering (INS) spectra. It is the lowest-energy soft mode of the correct symmetry that acts as both the phason and the amplitudon, and consequently the low-temperature specific heat still bears similar features as those here described [34,35]. These systems also show systematic deviations from the Debye behavior at low temperatures, as can be seen in the right panel in Fig. 1.

The simplest case of an IC superstructure emerging in an insulator from a purely structural phase transition is best

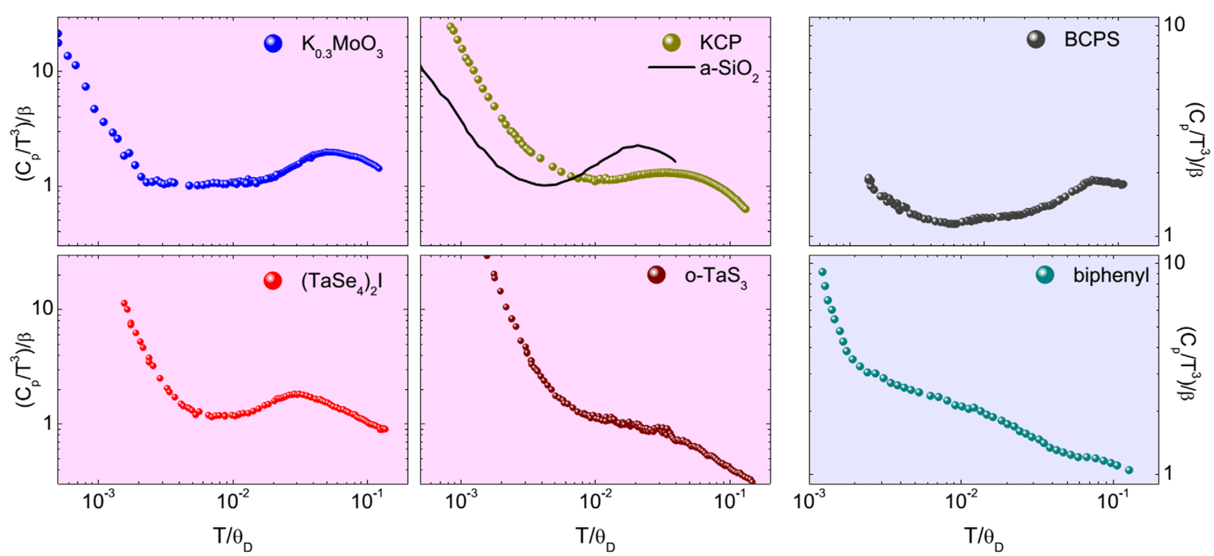

FIG. 1 (color online). $C_P/\beta T^3$ plots of several IC compounds, with β the coefficient of the Debye law. The left and middle panels are charge density wave compounds [$K_{0.3}MoO_3$ [20], $(TaSe_4)_2I$ [22], KCP [20], and TaS_3 [23]]. The $C_P/\beta T^3$ plot of vitreous silica is displayed as a comparison [19]. Right panel: Insulating compounds, BCPS [$(ClC_6D_4)_2SO_2$] [24] and biphenyl [25]. Error bars are smaller than the size of the symbol.

exemplified in ThB_4 [36]. This system undergoes a displacivelike transition to the 1**q**-IC modulated superstructure at 95 K, with T-independent (between 80 and 1.5 K) wave vector $\mathbf{q}_{IC} = 0.31\mathbf{c}^*$. This phase transition has been very well documented in the literature, and it is considered as one of the clearest examples of displacive dynamics with the presence of phason and amplitudon excitations below the transition temperature. Importantly, the spectrum of this system has been characterized by inelastic neutron scattering and Raman experiments with great accuracy down to 10 K. We thus performed low-temperature specific heat measurements for this system in order to further correlate these measurements with the spectrum in a no-fitting-parameter fashion [37].

The results of the specific heat measurements in $ThBr_4$ are shown in Fig. 2. They can be unfolded as follows [38].

(i) *Acoustic phonons.*—The background constant contribution in the $C_p(T)/T^3$ plot due to acoustic phonons. The Debye temperature $\theta_D = 62$ K has been calculated from the sound velocities measured by INS [36], yielding $\beta = 8 \times 10^{-3}$ J/mole $\cdot$ K^4.

(ii) *Amplitudon contribution.*—The peak in $C_p(T)/T^3$ around 10 K is attributed to the amplitude excitations (amplitudon) of the IC modulation. The amplitudon dispersion has been determined by INS in Ref. [36]. It is rather isotropic and to a good approximation can be reproduced with

$$\omega(q) = \sqrt{\omega_A^2 + B\sin^2(q - q_{IC})a}. \quad (1)$$

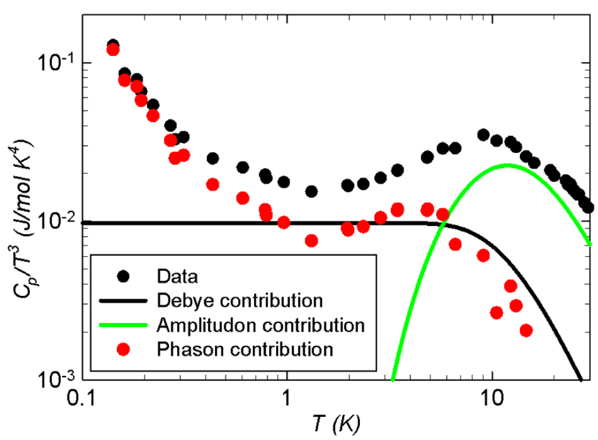

FIG. 2 (color online). Temperature dependence of the specific heat divided by T^3 in a log-log plot for $ThBr_4$. Experimental data are displayed with full black circles. The black line represents the Debye contribution calculated from sound velocities determined in a neutron scattering experiment [36], using the Debye model of the dispersion with $\theta_D \approx 62$ K, and corresponding to $\beta = 8 \times 10^{-3}$ J/mole $\cdot$ K^4. The green line is the amplitudon contribution estimated from the measured INS dispersion. Full red circles represent the contribution remaining after subtraction of previous contributions and assigned to the phason contribution. Experimental error bars are smaller than the size of the symbol.

Here ω_A determines the amplitudon gap and $\omega_{DA} = \sqrt{\omega_A^2 + B}$ the high-frequency cutoff, a is the lattice parameter along the direction of the IC modulation wave vector, and q_{IC} is the wave vector of the IC structure. Thus, the contribution to the specific heat of the amplitudon branch can be written as

$$C_A(T) = \delta C_0 \int_{x_0}^{x_1} dx \frac{x \arcsin^2\left(\sqrt{\frac{x^2 - x_0^2}{x_1^2 - x_0^2}}\right)}{\sqrt{(x^2 - x_0^2)(x_1^2 - x^2)}} \frac{x^2 \exp(x)}{[\exp(x) - 1]^2}, \quad (2)$$

with $x_0 = \hbar\omega_A/k_B T$ and $x_1 = \hbar\omega_{DA}/k_B T$. δC_0 is a prefactor that includes amplitudon mode weight normalization to the total density of states. With $\delta C_0 = 182$ J/mol $\cdot$ K, $\omega_A = 570$ GHz (19 cm^{-1}), the low-temperature optical gap measured by Raman scattering [39], and $\omega_{DA} = 1.2$ THz, the high-frequency cutoff of the original soft mode [36,40], we obtain the amplitudon contribution represented by the green line in Fig. 2.

(iii) *Phason contribution.*—This contribution remains upon subtracting (i) and (ii) off the original data. This is represented in Fig. 2 as red circles. It can be described as a small bump, with a maximum at $\approx$4 K, followed by a rise as the temperature decreases.

The two latter features have been regularly described in the literature as separated and having uncorrelated origins. However, in Ref. [41], it has been shown that both the shoulder and the subsequent rise can have a unified description revealing that they are two different manifestations of the very same phason mode: gap and damping. The shoulder indicates that the phason dispersion in $ThBr_4$ is not completely acousticlike as in textbook descriptions but contains a low-frequency gap (the phason dispersion is shown as an inset in Fig. 3). This is not very surprising, since, physically, the incommensurate superstructure is expected to be pinned to the underlying lattice rather than detached from it and totally free to move at no energy cost. According to Ref. [36], the upper limit of this gap is estimated to be $\approx$50 GHz. In addition, it was pointed out that the finite lifetime of the phason excitations can play a nontrivial role in the low-temperature properties of incommensurate systems. Such a finite lifetime has been experimentally observed by INS [40] within the temperature range of our specific heat data. This implies that, in contrast to the amplitudon modes, the phason excitations do not form a closed system. Consequently, the energy distributed in the phason subsystem can be transferred to another excitation within the time scale of our experiment. This transfer can be seen as a sort of redistribution of density of states that, phenomenologically, can be accounted as [41]

$$C(T) = k_B \sum_{i=1}^{3} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[\left(\frac{\hbar\lambda_i(\mathbf{q})}{2\pi k_B T} \right)^2 \psi' \left(\frac{\hbar\lambda_i(\mathbf{q})}{2\pi k_B T} \right) - \left(\frac{\hbar\omega_D}{2\pi k_B T} \right)^2 \psi' \left(\frac{\hbar\omega_D}{2\pi k_B T} \right) - 1 \right]. \quad (3)$$

Here $\psi' = d^2[\ln\Gamma(x)]/dx^2$ is the trigamma function, and λ_i are the roots of the equation $\lambda^3(\mathbf{q}) + \omega_D\lambda^2(\mathbf{q}) + [\omega^2(\mathbf{q}) + \Gamma\omega_D]\lambda(\mathbf{q}) + \omega_D\omega^2(\mathbf{q}) = 0$, where $\omega(\mathbf{q})$ gives the frequency of the phonon as a function of its wave vector, Γ^{-1} determines the phonon lifetime, and ω_D is a Drude cutoff for the phonon decay introduced for convenience [41,42]. The phason dispersion $\omega(\mathbf{q})$ is parametrized by the phason gap ω_ϕ and the high-frequency cutoff $\omega_{D\phi}$ as in Eq. (1).

The best fit of the experimental data, shown in Fig. 3, is obtained for $\Gamma = 3.8$ GHz, $\omega_\phi = 46$ GHz, and $\omega_{D\phi} = 430$ GHz. We have used for numerical calculations the value $\omega_D = 200$ THz, which does not affect the final results. The influence of damping on the amplitude mode contribution has been estimated as well, and it is, in view of the rather high energy of this mode at low temperatures, vanishingly small. We emphasize that the key ingredients are just the phason dispersion and the corresponding lifetime, which are in agreement with the results of inelastic neutron scattering [36,40].

This lifetime again evidences that the incommensurate superstructure cannot propagate freely. It will also be subjected to dissipation certainly due to the scattering with

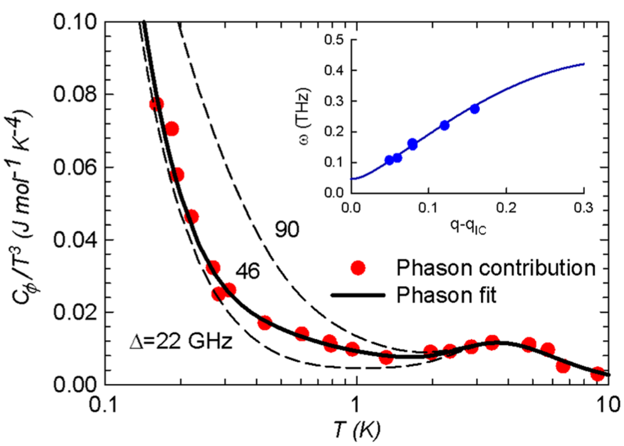

FIG. 3 (color online). Low-energy contribution to the specific heat of $ThBr_4$ divided by T^3 in a semilog plot. The red points correspond to the experimental data shown in Fig. 2 once the Debye and amplitudon contributions have been subtracted. The continuous black line is the result of the calculation from Eq. (3) with the phason gap of 46 GHz and damping of 3.8 GHz. The black dashed lines correspond to simulations using the same damping and different phason gaps of 22 and 90 GHz. The dispersion curve for the phason is drawn in the inset, with points representing the experimental data [36]. Experimental error bars are smaller than the size of the symbol.

impurities and/or disorder. This dissipation amounts to a redistribution of density of states [42] that, as a rule, is ignored when addressing thermodynamic properties. However, and as pointed out in Ref. [41], this redistribution cannot be neglected in incommensurate systems given the low frequency of their characteristic phason modes, which explains the origin of the uprise below 1 K. Analogous redistribution has been put forward in structural phase transitions, in the context of the central peak problem above T_C [43]. The central peak originates from the damping of the phonon excitations at the approach of T_C and yields an extra density of states at low energies. Once the source of anharmonicity disappears, away from the critical region, the central peak vanishes.

In summary, we have measured the low-temperature specific heat in the incommensurate insulator $ThBr_4$. These measurements reveal an excess of specific heat clearly seen in the C_p/T^3 plot. By carrying out a careful correlation with its spectrum of excitations, previously determined by means of inelastic neutron scattering and Raman experiments, we have established an unambiguous link between this excess of specific heat and the low-energy excitations of the incommensurate superstructure. Specifically, the bumps in the C_p/T^3 plot originate from the gaps in the phase and amplitude branches, while the low-temperature uprise is due to the finite lifetime of the phason excitations. This unambiguous link between structural dynamics and glasslike features is compatible with recent molecular dynamics simulations in glasses [4,6,44] and is expected to help in rationalizing the properties of more complex systems.

We acknowledge the funding obtained from the French Ministry of Higher Education and Research ECO-NET Project No. 21325VC and from the Croatian Ministry of Science, Education and Sports Project No. 035-0352827-2842. Crystals used in our experiment were synthesized by P. Delamoye and kindly lent by R. Currat.

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