Excess Low Temperature Specific Heat and Related Phonon Density of States in a Modulated Incommensurate Dielectric

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We report the first very low temperature (from 93 mK to 7.3 K) specific heat data of a modulated incommensurate dielectric $(ClC_6H_4)_2SO_2$. They reveal three different contributions in excess of that of normal acoustic phonons: low frequency excitations predominant below 0.2 K, a phason branch above 0.7 K, and optical phonon and amplitudon branches around 4.5 K. This analysis is done considering neutron scattering results also.

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Usually the lattice specific heat C_p of crystalline matter is well described by the Debye model if $T \ll \theta_D$ where $k_B\theta_D$ is a cutoff energy. It is now well known that this continuum model does not describe the low temperature specific heat of disordered solids, where additional degrees of freedom have to be considered. If the frequencies of these excitations are of the order of 10 GHz, they will contribute to C_p at some 100 mK. A specific example of extraphononic contributions is given by the two-level states of amorphous materials. In the crystalline state, the best examples are low-dimensional compounds undergoing a Peierls transition at a critical temperature [1] below which the electron charge density wave (CDW) shows a modulation that is incommensurate with the underlying lattice. In real one-dimensional conductors, the gapless character of the phason mode can be destroyed by various mechanisms, especially impurity pinning. In these compounds, C_p measurements have revealed at the lowest temperatures an excess contribution due to low-frequency excitations, which is strongly time dependent [2–5], and a contribution from the phason modes at somewhat higher temperatures [5]. However, the interpretation by the phason can be made more difficult by the contribution of low-frequency phonon branches due to the 1D character [6].

No such observation was reported up to now in other types of incommensurate systems, for instance, in dielectrics compounds. Fundamental differences exist between CDW and dielectric compounds. These differences are from both physical and experimental types. Concerning physical aspects, incommensurability in dielectrics is of structural origin, allowing direct analysis of the related lattice dynamics and also direct unambiguous observation of the characteristic incommensurate excitations such as the phason branches, by means of neutron investigation in biphenyl, $ThBr_4$, and BCPS [7,8]. From the experimental points of view, defects appear to play a crucial role in 1D CDW compounds in comparison to 3D dielectrics compounds which, in addition, can be obtained more easily in the form of large, quite pure, single crystals. The above discussed thermodynamic analyses request that the studied phase exists at the lowest temperature, which is rare in incommensurate systems. In this Letter, we present the first low temperature specific heat data in an insulator which presents a phase transition towards a persistent incommensurate modulated structure. It is the molecular compound of bis(4-chlorophenyl)sulfone, BCPS, whose incommensurate phase has been discovered recently and revealed very interesting experimental features [9–12]. The low temperature (<7 K) specific heat enables us to analyze the very low-frequency excitation spectrum and the possible metastable character of such a phase. The interpretation of the data is supported by measurements of both coherent and incoherent inelastic neutron scattering. Our main results concerning the collective excitations are as follows: the detection of a phason gap at $\nu_0 \approx 80$ GHz, in agreement with coherent neutron scattering data, and of optical and amplitudon branches at about 500 GHz. In addition, the metastable (or glassylike) character of the incommensurate phase is revealed by the presence of low-frequency excitations detected at very low temperature (below 200 mK) and by nonexponential energy relaxation on the time scale between 1 and 10^2 s.

At $T_I = 150$ K, BCPS, $(ClC_6H_4)_2SO_2$, presents a displacive incommensurate transition. Its modulation wave vector $\mathbf{q}_s = 0.78\mathbf{b}^*$ leads to peaks which are located far away from the Bragg ones, on both sides of a symmetry forbidden peak [9]. The observation of rather strong first and higher order diffraction satellites [13,14] is explained by a possible nonsinusoidal character of the static modulation. High resolution Raman scattering has shown that the amplitudon has an exceptionally weak damping and its frequency does not go to zero at T_I, with a gap of about 80 GHz [15]. This result is totally consistent with coherent neutron scattering, which reveals the existence of a phason gap in the frequency spectrum together with the

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appearance of a strong central peak, observed in the high temperature phase below 165 K [8]. The existence of a gapless phason has been assumed based on the analysis of the frequency dependence of the spin-lattice relaxation time T_1 in ^{1}H NMR [11], but as in biphenyl [16] this analysis neglected the role of the damping, which may hide the gap [17].

Specific heat measurements were performed from 7.3 K down to 93 mK in a dilution refrigerator with a transient heat-pulse technique. The BCPS single crystal (1.5×1.3 cm^2 in surface, 0.42 cm in thickness, and 1.206 g in weight) was coated with Apiezon N grease (2 mg in weight) and pressed between two large silicon plates. The heater was fixed on one plate, the thermometer and the thermal link to the regulated cold sink on the opposite plate. The specific heat of the addenda ($mC_{\rm add} = 3.95T + 8.41T^3$ ergs K^{-1} below 2 K) was determined by weighing the glue and the grease (a total of 3 mg) and by measuring separately the Si platelets of the sample holder. They contribute less than 10% to the total heat capacity above 0.4 K, but up to 45% for the minimum temperature (93 mK). A similar sample holder has recently been used to detect a sample heat capacity of the order of 0.1–0.2 erg K^{-1} at $T = 100$ mK in very sensitive experiments on Al-Si compounds [18]. This is of the same order as for the residual heat capacity of BCPS. The data were obtained by an automatic analysis of the exponential transients [19]. Because of the excellent thermal diffusivity of the single crystal, the accuracy of this technique is very good: a few percent between 0.2 and 7 K. Below 0.2 K, the uncertainty increases due to the progressive appearance of a deviation from exponential decay.

The raw data, corrected for the addenda, are represented in Fig. 1 as C_p/T^3 vs T in a log-log plot, in order to characterize deviations from the Debye T^3 law. Using the values of the sound velocity measured by Brillouin scattering [20], we have estimated the contribution $C_{\rm ac}$ of acoustic phonons to $C_{\rm ac} = 2\pi^2 k_B^4/5\rho\hbar^3\overline{v}^3$, ρ being the mass density $\rho = 1.5$ g cm^{-3}. The average sound velocity $\overline{v}$ is typically 1540 m s^{-1} and the resulting specific heat $C_{\rm ac}$ is assumed to obey an αT^3 law with $\alpha = 225$ ergs K^{-4} g^{-1}. Three dominant features are apparent in order of increasing temperature: (a) a strong departure from the T^3 law up to about 0.2 K, (b) a first increase around 0.5 K, and (c) a maximum around 4.5 K.

(a) An extra phonon contribution with a rapid variation becomes predominant below 0.2 K down to the lowest temperatures. Because of nonexponential transients in this temperature range, the specific heat is defined by the initial temperature decay just after the pulse, as explained in Ref. [2], which yields a minimum value. After subtraction of the acoustic phonon contribution ($225T^3$ ergs g^{-1} K^{-1}), there remains a small residual signal ΔC plotted on a log-log scale in Fig. 2. The dotted line shows a βT^γ law with $\beta = 5.4$ (in units of ergs g^{-1} K^{-1}) and $\gamma = 1.69$. The value of the exponent γ depends on the value assumed for α and it decreases to 1.44 for $\alpha = 235$ ergs K^{-4} g^{-1}. Another feature is the time dependence of the specific heat, an effect characteristic of the broad spectrum of relaxation times in disordered systems. Note at this point that the minimum value of C_p obtained in Fig. 2 represents only the part of the distribution with the shortest relaxation times. The sample is subjected to a permanent heat flow and the thermal increment has been applied successively during 0.5 s, 1 min, and 1 h. Following a previously presented procedure [2], after switching off the heat pulse, the relaxation cannot be fitted by a simple exponential function and the deviation increases with duration of the applied heat flow. From these results, we may assume that at $T_0 = 97$ mK the thermodynamical equilibrium has

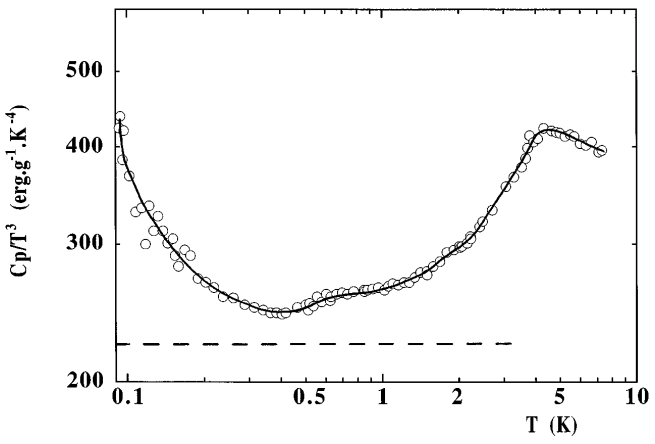

FIG. 1. Log-Log plot of the BCPS specific heat divided by T_3. Dashed line: Debye contribution calculated from acoustic data.

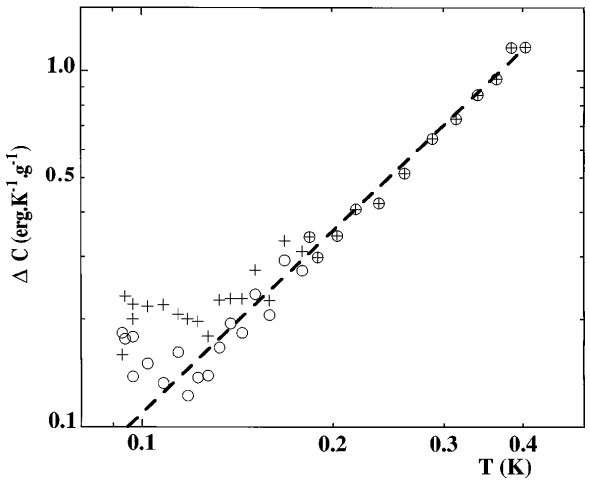

FIG. 2. Residual specific heat after subtraction of the contribution of phonons on a log-log plot. Two extreme possible values of C_p (circles and crosses), respectively, are deduced from the exponential laws, which can fit either the initial part (over a time space of 2 s) or the intermediate part (between 2 and about 10 s) of the temperature decay. The dotted line through the circles represents the power law $\beta T^{1.7}$.

been reached after about 1 min of thermalization of the compound, which indicates a very low activation energy for this slow relaxational process. It should be noted that these time-dependent relaxation effects disappear progressively above 200 mK. Such a features is usually attributed to the metastable character of the disordered ground state.

This behavior at very low temperatures could have the same origin as the low-energy excitations (LEE) observed in CDW compounds [2–5]. However, in that case, the residual LEE contribution was found to be much more important and varied less rapidly ($\gamma < 1$) [3]. This effect is less pronounced in our incommensurate modulated dielectric than in CDW compounds and its origin requires further clarification. In another incommensurate dielectric, biphenyl, NMR studies concluded for a glassy character of the lowest temperature phase [16]. Another aspect not considered up to now is the existence of the central peak in the phason fluctuation spectrum of incommensurate phases. As its spectral analysis is impossible (even with the best frequency resolution of a cold neutron triple axis spectrometer), its contribution to the very low temperature specific heat is unknown.

(b) The C_p/T^3 bumps seen in Fig. 1 above 0.5 K are more clearly illustrated in Fig. 3, under the form $\Delta C_p = (C_p - \alpha T^3 - \beta T^\gamma)/T^3$. Figure 3 clearly shows another contribution to C_p/T^3 around 0.7 K. Following an Einstein description this corresponds to excitations above 70 GHz. Coherent neutron scattering measurements have unambiguously shown that the resolved part of the phason spectrum presents a gap $\nu_0 = 80$ GHz at $\mathbf{q}_s$, with a slightly anisotropic dispersion and velocities 1700 m s^{-1} along $\mathbf{b}^*$ and 2600 m s^{-1} along $\mathbf{c}^*$ [8]. For a single phason branch, the specific heat may be expressed [5,21], assuming a truncated linear dispersion law at frequencies higher than the gap ν_0:

$$C_p = 3N_c k_B (T/\theta_c)^3 \int_{x_0}^{x_c} (x - x_0)^2 [x^2 e^x/(e^x - 1)^2]\, dx$$

$$\text{with } x_0 = h\nu_0/k_B T\,.$$

Here N_c is the number of phason mode excitations and $\nu_c = (k_B x_c/h)T = k_B\theta_c/h$ is a high-frequency cutoff. In order to describe the small region in reciprocal space around $\nu_0 = 80$ GHz where the phason branch is rather flat, and Einstein mode contribution with a small relative weight of 1% has been introduced. The resulting contribution is drawn as a dashed line in Fig. 3. From these C_p measurements, a mean velocity of 1980 m s^{-1} is found for the phason. A complete description of the specific heat is then obtained in this temperature range just by considering this phason mode. Figure 3 shows that the contribution of this mode at higher temperature is masked by the presence of other branches. Let us recall that in this description we used a modified Debye spectrum for the phase-mode excitations, with two characteristic frequencies: $\nu_0 = 80$ GHz corresponding to the gap and $\nu_c = 400$ GHz, assumed to be the high-frequency limit for the validity of Debye-like dispersion. The phason branch actually originates far away from the lowest transverse acoustic phonon in reciprocal space. Although it is in agreement with our coherent neutron scattering experiments [8], this value of ν_c is somewhat debatable, but this is of no fundamental importance. In fact in this temperature range several other contributions exist and the Debye assumption for the normal acoustic phonons becomes less and less valid.

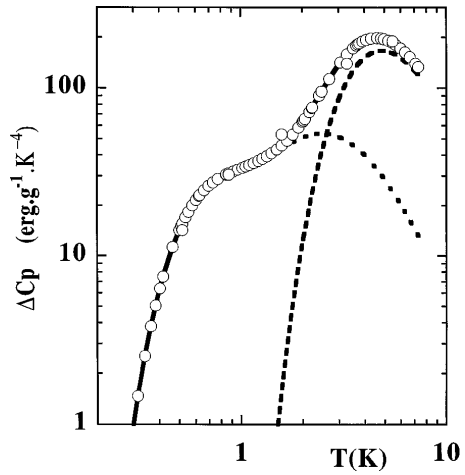

FIG. 3. Log-log plot of $\Delta C_p = (C_p - \alpha T^3 - \beta T^\gamma)/T^3$, as discussed in the text. The dashed curves indicate the contribution of the phason mode with two cutoffs ($\nu_0 = 80$ GHz and $\nu_c = 400$ GHz) and the contribution of an Einstein mode with $\nu_E = 500$ GHz. The solid curve is the sum of these two contributions.

(c) The last bump around 4.5 K is provided from low-frequency optical branches. An Einstein mode at $\nu_E \approx 500$ GHz indeed yields a maximum in C_p/T^3 at $\theta_E = 4.75$ K, i.e., a temperature 5 times smaller than calculated from ν_E. Raman scattering experiments [10] have shown that at low temperatures the amplitudon frequency saturates at approximately 400 GHz. Coherent neutron scattering spectra revealed the presence of other low-frequency excitations with temperature-independent frequencies at 320 and 470 GHz [22]. Our calculations indicate that other modes at higher frequencies do not contribute significantly to C_p/T_3 in this temperature range. This excess phonon density of states can be experimentally observed by incoherent neutron scattering. Such measurements have been performed on a polycrystalline sample using the time-of-flight spectrometer MIBEMOL of the Laboratoire Léon Brillouin (Saclay, France). The incident wavelength was $\lambda_0 = 6.2$ Å^{-1} giving a frequency resolution FWHM of 25 GHz. BCPS data measured in the incommensurate phase, at 80 K, are shown in Fig. 4, with the data analysis following Ref. [17]. As long as the Debye description is valid for acoustic phonons, their contribution to $g(\nu)/\nu^2$ and C_p/T^3 is constant. From lattice dynamics calculations [23] and coherent neutron scattering measurements [8], it follows that this Debye behavior is valid up

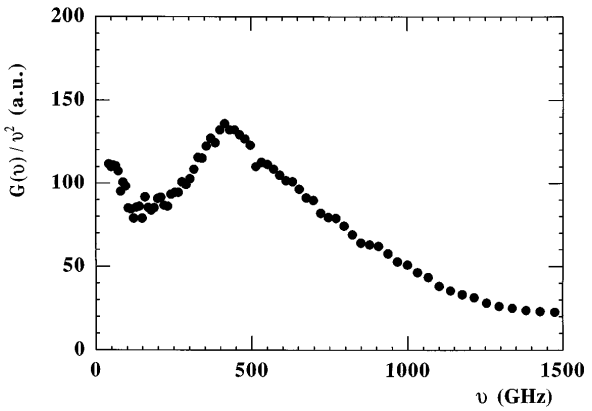

FIG. 4. Density of states $g(\nu)/\nu^2$ measured in the incommensurate phase ($T = 80$ K) by incoherent neutron scattering.

to about 500 GHz. A clear extra contribution to $g(\nu)/\nu^2$, superimposed on a maximum around 420 GHz, is consistent with the C_p/T^3 bump at 4.5–4.75 K. The intensity of the phenomenon observed can be explained by the nondispersive character of the optical-like modes. Hence even though the lowest frequency part of the amplitudon branch, which is not very dispersive around the satellite position $\mathbf{q}_s$, certainly contributes to the 4.5 K bump in C_p/T^3, the determination of its actual weight relative to other branches requires a measurement of the complete experimental dispersion or more precise lattice dynamics calculations.

In conclusion, the specific heat of the incommensurate modulated dielectric BCPS has revealed three extra terms in addition to the acoustic phonon contributions. The first one at $T < 0.2$ K is ascribed to low-frequency excitations whose microscopic origin (in both CDW incommensurate systems and glassy materials) remains a matter of debate. The second one, dominant around 1 K, is attributed to the phason excitations. This contribution is well described by a Debye dispersion of low-frequency modes with a flat gap at 80 GHz and a high-frequency cutoff that corresponds to the phason analogous of the Debye temperature and amounts to 19 K, in agreement with inelastic coherent neutron scattering results. The third extra contribution has a maximum at $T = 4.5$ K and, even if it is essentially due to optical phonons, it contains the contribution of the amplitudon branch.

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