Glassy anomalies in the heat capacity of an ordered 2-bromobenzophenone single crystal

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The heat capacity $C(T)$ of a 2-bromobenzophenone (2-BrBP) single crystal measured at temperatures from 0.4 to 30 K demonstrates anomalies inherent in disordered solids: Instead of the Debye law $C_D \propto T^3$, $C(T)$ shows a linear temperature dependence and a boson peak, i.e., peculiarities typical of solids with disorder. Computations for a pair of interacting 2-BrBP molecules revealed a few low-frequency states which are expected to actively couple to long-wave phonons. Raman scattering spectra demonstrate two strong spikes at energies close to the boson peak center at 26 cm^{-1}. We relate the Raman spikes to low-energy intramolecular modes, which are the rotational oscillations of the substituted phenyl ring around the C-C link to the ketone. Thus, we have found that a completely ordered crystal made up of molecules with low-energy intramolecular modes can show low-T properties, which are inherent in irregular solids such as various glasses, etc.

The Debye lattice dynamics model, in which the density of acoustic phonons is proportional to the phonon frequency squared, predicts the low-temperature heat capacity of nonmetal crystals to be $C_D \propto T^3$. Yet, if a solid contains any disorder, its low-T heat capacity follows a linear dependence $C \propto T$. This anomaly was explained [1,2] using the postulate that an intrinsic feature of irregular solids is the presence of two-level systems with small energy gaps. A more elaborate theory [3,4], which removed certain flaws in Anderson's approach and was able to treat the boson peak problem, postulates that irregular solids are best described by a soft potential model. Accordingly, within this approach the low-T heat capacity contains not only a linear term but also a term proportional to T^5. An important advantage of this theory is the conclusion that the coefficients at T and T^5 are rigidly interrelated [4].

The objects that perfectly obey the Debye law are noble gas cryocrystals. Diatomic and triatomic cryocrystals have extra degrees of freedom (rotations and intramolecular vibrations) but the respective energies are too high to affect the low-energy density of phonon states. There are many organic crystals with low-energy intramolecular modes, capable of distorting the low-energy density of states. In particular, pristine benzophenone and, especially, its monosubstituted derivatives such as ortho-bromobenzophenone (2-BrBP) belong here. As demonstrated earlier [5], the potential surface of the 2-BrBP molecule as a function of the rotation angle of the substituted ring around the link between the ring and the keton C=O is an ideal example of an asymmetric soft potential. Our main task was to accurately measure the heat capacities of ortho-bromobenzophenone crystals down to well below 1 K in order to establish to what extent the intrinsic properties of the 2-BrBP molecule can influence the low-frequency part of the energy spectrum.

In this Rapid Communication, we report the heat capacities of a single-crystal sample of 2-BrBP measured up to melting, with special attention given to the range from 0.4 to 10 K. In its regular polymorph state [5], the crystal has a $P2_1/c$ monoclinic lattice. The substance easily glassifies [6]; warming this glass state initiates [7] the formation of a metastable polymorphic phase, whose structure has yet to be determined.

The source 2-BrBP material was purified by recrystallization from ethanol solutions. Crystals grew during 5–6 days. The resulting single crystals had typical dimensions $1 \times 5 \times 8$ mm^3. Check phosphorescence measurements showed very low concentrations of lattice defects. Larger single crystals ($10 \times 10 \times 15$ mm^3) were grown from seeds in a supercooled phase according to a known procedure [8]. Transparent, colorless crystals with a nice cut were used in thermodynamic measurements. Heat capacities of a single crystal of weight 7.68 mg were measured from 0.4 to 305 K using a physical property measurement system (PPMS, Quantum Design) equipped with a ^{3}He option refrigerator. The sample was reliably secured in the measuring cell with Apiezon grease. The accuracy of the heat capacity measurements was better than 1%. Depolarized low-frequency Raman spectra of 2-BrBP samples were measured at room temperature in a 90° scattering configuration with a double monochromator (Jobin-Yvon Ramanor U 1000 spectrometer). The stray light rejection was 10^{-14} at 20 cm^{-1} from the Rayleigh line. The spectral slit width was 2 cm^{-1}. The spectra were recorded using the 514.5-nm line of an Ar$^+$ laser and the laser beam power focused on a sample was about 150 mW.

In order to understand the procedure of extracting the relevant parameters, we give below the expressions for the heat capacity contributions due to, respectively, the tunneling splitting and soft modes,
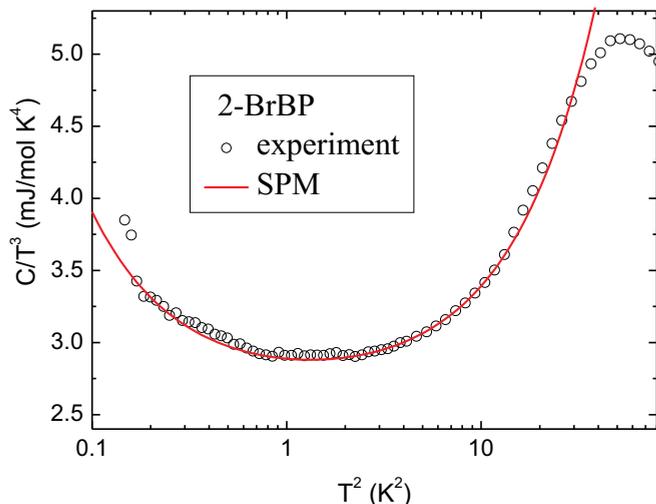
FIG. 1. The low-temperature part of the heat capacity C of crystalline ortho-bromobenzophenone in coordinates C/T^3 vs T^2. The red curves in this and subsequent figures are best fits to Eq. (3), which allowed us to estimate the three C_N parameters to be found Table I.

$$C_{\text{TLS}} = \frac{\pi^2}{6}\left(\frac{1}{9}\right)^{1/3} P_s k\left(\frac{kT}{W}\right)\ln^{1/3}\left(\frac{t_{\text{expt}}}{\tau_{\min}(T)}\right), \quad (1)$$

$$C_{\text{spm}} = \frac{2\pi^6}{21} P_s k\left(\frac{kT}{W}\right)^5. \quad (2)$$

Here, k is the Boltzmann constant; $W \simeq (1.8\text{–}2)kT$ is an important characteristic energy; P_s is the (constant) per mole density of localized low-frequency modes; t_{expt} is the characteristic experimental measurement time; $\tau_{\min}$ is the minimal relaxation time. For the sake of convenience, we represent the heat capacity $C(T)$ in the form

$$C(T) = C_1 T + C_3 T^3 + C_5 T^5, \quad (3)$$

the coefficients C_N having dimensions mJ/(mol K^{N+1}).

The plot of C/T^3 vs T^2 in Fig. 1 demonstrates that our data for T between 0.37 and 6 K fit nicely the predictions of the soft potential model (SPM) [4], which previously was applied only to solids with explicitly present disorder of any kind. Extraction of the linear contribution parameter C_1 due to two-level systems (0.12 mJ/mol K^2) is demonstrated in Fig. 2. In the C/T^3 vs T representation (Fig. 3) our data show a broad boson peak at $T_{\max} \simeq 7.2$ K. The peak energy is evaluated to be $E_{\text{BP}} \simeq 5T_{\max} = 36$ K or 26 cm^{-1}. Summing up, we show that our data include the Debye contribution, the boson peak, and the two-level signature [1,4]. Room-temperature Raman scattering data show two intensive spikes at frequencies 21.1 and 30.8 cm^{-1} (intensity ratio roughly 4). These two correspond quite reasonably to the boson peak center at 26.1 cm^{-1} (36 K).

All the above characteristics are summarized in Table I, together with the values for a few molecular crystals in which disorder was observed and identified. It should be mentioned that glycerol was in the "complete" glass state (i.e., positional disorder was also present); the other systems, pentachloronitrobenzene (PCNB) and ethanols, did not contain
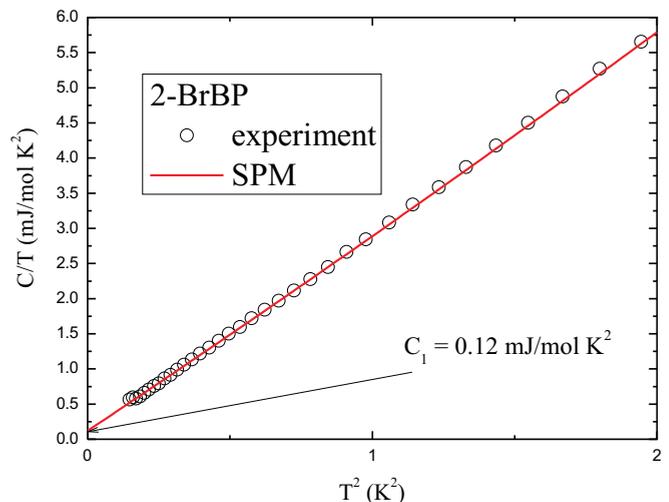

FIG. 2. Estimation of the linear contribution in the heat capacity of crystalline ortho-bromobenzophenone.

positional disorder but were only orientationally disordered. Here, we note that the heat capacity of *crystalline* glycerol (without any disorder whatsoever) fits the Debye law down to the lowest temperatures reached [11].

To understand how the energy spectrum of the 2-BrBP crystal forms, below we compare the spectra of an isolated 2-BrBP molecule with that of a pair. The vibrational spectra of the 2-BrBP monomer and dimer were computed using the Becke three-parameter Lee-Yang-Parr (B3LYP) density functional [12–14] with empirical dispersion corrections. We used the D3 version of Grimme's dispersion with Becke-Johnson damping [15,16] via the "GD3BJ" keyword. Our choice of the computational method is explained by the need to calculate the vibrational spectrum of a 2-BrBP dimer, which is formed by the stacking interactions between π-conjugated fragments of the two 2-BrBP molecules. The initial geometry of the dimer was derived from the crystal unit cell [5].
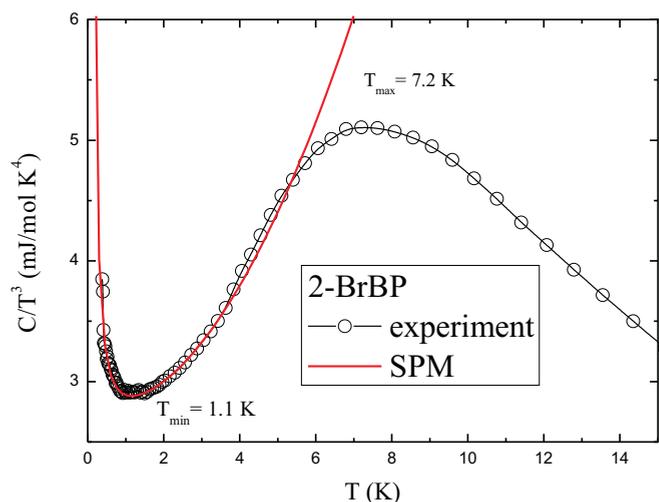

FIG. 3. Evaluation of the T^5 contribution to the heat capacity of crystalline ortho-bromobenzophenone to reveal a token of the boson peak.

TABLE I. Parameters of the low-temperature heat capacity of crystalline 2-bromobenzophenone and some disordered organic solids. Dimensions of the C_N contributions as in Eq. (3); the characteristic temperatures are in degrees Kelvin.

Material	C_1	C_3	C_5	T_{min}	T_{max}
2-BrBP	0.12	2.7	0.068	1.1	7.2
PCNB [9]	1.06	6.82	0.072	4.8	7.85
H-ethanol [10]	1.27	1.45	0.0288	6.8	2.2
D-ethanol [10]	1.13	1.72	0.0419	6.4	2.6
Glycerol [10]	0.157	0.855	0.0139	8.7	1.4

A fully optimized structure of the dimer turned out to be very close to the dimer moiety in the 2-BrBP crystal. The density functional theory (DFT) calculations were performed with the standard augmented correlation-consistent polarized valence double zeta (aug-cc-pVDZ) basis set. The inclusion of diffuse functions on this basis set is important because of the intramolecular noncovalent interactions between the phenyl moieties. The potential surface of a single molecule as a function of the torsional angle of the substituted phenyl ring is presented in Fig. 4. This surface was calculated at the second-order Møller-Plesset (MP2)/aug-cc-pVDZ level of theory which allows a more accurate account of noncovalent interactions as compared to the DFT/B3LYP method. The accuracy of our present calculations is higher compared to that published earlier by Baumer *et al.* [5], where the relevant calculations were carried out at the MP2/cc-pVDZ level, i.e., without the diffuse functions. Our present calculations show that only one minimum is present on the potential surface (Fig. 4) instead of two (one being shallow), as published by Baumer *et al.* [5]. All present computations were performed using the GAUSSIAN 09 program package [17]. The calculated energies for both a single molecule and a dimer are indicated in Fig. 5 as vertical lines.

Below, we propose a reasoning to better understand how the spectra of a single molecule and a pair are interrelated. Let N_1 be the number of atoms in a molecule (for 2-BrBP, $N_1 = 24$), then the number of intramolecular oscillatory modes is $3N_1 - 6$, where 6 is the number of degrees of freedom of
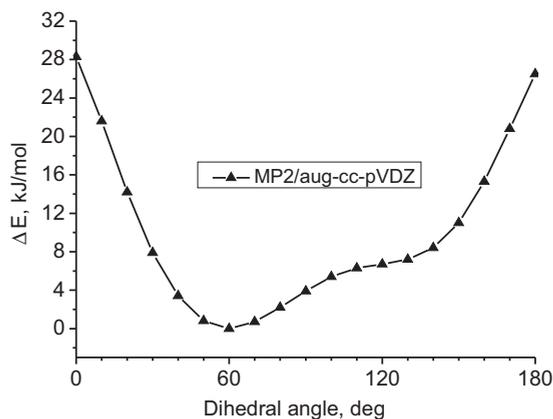

FIG. 4. Energy of the 2-bromobenzophenone molecule as a function of the torsion angle of the substituted ring.
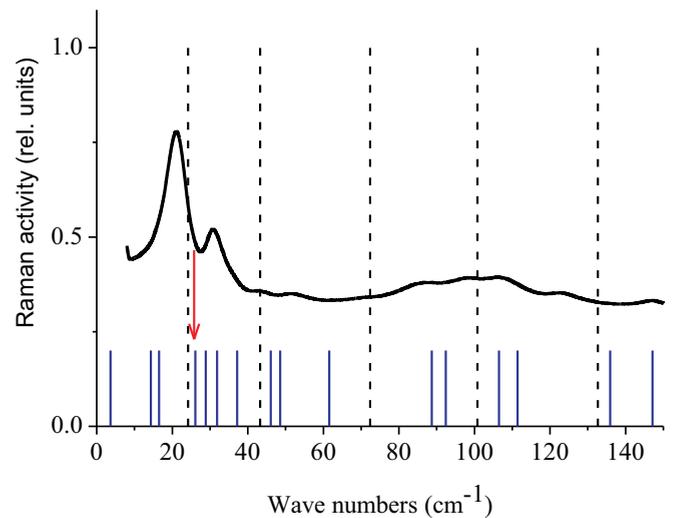

FIG. 5. Comparison of the low-frequency parts of the vibrational spectra of a single 2-BrBP molecule (long dotted lines) and a pair cluster (short blue lines), in which mutual molecular positions are close to that in the crystal. The red arrow indicates the boson peak energy. The curve is the low-energy part of our room-T Raman spectrum.

the molecule as a whole. If two molecules are not coupled, the total number of intramolecular modes is simply $2(3N_1 - 6) = 6N_1 - 12$. But if they are coupled, then the aggregate pair cluster has the total number in it, $N_2 = 2N_1$ and the number of intracluster modes will be $3N_2 - 6 = 6N_1 - 6$. Thus, a pair cluster has six extra modes, which can be treated as belonging to the cluster. In Fig. 5 we show a schematic representation of the eigenfrequencies of the pair cluster together with similar frequencies of the isolated molecule. We note here that the other parts (not shown) of the two spectra at higher frequencies are a set of frequencies for a single molecule plus a "set" of pairs of frequencies near the respective eigenfrequencies of the single molecule. This tendency of frequency "pairing" is clearly seen already in the range 100–140 cm^{-1} in Fig. 5. Thus, the spectrum of a pair includes six "extra" frequencies, part of which is below the lowest eigenfrequency of the isolated molecule. These modes will participate in the formation of phonon excitations, yet some of them will remain (quasi)local, which will inevitably result in phenomena typical of disordered systems and, as a consequence, the heat capacity will get a contribution linear in T. The curve in Fig. 5 explicitly shows that the boson peak is directly related with the two powerful Raman-sensitive modes.

Our low-temperature heat capacity data obtained on high-quality 2-bromobenzophenone single crystals show that this crystal reveals properties which are typical of irregular systems such as glasses or disordered solids. It should be remarked here that the only parameter C_1, which is related with two-level systems, in 2-BrBP is smaller (cf. Table I) than in the noncrystalline states quoted.

The respective parameters responsible for glasslike effects in 2-BrBP are substantially smaller than those typical for noncrystalline states (cf. Table I): As shown, the C_1 and C_5 parameters are smaller compared to their analogs in disordered systems.

An important factor, which is possibly important for understanding the nature of the unexpected effects, is the dependence of the inner energy of the 2-BrBP molecule on the torsion angle of the substituted phenyl ring. In other benzophenone derivatives this energy surface is shaped as two potential "wells" separated by a high (of order 3–5 cal/mol) barrier. In the 2-BrBP this dependence has the shape of a single *asymmetric* "trough" or, in other words, a typical soft potential. This means that even an ideally periodic structure of the 2-BrBP crystal features a factor that should be treated within the soft potential theory [3,4] and, hence, is expected to promote heat capacity effects which are inherent in glasslike solids, if only weaker, as shown in Table I.

What other possibilities exist to explain the heat capacity anomalies reported in our Rapid Communication? In a recent paper [18] an idea concerning the nature of boson peaks was dealt with theoretically on a model atomic solid with a special type of disorder (random network and randomly removed bonds). The basic conclusion is the statement that the most important feature, which results in a boson peak, is the (site-random) breaking of inversion symmetry or randomly removed bonds. These ideas are hardly applicable to our case for two reasons. First, the solid ortho-bromobenzophenone of our studies is a *regular* molecular single crystal with ideal inversion symmetry properties [5], and, second, as shown below, the levels of any lattice imperfections are too low to affect our results and considerations.

In another theoretical model [19] (which did not deal with the problem of Bose peaks) the $C \propto T$ dependence is explained as being due to defects. In our case of single-crystal samples the most likely defects are dislocations with typical densities $\rho \simeq 10$–100 cm^{-2}. If the sample is a cube with a rib of Na length (a being the distance between nearest molecules of a total number N), then the relative total number of molecules in the defective environment will be $\rho Na^2/N^3 = \rho a^2/N^2$. Thus,

the crossover temperature will be $T^\star = \sqrt{\rho a^2/N^2} \sim 10^{-12}$ if normalized to the Debye temperature.

In conclusion, a modern and brilliantly formulated view of the heat capacity term $\propto T$ due to two-level entities, for sure present in any irregular solids, can be found in Varma's commentaries [20].

Summing up: First, the behavior of $C(T)$ of 2-bromobenzophenone single crystals at lowest temperatures can be consistently described within the framework of the known theory [3,4] for irregular solids, the relevant characteristic parameters in 2-BrBP being roughly of the same order of magnitude as in typical glasslike molecular solids. Second, our computations for a pair of 2-BrBP molecules in an equilibrium mutual orientation (which turned out to be quite close to that in the crystal [5]) give us grounds to state that the energy spectrum of the 2-BrBP crystal includes a sufficiently large number of low-energy nonphonon modes with anomalously low frequencies. Third, quantum chemical computations of the intramolecular energy of 2-BrBP as a function of the dihedral angle (which determines the orientation of the substituted phenyl ring) show that the corresponding dependence is an intrinsic intramolecular potential capable of strongly influencing the heat capacity of crystalline 2-BrBP at low temperatures. Fourth, our Raman scattering experiments show that the boson peak in 2-BrBP embraces the energies where the intensive Raman lines have been registered. Thus, our heat capacity and Raman measurements as well as computations give us solid grounds to claim that owing to the unusual properties of the 2-BrBP molecule, the crystalline 2-bromobenzophenone at lowest temperatures reveals properties which are inherent in glasses.

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