

# Effects of site-occupation disorder on the low-temperature thermal conductivity of molecular crystals

A. I. Krivchikov, G. A. Vdovichenko, O. A. Korolyuk

*B. Verkin Institute for Low Temperature Physics and Engineering of NAS Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine*

F.J. Bermejo

*Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, CSIC, Serrano 123, 28006 Madrid, Spain*

L. C. Pardo, J. Ll. Tamarit

*Grup de Caracterització de Materials, Departament de Física i Enginyeria Nuclear, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Catalonia, Spain\**

A. Jezowski, D. Szewczyk

*Institute for Low Temperature and Structure Research, Polish Academy of Science, Poland*

The thermal conductivity of  $\text{CBr}_n\text{Cl}_{4-n}$ , ( $n=0,1,2$ ) and 2-adamantanone ( $\text{C}_{10}\text{H}_{14}\text{O}$ ) crystals which exhibit substitutional disorder has been measured for temperatures between 2 K and 150 K. Such temperatures comprise signatures of dynamical processes involving the site occupancy of the chlorine and bromine atoms for  $\text{CBr}_n\text{Cl}_{4-n}$ , ( $n=0,1,2$ ) and the oxygen atom for ( $\text{C}_{10}\text{H}_{14}\text{O}$ ), as it has been revealed by both, calorimetry and spectroscopic techniques. The data analysis is carried out in terms of several phonon scattering channels contributing to a resistive relaxation rate which can be represented by two contributions due to propagating phonons whose mean-free path exceeds half the phonon wavelength as well as a term attributed to localized short wavelength modes. The implications of the present findings for studies pertaining glassy dynamics are briefly discussed.

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## I. INTRODUCTION

Our current understanding of glassy behavior portrays it as that exhibited by dynamical processes taking place in whatever physical systems which are non-stationary on the time scales amenable to direct observation. Such processes are often encountered in systems which may explore a large number of metastable configurations [1]. Up to now, the behavior in question has been observed in very different systems, including granular materials or even non-physical systems such as traffic flow and models of biological evolution [2]. In addition, glassy systems seem to involve some sort of competing interactions which hinder the attainment of a stationary ground state. As a direct consequence, the system becomes trapped into long lived metastable states.

While the very concept of glassiness as well as the glass-transition have developed from studies on the canonical liquid  $\rightarrow$  glass transition, some of its characteristic features have also been found in other condensed matter systems. In fact, detailed theoretical consideration of molecular liquids [3] and some classes of molecular crystals [4] have enabled the establishment of some connections with theoretical results derived from several statistical mechanics approaches where glassiness appears in the dynamics of simple, idealized objects [2]. Such model

systems show trivial, non-interacting, equilibrium behaviors but nonetheless, interesting slow dynamics features appear due to restrictions on the allowed transitions between configurations.

In the quest for simple systems exhibiting dynamical behaviors which may at least partially be understood by recourse to results obtained from idealized models, some disordered molecular crystals known as *rotator-phase* or *plastic-crystals*, exhibit fully developed glassy behavior. Moreover, thermodynamic signatures akin to those common to vitrifying liquids are shown at transitions between disordered crystal states where basically free-rotations are executed by molecules executing reorientations at the nodes of a crystal lattice and a frozen orientationally disordered crystal attained by cooling such rotator-phase crystal into a orientationally disordered (OD) state [5]. Furthermore, in some favorable cases [6], a direct comparison between a theoretical prediction derived from a simple kinetic model for particle reorientations and experimental results for the onset of reorientational motions above  $T_g$  have been achieved. Such studies lend further support to the view which sees the physical origin of glassy behavior as not necessarily linked to mass-transport properties but rather to the arrest below some  $T_g$  of any dynamical degree of freedom.

On the other hand, experiments on simpler crystalline solids such as the substitutional defective alkali halide-alkali-cyanide crystals such as  $(\text{KBr})_{1-x}(\text{KCN})_x$  or  $(\text{KCl})_{1-x}(\text{KCN})_x$  have been shown to exhibit most of the universal low-temperature properties of glasses such as a bump in the specific heat if plotted as  $C/T^3$  or the

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\*Electronic address: josep.lluis.tamarit@upc.edu

appearance of a characteristic plateau in the thermal conductivity [7]. The interest in these systems stems from their role as models to study glassy phenomena which arises from the action of rotational degrees of freedom. These concern the effects of the barrier potential which arises from the interactions of the  $\text{CN}^-$  molecular impurity with the surrounding alkali lattice. At temperatures above those corresponding to the barrier potential height, the  $\text{CN}^-$  ions execute basically free rotations, whereas at lower temperatures the reorientational motion is hindered leading to the emergence of angular oscillations or librations. In turn, the librational ground state splits into tunneling levels due to the crystal potential enabling transitions between tunneling states which may scatter lattice phonons [8] as revealed by a double dip structure in the temperature dependence of the thermal conductivity [9]. Their origin is now understood on quantitative grounds by recourse to some models such as that developed in Ref.[10] which portrays the interactions of the  $\text{CN}^-$  ions in terms of randomly placed elastic dipoles which strongly interact with the neighboring K atoms and leads to the appearance of harmonic excitations with terahertz frequencies which resonantly scatter heat-carrying phonons to produce the plateau in the thermal conductivity. Such excitations are in fact librations of the  $\text{CN}^-$  moiety which show a well defined density of librational states [10].

Motivated by the promising results found in studies on rotator-phase crystals as well as on the substituted alkali halides just mentioned above, we have previously carried out studies on the structure and dynamics of materials composed by tetrahedral molecules of general formula  $\text{CBr}_n\text{Cl}_{4-n}$ ,  $n=0, 1, 2$ , as well as on a material composed by a rigid molecule, 2-adamantanone ( $\text{C}_{10}\text{H}_{14}\text{O}$ ). These compounds exhibit a series of solid-solid phase transitions with increasing temperature before melting which arise from rotational degrees of freedom which remain thermally activated within the crystalline state. In turn, cooling the room temperature liquids at moderate rates leads to rotationally disordered crystalline phases which show translational face-centered cubic or rhombohedral lattices with the center of mass of molecules sitting at the lattice nodes [11]. As far as the  $\text{CBr}_n\text{Cl}_{4-n}$  materials are concerned, further cooling leads to a transformation into complex monoclinic,  $C2/c$  structures with  $Z = 32$  molecules per unit cell and an asymmetric unit with  $Z' = 4$  [12]. The transition temperatures for materials here considered are 226 K, 238 K, and 259 K for  $\text{CCl}_4$ ,  $\text{CCl}_3\text{Br}$ , and  $\text{CCl}_2\text{Br}_2$ , respectively. Molecular motions within such monoclinic crystals persist down to  $\approx 90$  K where a calorimetric transition [13] much alike that exhibited by the canonical glass-transition signals the transition into a orientationally disordered state where molecular reorientations cannot be detected with the available experimental means. The dynamics of such materials within these phases has been studied by means of dielectric spectroscopy and nuclear quadrupole resonance (NQR)[14, 15] spectroscopy. The former technique allows

the measurement of the dynamic response within a broad time scale but it is insensitive to fine details of molecular motions, whereas the latter has a restricted time window but monitors the movement of individual chlorine atoms. Results derived from the concurrent use of NQR and molecular simulations show that large-angle rotations of tetrahedra about their higher symmetry axes ( $\text{CCl}_3\text{Br}$ , and  $\text{CCl}_2\text{Br}_2$  with  $C_{3v}$  and  $C_{2v}$  point-group symmetries, respectively) lead to a statistical occupancy of 75% for Cl and 25% for Br atoms in the case of  $\text{CCl}_3\text{Br}$ , and 50% for Cl and 50% for Br atoms for  $\text{CCl}_2\text{Br}_2$ . In addition, broadband spectroscopy carried out by means of dielectric relaxation [15] shows a main peak or  $\alpha$ -relaxation, together with a shoulder in its high-frequency edge or ( $\beta$ -relaxation). The analysis of such data in conjunction with NQR results has shown that both relaxations correspond to the dynamics of three ( $\alpha$ -relaxation) and one ( $\beta$ -relaxation) molecules within the asymmetric unit cell, which due to the nonequivalent molecular environments are forced to execute reorientational jumps on rather different time scales. In addition, the high temperature phase I of 2-adamantanone ( $\text{C}_{10}\text{H}_{14}\text{O}$ ) is known to consist of molecules within a fcc lattice exhibiting reorientational motions of the dipolar axis ( $C_3$ ) along the six fourfold (001) directions, while about the  $\text{C}=\text{O}$  axis the molecules can take two positions related by a  $\pi/2$ -rotation [16]. On cooling from phase I, an orientationally ordered phase II, monoclinic  $P2_1/c$  with one molecule per asymmetric unit appears [17]. The most striking characteristic of this phase is the existence of statistical disorder concerning the occupancy of the oxygen atom along 3 different sites (occupancies are 50%, 25% and 25%). Such a disorder has been highlighted by means of dielectric spectroscopy revealing glass-like behavior with appearance of  $\alpha$ - and  $\beta$ -relaxation processes identified with the strongly hindered reorientational motions within the long-range ordered crystalline lattice whereas the second one displays all the properties of an original Johari-Goldstein  $\beta$ -relaxation.

Previous experimental results indicate that the dynamics of these translationally-ordered phases which still show rotational or substitutional disorder, exhibit several features in common with glassy systems. Thus the question we want to address here is whether the low-temperature thermal properties of these disordered crystal systems have some common features with those found for frozen OD systems [18], that is, whether the temperature dependence of the thermal conductivity shows any of the signatures attributed to glassy dynamics. In other words, the rationale behind this is to test whether the presence of intrinsic disorder with respect to site-occupancy well within the deeply frozen state may give rise to phenomenology akin to that known to be the most characteristic feature of amorphous systems.

## II. EXPERIMENTAL

Samples of  $\text{CCl}_4$  and  $\text{CCl}_3\text{Br}$  were obtained from Across with purity better than 99% and used as such.  $\text{CCl}_2\text{Br}_2$  was purchased from Aldrich with a stated purity of 98% and fractionally distilled. The sample of 2-adamantanone was purchased from Aldrich Chem. Co., Inc., with purity of 99% and used as received. The samples were prepared as polycrystals and as such have been characterized by diffraction [12], dynamic measurements [14] and thermodynamic [13] means.

For the halogen compounds the explored temperature range was 2 K -150 K. Measurements were performed under equilibrium vapor pressure using the steady-state method and the experimental setup described in Ref. [19]. The sample container was filled with liquid samples under  $^4\text{He}$  gas flow. The thermal history followed in the present measurements started from the OD phase attaining crystallization into the low-temperature phase by cooling at  $\approx 1 \text{ K min}^{-1}$ . The thermal conductivity was then measured at gradually decreasing temperature from *ca.* 200 K down to 2 K. A heating cycle followed, increasing then the temperature up to 150 K for halogen compounds and up to 200 K for 2-adamantanone. The statistical error in the thermal conductivity coefficient was below 3% for the whole temperature range. A sample of 2-adamantanone cylindrical in shape was prepared in order to enable measurements using standard cryostat set-up for axial stationary heat flux method. The sample was obtained by mechanical pressing of powders with applied force of 2000 kg. Thermal conductivity measurements were carried out within the temperature range 4 K - 200 K. The experiment was performed under high vacuum conditions. The sample underwent cooling from room temperature to 5 K at the rate of  $\approx 3 \text{ K min}^{-1}$ . The measurement of the thermal conductivity coefficient was performed every 5 K from 200 K to 5 K after conditions were stabilized. Particular care was taken to avoid heat transfer between the sample and the environment. The total measurement error  $\approx 10\%$ , mainly arises from systematic errors incurred in the measurement of geometrical parameters (e.g. the inner container cross section and spacing between thermometers).

## III. DATA ANALYSIS AND RESULTS

The results from measurements of the thermal conductivity are displayed on Fig.1 in a double logarithmic scale. A glance to the figure shows that  $\kappa(T)$  for  $\text{CCl}_4$  exhibits a temperature dependence characteristic of ordered molecular crystals, although  $\kappa(T)$  within the low-temperature range does not follow the behavior expected for ordered crystals, that is  $\kappa(T) \propto T^3$ . In fact, our data for the four samples is best described by  $\kappa(T) \propto T^m$  with an exponent  $m < 2$ . Data for  $\text{CCl}_4$  shows a maximum at 5.6 K with a value of  $\kappa(T)_{max}$  of  $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ . Similar behavior is observed for  $\text{CCl}_3\text{Br}$  and  $\text{CCl}_2\text{Br}_2$ , with max-

TABLE I: Best fit parameters describing data below the conductivity maximum as  $\kappa(T) = DT^m$

Material	Temp-Range (K)	D ( $\text{W m}^{-1} \text{ K}^{1-m}$ )	m
$\text{C}_{10}\text{H}_{14}\text{O}$	6 - 9	$0.032 \pm 0.02$	$1.25 \pm 0.05$
$\text{CCl}_4$	2.1 - 3.8	$0.29 \pm 0.02$	$1.40 \pm 0.05$
$\text{CCl}_3\text{Br}$	2.5 - 4.2	$0.16 \pm 0.02$	$1.25 \pm 0.05$
$\text{CCl}_2\text{Br}_2$	2.4 - 3.6	$0.073 \pm 0.02$	$1.25 \pm 0.05$

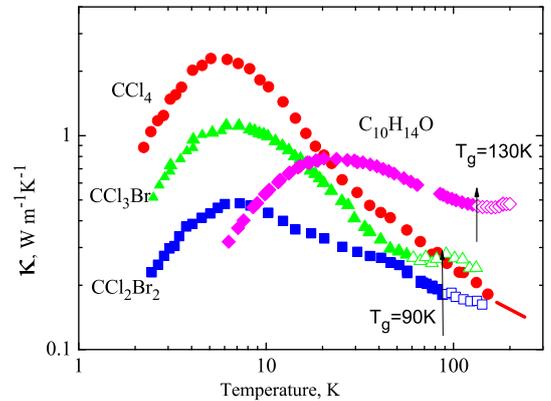


FIG. 1: (Color online) The temperature dependence of the thermal conductivity of  $\text{CCl}_4$  (red circles),  $\text{CCl}_3\text{Br}$  (green triangles),  $\text{CCl}_2\text{Br}_2$  (blue squares) and  $\text{C}_{10}\text{H}_{14}\text{O}$  (pink diamonds). Literature data for  $\text{CCl}_4$  [20] (red line at about 200 K). Arrows indicate the temperature at which the dynamics of the statistical occupational disorder freezes as monitored by calorimetric measurements.

ima at  $\approx 6.6 \text{ K}$  with  $\kappa(T)_{max}$  of  $1.1$  and  $0.48 \text{ W m}^{-1} \text{ K}^{-1}$ , respectively. In turn, for  $\text{C}_{10}\text{H}_{14}\text{O}$ , the maximum appears at *ca.* 20 K, with a value of  $0.78 \text{ W m}^{-1} \text{ K}^{-1}$ . For polycrystal samples as ours, the appearance of such a maxima in  $\kappa(T)$  is known to arise from an increase in density of thermally activated phonons which by means of the Umklapp-processes strongly limit the conductivity.

The best fit parameters describing the behavior of the conductivity below the maximum are shown in table I.

The most striking result from data listed in the table concerns the remarkably low value of the power which compares with findings in amorphous systems.

As mentioned above, most pure (i.e. free from imperfections) crystals show  $\kappa(T)$  increasing as  $T^3$ , reaching a maximum value. The conductivity is there limited by boundary scattering effects, that is, it becomes limited by the crystal size only, whereas other sources of phonon scattering are far smaller compared to that, especially at low temperatures. In contrast, point defects and/or dislocations as well as phonon collisions where the sum of the phonon wavevectors is changed by a reciprocal lattice vector (i.e. Umklapp-processes) provide frequency dependent phonon scattering channels which become more important as the temperature increases and gives rise to a

decrease of the exponent in the T-dependence of  $\kappa(T)$  for temperatures below the maximum and cause a shift of the maximum value of the conductivity towards higher temperatures. In fact, order of magnitude estimates [21] for the conductivity of crystals show that the contributions arising from phonon-defect scattering is inversely proportional to the temperature, whereas the contribution from Umklapp-processes should follow  $\kappa(T) \propto \exp(\Theta_D)/T$  where  $\Theta_D$  stands for the Debye temperature. In consequence, the experimental quantities may show a complicated behavior resulting from the combined effects of several scattering mechanisms which cannot be easily predicted from the outset. On the other hand, a low temperature behavior following  $\kappa(T) \propto T^m$  with the power somewhat smaller than two is known to be a characteristic exhibited by most amorphous dielectric solids [22].

From data shown in Fig.1 it can also be seen that the increase in the number of Br atoms leads to a decrease of the maximal values for the conductivity as compared to  $\text{CCl}_4$ . Substitution of Cl by Br atoms leads to an increase in molecular mass and on such grounds one would expect a decrease in conductivity with increasing substitution. A rough estimate of the mass effect yields  $\kappa \propto M^{-1/2}$ . These results however contrast with previous studies on other materials which have shown that the increase in molecular mass decreases the rate of phonon scattering [23, 24]. The typical bell-like shape for  $\kappa(T)$  for ordered phases in such a log-log plot is clearly observed and thus, after the maximum,  $\kappa(T)$  decreases with temperature. As far as the 2-adamantanone compound is concerned, the conductivity shows common features with those measured for the ordered phases of cyclic molecules as cyclohexanol [25].

Apart from a purely mass-effect, increasing the number of Br atoms from the  $\text{CCl}_4$ , a molecule devoid of electric dipole moment but with a relatively large molecular quadrupole moment, to  $\text{CCl}_2\text{Br}_2$  leads to an increase in strength of electrostatic interactions due to the finite molecular dipole moments of the other the bromine substituted materials [26]. On such grounds one could expect that librating molecules of  $\text{CCl}_3\text{Br}$  and  $\text{CCl}_2\text{Br}_2$  should experience a strong hindering of molecular motions which in turn leads to an increase in the interaction between molecular librations and crystal phonons.

For temperatures beyond the conductivity maximum the  $T^{-1}$  dependence of  $\kappa(T)$  can be empirically parametrized as,

$$\kappa(T) = \frac{A}{T} + C \quad (1)$$

where, the  $A/T$  term could be assigned to phonon-phonon scattering (three-phonon Umklapp processes) and  $C$  comprises all other mechanisms leading to the expected deviation from the  $T^{-1}$  beyond the phonon maximum. The Fig.2 plots the experimental data for the three halogen materials and Fig.3 for the  $\text{C}_{10}\text{H}_{14}\text{O}$  compound in the form of  $\kappa(T) \cdot T$  as a function of T.

From Fig.2 and Fig.3 two different temperature re-

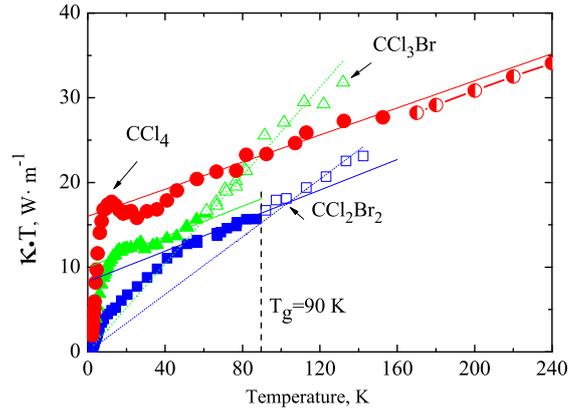


FIG. 2: (Color online) Temperature dependence of the thermal conductivity of  $\text{CCl}_4$ ,  $\text{CCl}_3\text{Br}$ ,  $\text{CCl}_2\text{Br}_2$  times the temperature (Symbols as in Fig.1). The half-filled circles show smoothed data taken from the literature for  $\text{CCl}_4$  [20]. The solid and dotted lines are fits according to Eq. [1] which yield the parameter values given in Table II.

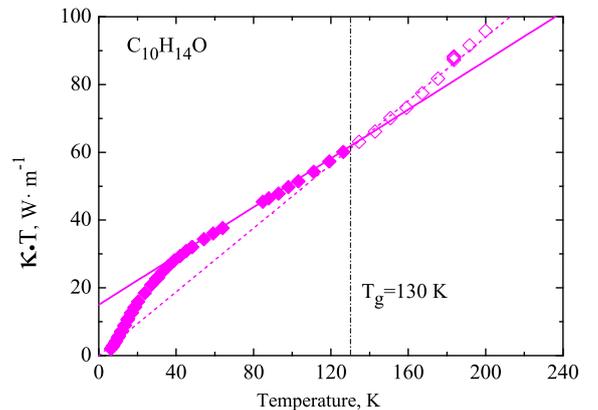


FIG. 3: (Color online) Temperature dependence of the thermal conductivity of  $\text{C}_{10}\text{H}_{14}\text{O}$  times the temperature. The solid and dotted lines are fits according to Eq. [1] which yield the parameter values given in Table II.

gions can be gauged for the Br-substituted samples and 2-adamantanone which manifest themselves as different slopes in the  $\kappa(T) \cdot T$  vs.  $T$  plots. In contrast, data for  $\text{CCl}_4$  beyond the conductivity maximum roughly follows a linear trend. The temperatures dividing such two regions roughly correspond to those at which the statistical occupational disorder freezes in. In other words, the conductivity above some 90 K where molecular motions become thermally activated shows a somewhat different temperature dependence than that measured for lower temperatures. The values for parameters entering Eq.1 as well as the temperature ranges just referred to are given in Table II. The values listed in such table show that

TABLE II: Parameter values corresponding to Eq. [1] for the different temperature range.

Material	Temp-Range (K)	A ( $\frac{W}{m}$ )	C ( $\frac{W}{mK}$ )
C <sub>10</sub> H <sub>14</sub> O	45 - 130	15±0.5	0.36±0.02
CCl <sub>4</sub>	50 - 150	16±0.5	0.08±0.02
CCl <sub>3</sub> Br	30 - 65	10±0.5	0.09±0.02
CCl <sub>2</sub> Br <sub>2</sub>	50 - 90	8.3±0.5	0.09±0.02
C <sub>10</sub> H <sub>14</sub> O	130-200	0	0.47±0.02
CCl <sub>3</sub> Br	60 - 130	0	0.26±0.02
CCl <sub>2</sub> Br <sub>2</sub>	90 - 140	0	0.17±0.02

the  $A$  value decreases with the increasing number of Br atoms, thus suggesting a significant enhancement of the rate of phonon scattering arising from an increase in site disorder. In fact, it is evidenced that the largest value for parameter  $A$ , which reflects the strength of the phonon-phonon scattering processes, corresponds to the well-ordered CCl<sub>4</sub> compound. The high-temperature data for CCl<sub>3</sub>Br, CCl<sub>2</sub>Br<sub>2</sub> and C<sub>10</sub>H<sub>14</sub>O is thus accounted for in terms of Eq.[1] by means of straight lines with zero  $A$  values, which means that phonon-phonon scattering at that temperatures vanishes and additional scattering mechanisms dominate. In other words,  $\kappa(T)$  remains almost constant as it happens for orientationally disordered phases.

It is worth pointing out here the significant difference found between these materials and those plastic phases and alkali halides where rotational disorder involves the overall tumbling motion of the whole molecule. Here the site occupancies, that is the fractional occupancies for the low-temperature phases of CCl<sub>3</sub>Br, CCl<sub>2</sub>Br<sub>2</sub> and C<sub>10</sub>H<sub>14</sub>O are well defined quantities and thus motions within the higher temperature phase will take place between discrete molecular orientations.

The appearance of a well defined maximum in the conductivity calls for an analysis of its temperature dependence to be carried out following established routes for ordered molecular crystals. As it is well known, the conductivity of complex crystals [27] while following the same trend than that observed for simple solids, shows a temperature dependence above the maximum much weaker than  $T^{-1}$  which in some cases becomes temperature independent, thus sharing some similitude with the high temperature conductivity of amorphous materials. This results from the fact that at high temperatures the phonon mean free path  $l$  decreases down to a scale comparable to the unit cell dimensions so that heat is transported by activation or hopping of localized modes. To account for such effects we proceed on phenomenological grounds assuming that the measured quantity can be decomposed into a sum,

$$\kappa(T) = \kappa(T)_{ph} + \kappa_{min}(T) \quad (2)$$

where the first term stands for propagating acoustic phonons having long relaxation times  $\tau_R(\omega, T)$  charac-

teristic of resistive phonon scattering, whereas the second component,  $\kappa_{min}(T)$ , comprises all short wavelength phonons having relaxation times above a minimum value of the phonon relaxation time  $\tau_{min} = \pi/\omega$  as specified by the Cahill-Pohl model of minimal conductivity [28], the validity of which has been recently scrutinized by experimental means [29].

The contribution  $\kappa_{ph}(T)$  can in turn be modeled using the standard Debye-Peierls relaxation time model, that yields,

$$\kappa_{ph}(T) = \frac{k_B^4 T^3}{2\pi^2 \hbar^3 c_s} \int_0^{\Theta_D/T} \tau_R(x) \frac{x^4 e^x}{(1 - e^x)^2} dx \quad (3)$$

where  $x = \hbar\omega/k_B T$ ,  $\Theta_D$  is the Debye temperature,  $c_s$  is a sound velocity averaged over longitudinal and transverse polarizations and  $\tau_R(x)$  is an effective relaxation time for phonon scattering which comprises the different scattering phenomena participating and limiting the heat transfer. On the other hand, the minimal conductivity component  $\kappa_{min}(T)$  can be evaluated from the Cahill-Pohl model developed for the interpretation of the thermal conductivity of amorphous solids at high temperatures, and yields,

$$\kappa_{min}(T) = \frac{k_B^3 T^2}{2\pi^2 \hbar^3 c_s} \int_0^{\Theta_D/T} \frac{x^3 e^x}{(1 - e^x)^2} dx. \quad (4)$$

The above prediction tells that at high temperatures  $\kappa_{min}(T)$  should become temperature independent. To evaluate such a component we have made use of the pertinent values for the sound velocity and Debye temperatures which are compiled in Table III. The estimation of such a component shows that it is very small for temperatures below 10 K and it dominates the conductivity within the higher temperature range detailed in Table II. In fact, its value becomes comparable to the total conductivity once the limiting temperatures  $T_g$  are crossed from below. Put into real numbers, at high temperatures  $\kappa_{min}(T)$  amounts an average value of the order of 0.2 W K<sup>-1</sup>m<sup>-1</sup> for the halogen compounds and about 0.5 W K<sup>-1</sup>m<sup>-1</sup> for adamantanone. On the other hand, and from rather simple considerations it may be seen that this component approaches the value of parameter  $C$  given by Eq. 1 at high temperature, where phonon-phonon scattering is the dominant mechanism.

The relative strength of the component  $\kappa_{ph}(T)$  accounting for the propagating acoustic phonons with longer relaxation times was estimated from the difference between the experimentally measured values of the total conductivity and the minimal conductivity component  $\kappa_{min}(T)$  and the results are plotted in Fig.4.

The analysis of  $\kappa_{ph}(T)$  once isolated from the total conductivity has been carried out within the frame of the Debye-Peierls model given by Eq.3 as usually done for ordered crystals, assuming that the resistive relaxation time  $\tau_R(\omega, T)$  is the result of three main mechanisms. For relatively simple crystals such mechanisms

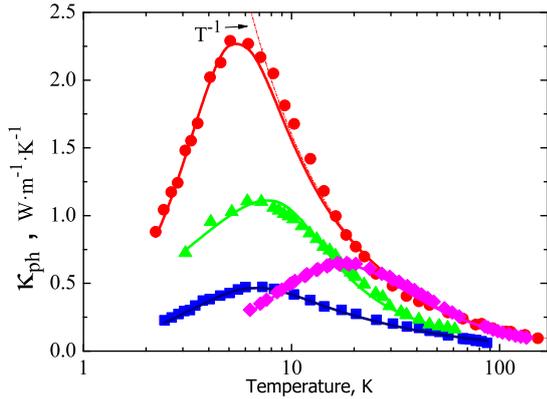


FIG. 4: (Color online) The temperature dependence of the phonon part  $\kappa_{ph}(T)$  of the thermal conductivity of  $\text{CCl}_4$ ,  $\text{CCl}_3\text{Br}$ ,  $\text{CCl}_2\text{Br}_2$  and  $\text{C}_{10}\text{H}_{14}\text{O}$  (symbols as in Fig.1). Solid lines are fitted curves calculated with the Debye-Peierls model (see text)

would comprise anharmonic Umklapp processes, with relaxation time  $\tau_U^{-1}$ , a second term accounts for phonon scattering from crystal dislocations,  $\tau_{dis}^{-1}$ , and a third mechanism from Rayleigh scattering from point lattice defects or mass-differences  $\tau_{imp}^{-1}$ . All the three combine according to the Matthiessen rule, to yield the relaxation time as,

$$\tau_R(\omega, T)^{-1} = \tau_U^{-1} + \tau_{dis}^{-1} + \tau_{imp}^{-1} \quad (5)$$

where the individual terms are given by,

$$\tau_U^{-1} = B\omega^2 T \exp\left(\frac{-E_U}{T}\right) \quad (6)$$

corresponding to Umklapp processes,

$$\tau_d^{-1} = D_d \omega \quad (7)$$

for dislocations and

$$\tau_{imp}^{-1} = C_{imp} \omega^4 \quad (8)$$

for impurity scattering.

In the above equations  $B$  stands for a frequency factor,  $E_U$  for the activation energy of the Umklapp processes,  $D_d$  is the scattering strength for the dislocations, and  $C_{imp}$  is the parameter accounting for the strength of Rayleigh scattering of phonons by imperfections or by mass-difference scattering. Additional terms concerning strings from impurities having a frequency dependence  $\tau^{-1} \propto \omega^3$  have appeared in the literature [30]. We have however restricted the analysis to terms having the frequency and temperature dependences given by Eq.5 in

TABLE III: Parameters entering Eqs.5 to 8 obtained from the fits of thermal conductivity as derived from fits to  $\kappa_{ph}(T)$  data with errors lower than  $\approx 10\%$ . Superscripts: *a* Ref.[33], *b* Ref.[31], *c* Ref.[13], *d* Ref.[12], *e* Ref.[32].

Material	V ( $\frac{\text{cm}^3}{\text{mol}}$ )	$c_s$ ( $\frac{\text{m}}{\text{s}}$ )	$\Theta_D$ (K)	$D_d \cdot 10^4$	$C_{imp} \cdot 10^{40}$ ( $\text{s}^3$ )	$B \times 10^{16}$ ( $\frac{\text{s}}{\text{K}}$ )	$E_U$ K
$\text{C}_{10}\text{H}_{14}\text{O}$	121.6 <sup>a</sup>	2200 <sup>b</sup>	112 <sup>b</sup>	46	0.2	3.8	30
$\text{CCl}_4$	82.4 <sup>d</sup>	1850	106.7 100.3 <sup>e</sup>	1.9	5.1	4.3	20
$\text{CCl}_3\text{Br}$	78.8 <sup>d</sup>	1240	73.0 63.8 <sup>c</sup>	3.7	31	4.3	20
$\text{CCl}_2\text{Br}_2$	82.0 <sup>d</sup>	1112	64.4 58.4 <sup>c</sup>	11	65	6.8	20

order to keep the number of adjustable parameters within reasonable limits.

For complex, defective crystals a clear cut separation between sound scattering phenomena leading to relaxation rates with different frequency dependences, seems to be beyond reach. In consequence the numerical values for the parameters entering Eqs.6 to 8 will most probably lump together several effects having similar frequency dependences. Further discussion on this is deferred to the discussion section.

The Table III compiles the results obtained from fits to experimental data carried out under the assumption of the combined model given by Eq.3 and Eqs. 5 to 8. The values of  $c_s$  and  $\theta_D$  were obtained from the published specific-heat measurements [32] whereas molar volumes were obtained from references [11, 12] for  $\text{CCl}_4$ ,  $\text{CCl}_3\text{Br}$  and  $\text{CCl}_2\text{Br}_2$  and from ref. [31] for  $\text{C}_{10}\text{H}_{14}\text{O}$ . The solid lines drawn in Fig.4 display the ability of the Debye-Peierls model to account for the phonon conductivity  $\kappa_{ph}(T)$  of the low temperature monoclinic phases of  $\text{CCl}_{4-n}\text{Br}_n$ ,  $n = 0,1,2$  and  $\text{C}_{10}\text{H}_{14}\text{O}_n$  compounds. The figure also highlights the agreement at high-temperature in which the  $T^{-1}$  law works.

The Table III lists the values for parameters entering the relaxation time  $\tau_R(\omega, T)^{-1}$  as well as the other quantities such as molar volume, sound velocity and Debye temperatures to enable the calculation of the phonon thermal conductivity. The most striking result concerns the strong increase of the  $C_{imp}$  parameter for the  $\text{CCl}_{4-n}\text{Br}_n$ ,  $n = 0,1,2$  series which shows roughly a ten-fold increase with increased substitution of Br atoms. Finally, as far as the parameters characterizing the anharmonic Umklapp process are concerned, both the pre-exponential coefficient and the activation energies show closer values, account made of the statistical error involved.

## IV. DISCUSSION

### A. Some remarks on the analysis of the conductivity data

The data analysis procedure sketched above relies upon a separation of the measured conductivity  $\kappa(T)$  given by Eq. 2 into a component pertaining heat transport processes mediated by phonons having a mean-free-path larger than the lattice parameter  $\kappa_{ph}$  and a contribution  $\kappa_{min}$  comprising processes mediated by random walks of thermal energy transported between molecules vibrating with random phases, which dominates heat transport at temperatures well above the conductivity maximum. Most crystals composed by molecules interacting via van der Waals interactions show that at melting the ratio  $\kappa_{ph}/\kappa_{min} \simeq 1.2 - 2$  [34] a fact also witnessed by the current measurements.

In what follows we briefly discuss the physical relevance of parameters listed in III. In doing so we shall bear in mind that while the thermal conductivity tensor for a crystalline dielectric can be explicitly calculated from solution of the transport equation, this has only been achieved for substances much simpler than those here considered. The case of molecular crystals represents an additional complication since in addition to the lattice modes one has to deal with the molecular modes. For molecules composed by relatively light atoms which interact by mostly by means of van der Waals forces one may try a separation between molecular rigid-body and lattice motions. This will surely not be the case of the halomethane compounds which because of their heavier atom masses one needs to consider the full 15 modes. In addition, the large 32-molecule unit cells makes a full microscopic treatment beyond reach. Under such circumstances the best we can attempt is to follow the procedures customarily employed for simpler materials and discuss the physical meaning of the fitted parameters on semi-quantitative grounds at best.

The term which is characteristic of dislocations  $D_d$  exhibits a large coefficient for 2-adamantanone which correlates well with structural crystallographic and microscopy findings [33], as well as with our own experience in preparing such sample. In fact, since dislocations are non-equilibrium defects they would leave the crystal if conditions for it to relax are supplied (i.e. annealing or thermal cycling), which in fact happens with this particular sample.

The coefficient  $D_d \propto N_d$ , should be directly proportional to the number of dislocations per unit area, a figure that is available for adamantane that yields some  $10^7 - 10^{10}$  dislocations per cubic centimeter [35] which means that a fairly substantial portion of the molecules composing the crystal are somewhat distorted from its equilibrium position.

The fitted value for  $D_d$  found for  $\text{CCl}_2\text{Br}_2$  comes close to one order of magnitude larger than that for  $\text{CCl}_4$  suggesting the presence within the crystal of a large amount

of dislocations. Although specific structural data pertaining this kind of crystal imperfections for the former material does not seem to be available, literature data reported for the latter compound shows that a fairly large number of vacancies ( $\approx 2\%$  [36]) is present at the triple point, a feature common to other organic plastic crystals, which will lead to dislocations, some of which may well survive after the phase transformation into the monoclinic crystal. As regards the other two halomethanes, up to the authors knowledge the dearth of pertinent data makes it difficult to rationalize our findings in terms of far larger density of dislocations for such compounds.

Lets now deal with findings pertaining impurity scattering. Such effects account for both differences in atomic masses between the atoms composing the molecules as well as the isotopic abundances. In general terms,  $C_{imp}$  is given by [37],

$$C_{imp} = \frac{\Gamma_{md}\Omega}{4\pi\bar{c}^3} \quad (9)$$

where  $\Omega$  stands for the unit cell volume and  $\bar{c}^3$  is defined by  $3/\bar{c}^3 = \sum_s c_s^{-3}$ . The coefficient  $\Gamma_{md}$  will in general comprise some statistic concerning the mass deviation of the impurity from that of the average atom, the sound velocity as well as combination of elastic constants in a way dependent upon the crystal symmetry. In short,

$$\Gamma_{md} = \sum_i f_i \left( \frac{\Delta M_i}{\bar{M}} \right)^2 \quad (10)$$

where it has been assumed that the dominant factor for the cases under consideration involves mass differences only since a term on  $6\gamma\Delta d/\bar{d}$  involving the Grüneisen parameter and the fractional change of the average distance  $\Delta d/\bar{d}$  upon introduction of the impurity could be safely disregarded.  $\bar{M}$  is the average mass,  $f_i$  the fraction of atoms having mass  $M_i$  and  $\Delta M_i$  the mass difference of the individual atoms in the crystal with respect to the average mass. Data listed in III for the three halomethanes yield relative values of roughly 1: 6 :12 with increasing Br content and a rather small value of 0.2 for 2-adamantanone, that is roughly 0.04 times the coefficient for  $\text{CCl}_4$ . In turn, the calculated values for  $\Gamma_{md}$  for the three haloethanes yield, 0.62, 2.60 and 2.51 respectively and 8.2 for 2-adamantanone. Account made of the volume and sound velocity factors yields a proportions close to 1:13:19 for the halomethanes, and 12 for 2-adamantanone.

The results here discussed thus suggest that the analysis procedure grasps some relevant details of heat transport in these materials at some semi-quantitative level. In particular,

- The dominant phonon scattering channel in the halomethanes concerns Rayleigh proceses due to the differences in atomic masses. This is rationalized account made of preliminary lattice dynamics

results for  $\text{CCl}_4$  [38] which show that the acoustic branches are confined to frequencies below  $15 \text{ cm}^{-1}$  with two dense meshes of optical branches extending from  $15 \text{ cm}^{-1}$  -  $70 \text{ cm}^{-1}$  and  $700 \text{ cm}^{-1}$  -  $750 \text{ cm}^{-1}$  as well as three sharp molecular internal vibration peaks at about  $200 \text{ cm}^{-1}$ ,  $320 \text{ cm}^{-1}$  and  $440 \text{ cm}^{-1}$  together with less intense features. The calculation which compares favorably with preliminary experiments carried out using the MARI spectrometer at ISIS [39] tells that the lowest-lying molecular modes are strongly hybridized with those pertaining to lattice modes. Under such conditions atomic vibrations cannot be separated into those of intra- and intermolecular nature. Phonon scattering is thus sensitive to *mass-differences between atoms composing a given molecule*. The available recipes to calculate the strength of this scattering contribution reproduce the trend of values for  $C_{imp}$  in a semi-quantitative way.

- The result for  $C_{imp}$  for 2-adamantanone tells that there is a scant need for a term having a  $\omega^4$  dependence in Eq.8 to explain the conductivity of this material. Put into different words, the result tells that molecular motions within this sample can be considered as of rigid body kind, account made of the light atoms involved. In consequence, any relevant mass difference will have to regard the molecular mass instead of that of individual atoms.
- Scattering from lattice imperfections becomes dominant for 2-adamantanone, a fact that agrees with preliminary conductivity experiments that have shown that the material once frozen from the liquid contains a large number of defects which make the conductivity to attain significantly lower values than those here reported on as well as does not show the presence of a peak at 25 K. The results showing the crystal-like peak require the sample to undergo a specific thermal treatment to release some of those defects. As regards data pertaining  $D_d$  for the three halomethane compounds we defer any further discussion until crystallography or microscopic data is available to judge whether or not such a different density of defects as predicted from analysis of the conductivity is borne out by direct measurement.

As a final remark, data concerning the anharmonic, Umklapp term does not allow to make any definite statement. A rough, order of magnitude estimate of the anharmonic terms, in particular of the third order anharmonic coefficients  $b_{i,j,k}$  which govern the strength of such interactions can be provided in terms of average quantities such as the atomic mass  $\bar{M}$ , sound velocity  $\bar{v}$  and intermolecular distance  $\bar{d}$  [40] as,

$$b_{i,j,k} \simeq \frac{\bar{v}^2}{\bar{d}^3}. \quad (11)$$

An estimate was made using for the purpose the velocity of sound values listed in III, and setting  $\bar{d}$  to the average distances between molecular centers-of-mass derived from diffraction data. The results given in terms of proportions with respect to  $\text{CCl}_4$  yield 1: 0.64: 0.36 for the halomethanes and 1.65 for 2-adamantanone, to be compared with the ratios 1: 1: 1.58 and 0.88 respectively calculated from the  $B$  pre-exponential factor listed in table III. Such a comparison again tells that the values for the fitted coefficients should be taken as order-of-magnitude estimates. Finally, the fitted values for the activation energies and the pre-exponential term are comparable to those measured for other systems [25, 41].

## B. Absence of characteristic glassy features

The results here reported on may, at a first glance, be at variance with the scenario postulated in the opening paragraphs. There, molecular rotational motions or rotational librations are assigned as the prime quantities to account for strong phonon scattering processes leading to a distinctive plateau in the thermal conductivity at intermediate temperatures.

Our motivation to carry out the measurements here reported on did stem from the dynamics and calorimetric results which evidenced behaviors similar to others exhibited by rotator-phase/orientationally disordered crystals, including those regarding the well studied case of substituted alkali halides. As a matter of fact, the higher temperature phases of all the materials under scrutiny exhibit rotator phases which have been extensively investigated in the past by optical spectroscopic means [42]. Curiously enough, the Raman spectra of tetrahalides  $\text{CX}_4$ ,  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$  within their rotator phases show small differences with respect to those measured for the liquids [43] and in fact, the orientational correlation times if plotted versus reciprocal temperature shows no discontinuity at the liquid-plastic crystal phase transition which was understood as a result of similar short-range order existing in both phases. Molecular reorientations within the rotator-phase crystal thus seem to be pretty free and only limited by potential barriers arising from angle-dependent forces within the lattice. As referred to above, molecular motions still persist within the monoclinic phases down to a temperature signalled by a calorimetric anomaly. Since most data refer to the  $\text{CBr}_n\text{Cl}_{4-n}$  derivatives we focus the discussion onto such samples. Combination of dielectric and NQR data show that above some 95 K, that is some 5 K above the calorimetric transition, the reorientational correlation times attain values within the range 0.01 s - 10 s, and even at a given temperature, different sets of correlation times are found due to the presence of several dynamically inequivalent molecules within the unit cell. Such experimentally determined correlation times behave with temperature following an Arrhenius law and reach some  $10^{-9}$  s at the highest explored temperatures within

the same crystal phase. Moreover, the dynamics data derived from the NQR measurements referred to above [14], while identifying torsional librations as the motions responsible for spin-lattice relaxation, show very large activation energies ( $2382.4 \text{ cm}^{-1}$ ) and also extremely large pre-exponential factors within the  $10^{-15}$  -  $10^{-17}$  s range.

The emergence of a plateau in the conductivity is, on the other hand understood, at least for the well studied case of  $(\text{KBr})_{1-x}(\text{KCN})_x$  [10], as a consequence of strong scattering of heat carrying phonons with frequency  $\omega$  by librations on  $\text{CN}^-$  ions so that  $\omega\tau \simeq 1$ . Such librations show a peaked density of states and display well defined features in the infrared spectrum [44] consistent with rotational transitions with frequencies given up to first order by,

$$F_\omega = B_r J(J+1) - D_c J^2 (J+1)^2, J = 0, 1, 2 \quad (12)$$

where the first term stands for the rotational constant of the ion  $B_r = h/8\pi^2 cI$  and,  $I$  for its moment of inertia within the vibrational ground state and  $D_c$  is a lowest-order correction to account for the coupling to vibrations. The parameter values for this free-rotor model constants yield values for the rotational constants of  $B_r \approx 60 \text{ GHz}$ , depending upon the chosen isotopes for C and N, while  $D_c$  comes to be six orders of magnitude smaller. A dressed-rotor model which accounts for the elastic interactions with the rotating cyanide ion yields values significantly smaller for  $B_r$  (within the range  $14 \text{ GHz} - 25.5 \text{ GHz}$ ), depending upon the temperature, which anyhow will give transition frequencies well within the GHz range.

Lets consider the simplest case such is  $\text{CCl}_4$ . Calculation of the rotational constant in the gaseous state comes close to the experimental value of  $B_r \approx 1.7 \text{ GHz}$ . However, molecular interactions within the crystal are expected to largely decrease its value well below GHz values and in fact, dynamics data show that only at high temperatures, the characteristic reorientational times become comparable to those corresponding to lowest free rotor frequency  $F_\omega = 3.4 \text{ GHz}$ . As the temperature decreases, motions become strongly hindered making rotational jumps far too infrequent to be effective as a strong phonon scattering mechanism. To see this, lets compare the experimentally determined frequencies (reciprocal of reorientational times) with the characteristic phonon frequency which could be roughly estimated by recourse to the dominant-phonon approximation that gives for the phonon wavelength[22],

$$\lambda_{dom} = 0.235 \frac{hc_s}{k_B T} \quad (13)$$

and yields a frequency at temperatures about the maximum of  $\kappa(T)$  of  $540 \text{ GHz}$ . Such value is thus orders of magnitude larger than those explored by spectroscopic means at temperatures within the measured range. In consequence, such figures thus rule out resonant scattering processes of GHz phonons by librational motions similar to those operative for the alkali halides. The same

considerations apply for the Br-substituted compounds with heavier molecular masses and stronger intermolecular interactions.

Put into different words, the change in the observed rotational excitations from whole molecule motions within the liquid and plastic phases to those within the monoclinic phases which are assigned as low-angle librations [45] can be related to changes of the effective potential experienced by a single molecule within the lattice. Within the plastic crystal the total potential can be regarded as soft if compared to the rotational constant of the molecule and consequently rotations are limited mostly due to the fluctuating part of the intermolecular potential. In contrast, the situation witnessed within the monoclinic phases tells that interactions mostly arise from strong, static forces having a strength far larger than  $B_r$ . Account made of this, we consider motions for the  $\text{CBr}_n\text{Cl}_{4-n}$  derivatives as strongly hindered by intermolecular interactions within the lattice thus being ineffective as a resonant scattering source for phonons. In absence of such strong scattering mechanism, one does not expect a plateau to develop as a result of the rest of phonon scattering processes, although the Rayleigh scattering term with its strong frequency dependence, could yield a plateau if its strength  $C_{imp}$  were set some three orders of magnitude above the fitted value.

To end this section, it is worth recalling that a plateau in the thermal conductivity of crystalline materials containing impurities or isotopic mixtures has already been reported in the available literature. In fact, samples of *para*- $\text{H}_2$  containing minute amounts of a Ne impurity [46], exhibit a noticeable plateau between 2 K and 5 K as also does a  $\text{CH}_4 - \text{CD}_4$  solid solution. The appearance of such a *glassy feature* is there explained as arising from the enhancement of the interaction of rotations with crystal phonons since the rotational constant  $B_r$  for  $\text{CD}_4$  comes to be one half of that of  $\text{CH}_4$  which amounts to  $158 \text{ GHz}$ . The authors of Ref. [47] attribute the appearance of the plateau to the disturbance of the molecular field due to the presence of  $\text{CD}_4$  molecules which lead to an increase in strength of the phonon-libration coupling, thus lowering the thermal conductivity relative to pure crystals. In fact, the authors follow the same line of reasoning sketched in the introduction section where ground spin-rotational states of almost freely rotating molecules of  $\text{CH}_4$ , which strongly interact with the acoustic field take there the role played by librations of cyanide ions in mixed alkali halides.

## V. CONCLUSIONS

The results herein described show that the thermal conductivity of molecular crystals with substitutional disorder due to the different but well-defined probabilities of site occupancies, displays two distinct temperature regions the boundary of which roughly coincides with temperatures where dynamic and calorimetric sig-

natures indicative of freezing or orientational jumps are located.

The analysis in detail of the experimental conductivity data is carried out at a phenomenological level, subtracting first an estimate due to a minimal conductivity, which becomes significant at high temperatures, particularly in case of 2-adamantanone.

The relative weights of terms employed to fit the phonon part of the conductivity can be rationalized on semiquantitative grounds and yield a significantly different scenario concerning heat transport in halomethanes and 2-adamantanone.

The absence of a distinctive plateau at intermediate temperature is understood as a consequence of a large mismatch between frequencies characteristic of heat-carrying phonons and those of possible reorientational

or librational events.

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- [1] G. Radons, W. Just and P. Haussler (Eds.) *Collective Dynamics of Nonlinear and Disordered Systems*, Springer, 2005; D. Popovic in *Conductor-Insulator Phase Transitions*, V. Dobrosavijevic *et al.* Eds., Oxford Univ. Press, 2012, chapt. 8, p. 256; P. E. Anderson, H. J. Jensen, L. P. Oliveira and P. Sibani, *Complexity* **10**, 49 (2004); C. Josserand, A.V. Tkachenko, D.M. Mueth and H.M. Jaeger, *Phys. Rev. Lett.* **85**, 3632, (2000); J. Sun, D.J. Earl and M.W. Deem, *Phys. Rev. Lett.* **95**, 148104 (2005).
- [2] F. Ritort and P. Sollich, *Adv. Phys.* **52**, 219 (2003).
- [3] R. Schilling, *J. Phys.: Condens. Matter* **12**, 6311 (2000).
- [4] M. Ricker and R. Schilling, *Phys. Rev. E* **72**, 011508 (2005).
- [5] M. Jimenez-Ruiz, *et al.*, *Phys. Rev. B* **59**, 9155 (1999); A. Criado, *et al.*, *Phys. Rev. B* **61**, 12082 (2000); C. Cabrillo *et al.*, *Phys. Rev. B* **69**, 134202 (2004); F. Affouard, *J. Chem. Phys.* **123**, 084501 (2005); A. Drozd-Rzoska, S. J. Rzoska, S. Pawlus, and J. Ll. Tamarit, *Phys. Rev. B* **74**, 064201 (2006); A. Drozd-Rzoska, S. J. Rzoska, S. Pawlus, J. C. Martinez-Garcia, and J. Ll. Tamarit, *Phys. Rev. E* **82**, 031501 (2010); L. C. Pardo, P. Lunkenheimer, and A. Loidl, *Phys. Rev. E* **76**, 030502(R) (2007); K. L. Ngai and M. Paluch, *J. Chem. Phys.* **120**, 857(2004); A. Drozd-Rzoska *et al.*, *Phys. Rev. B* **73**, 224205 (2006); J. C. Martinez-Garcia, J. Ll. Tamarit and S. J. Rzoska, *J. Chem. Phys.* **134**, 24512 (2011); J. C. Martinez-Garcia, J. Ll. Tamarit and S. J. Rzoska, *J. Chem. Phys.* **134**, 144505 (2011); K. L. Ngai, *et al.*, *J. Phys. Chem. B* **109**, 17356 (2005); S. Capaccioli and K. L. Ngai, *J. Chem. Phys. B* **109**, 9727 (2005); K. L. Ngai, S. Capaccioli and N. Shinyashiki, *J. Chem. Phys. B* **112**, 3826 (2008).
- [6] M. Jimenez-Ruiz, A. Criado, F. J. Bermejo, G. J. Cuello, F. R. Trouw, R. Fernandez-Perea, H. Löwen, C. Cabrillo, and H. E. Fischer, *Phys. Rev. Lett.* **83**, 2757 (1999).
- [7] J. J. De Yoreo, W. Knaak, M. Meissner and R. O. Pohl, *Phys. Rev. B* **34**, 8828 (1986).
- [8] V. Narayanamurti and R.O. Pohl, *Rev. Mod. Phys.* **42**, 201 (1970).
- [9] D.P. Singh and G.S. Verma, *Phys. Rev.* **4**, 4647 (1971).
- [10] E.R. Grannan, M. Randeria and J.P. Sethna, *Phys. Rev. B* **41**, 7799 (1990).
- [11] L. C. Pardo, *et al.*, *Chem. Phys. Lett.* **308**, 204 (1999); *ibid* *Phys. Chem. Chem. Phys.* **3**, 2644 (2001); L. C. Pardo *et al.*, *J. Phys. Chem. B* **105**, 10326 (2001); *ibid.* *Chem. Phys. Lett.* **321**, 438 (2000); M. Barrio *et al.*, *J. Phys. Chem. B* **108**, 11089 (2004); P. Negrier *et al.*, *Chem. Phys.* **336**, 2, 150 (2007); M. Barrio, *et al.*, *J. Chem. Phys. B* **110**, 12096 (2006).
- [12] B. Parat *et al.*, *Chem. Mater.* **17**, 3359 (2005); M. Barrio, J. Ll. Tamarit, P. Negrier, L. C. Pardo, N. Veglio, and D. Mondieig, *New J. Chem.* **32**, 232 (2008); J. Ll. Tamarit, M. Barrio, L. C. Pardo, P. Negrier, and D. Mondieig, *J. Phys.: Condens. Matter* **20**, 244110 (2008).
- [13] T. Ohta, O. Yamamuro, and T. Matsuo, *J. Phys. Chem.* **99**, 2403 (1995).
- [14] M. J. Zuriaga, S. C. Perez, L. C. Pardo, and J. Ll. Tamarit, *J. Chem. Phys.* **137**, 054506 (2012); N.B. Caballero, M. Zuriaga, M. Carignano, and P. Serra, *J. Chem. Phys.* **136**, 094515 (2012).
- [15] M. Zuriaga, L. C. Pardo, P. Lunkenheimer, J. Ll. Tamarit, N. Veglio, M. Barrio, F. J. Bermejo, and A. Loidl, *Phys. Rev. Lett.* **103**, 075701 (2009).
- [16] M. Bee and J. Amoureux, *Mol. Phys.* **83**, 533 (1982).
- [17] M. Romanini, Ph. Negrier, J. Ll. Tamarit, S. Capaccioli, M. Barrio, L. C. Pardo and D. Mondieig, *Phys. Rev. B* **85**, 134201 (2012).
- [18] R.C. Zeller and R.O. Pohl *Phys. Rev.* **B 4**, 2029 (1979).
- [19] A. I. Krivchikov, B. Ya. Gorodilov and O. A. Korolyuk, *Instruments and Experimental Techniques*, **48**, 417 (2005).
- [20] R.G. Ross, P. Andersson and G. Backstromm, *Mol. Phys.* **38**, 527 (1979); R.G. Ross and P. Andersson, *Mol. Phys.* **36**, 39 (1978).
- [21] V.L. Gurevich, *Transport in Phonon Systems*, in *Modern Problems in Condensed Matter Sciences*, V.R. Agranovich and A.A. Maradudin (Eds.), North-Holland, chapt. 2, p. 110, Amsterdam 1986.
- [22] R.O. Pohl, X. Liu and E. Thompson, *Rev. Mod. Phys.* **74**, 991 (2002).
- [23] A. I. Krivchikov, F. J. Bermejo, I. V. Sharapova, O. A. Korolyuk, and O.O. Romantsova, *Fiz. Nizk. Temp.* **35**, 1143 (2009), [*Low Temp. Phys.* **35**, 891 (2009)].
- [24] A. I. Krivchikov *et al.*, *Low Temp. Phys.* **37**, 517 (2011).
- [25] A. I. Krivchikov *et al.*, *Phys. Rev. B* **85**, 014206 (2012).

- [26] Sz. Pothoczki, A. Ottochian, M. Rovira-Esteva, L. C. Pardo, J. Ll. Tamarit, and G. J. Cuello, *Phys. Rev. B* **85**, 014202 (2012).
- [27] G.P. Srivastava, *The Physics of Phonons*, sect. 7.4, p. 245, Adam Hilger, Bristol, U.K. 1990.
- [28] D.G Cahill and R.O. Pohl, *Ann. Rev. Phys. Chem.*, **39**, 93 (1988); D.G Cahill and R.O. Pohl, *Phys. Rev. B* **35**, 4067 (1987); D.G Cahill, S.K. Watson and R.O. Pohl, *Phys. Rev. B* **46**, 6131 (1992).
- [29] W-P. Hsieh, M. D. Losego, P.V. Braun, S. Shenogin, P. Keblinski, and D. G. Cahill, *Phys. Rev. B* **83**, 174205 (2011).
- [30] R. Berman, *Thermal Conductivity of Solids*, Clarendon Press, Oxford, 1976.
- [31] A.B. Bazyleva, A. V. Blokhin, G. J. Kabo, A. G. Kabo and V. M. Sevruck, *Thermochim. Acta* **451**, 65 (2006).
- [32] T. Atake and H. Chihaha, *J. Chem. Thermodyn.* **3**, 51 (1971), T. Ohta, O. Yamamuro and T. Matsuo, *J.Phys.Chem.* **99**, 2403 (1995).
- [33] Ph. Negrier, M. Barrio, M. Romanini, J. Ll. Tamarit, A. Krivchikov, L. Kepinski, A. Jezowski, D. Szewczyk, *Cryst. Growth & Des.*, in press (DOI: 10.1021/cg500313m) (2014).
- [34] V.A. Konstantinov, in *Heat Transfer - Theoretical Analysis, Experimental Investigations and Industrial Systems*, A. Belmiloidi (Ed.) InTech Publishing (2011). Available from <http://cdn.intechopen.com/pdfs-wm/13188.pdf>.
- [35] S.D. Lubetkin and W.J. Dunning, *J. Cryst.Growth*, **43**, 77 (1978).
- [36] P.F. Higgins, R.A.B. Ivor, L.A.K. Staveley and J.J. des C. Virden, *J.Chem.Soc.*, 5762 (1965) (DOI: 10.1039/JR9640005762).
- [37] Ref. [27], p. 181.
- [38] T. Ramirez-Cuesta, personal communication. A previous lattice dynamics calculation reported by R. Righini and M.L. Klein, *Chem.Phys.Lett.* **87**, 604 (1982) on a high-pressure monoclinic phase, also reports strong rotation-translation coupling of the lowest Raman active mode having a frequency of  $28\text{ cm}^{-1}$ .
- [39] Measurements carried out using the MARI spectrometer at the ISIS spallation neutron source made at 5 K using two incident energies. The spectrum at low energies displays a strong rotational peak centered at  $40\text{ cm}^{-1}$  and a series of narrower features starting at some  $80\text{ cm}^{-1}$ .
- [40] Taken from Ref.[21], p. 60.
- [41] A. I. Krivchikov, A. N. Yushchenko, O. A. Korolyuk, F. J. Bermejo, R. Fernandez-Perea, I. Bustinduy, and M. A. Gonzalez, *Phys. Rev. B* **77**, 024202 (2008); M. A. Ramos, C. Talon, R. J. Jimenez-Rioboo and S. Vieira, *J.Phys: Condens.Matter* **15**, S1007 (2003); A. I. Krivchikov, A. N. Yushchenko, V. G. Manzhelii, O. A. Korolyuk, F. J. Bermejo, R. Fernandez-Perea, C. Cabrillo, and M. A. Gonzalez, *Phys. Rev. B* **74**, 060201(R) (2006); V. V. Sumarokov, P. Stachowiak, J. Mucha, and A. Jezowski, *Phys. Rev. B* **74**, 224302 (2006).
- [42] R.P. Fournier, R. Savoie, F. Bessete and A. Cabana, *J.Chem.Phys.* **49**, 1159 (1968); M. Gilbert and M. Driford *J.Chem.Phys.* **66**, 3205 (1977); G.J. Davies, G.J. Evans and M. Evans, *J.Chem.Soc. Faraday II*, **72**, 2147 (1976); S. Sunder and R.E.D. McClung, *Chem.Phys.* **2**, 467 (1973); L. Temleitner and L. Pusztai, *Journal of Physics : Condensed Matter*, **25**, 454209 (2013).
- [43] J.N. Sherwood, *The Plastically Crystalline State*, chapt. 7 . p. 265, Wiley, New York, 1979.
- [44] C.E.Mungan, R.C. Spitzer, J.P. Sethna and A.J. Sievers, *Phys.Rev.B* **43**, 43 (1991).
- [45] M. Zuriaga, M. Carignano, and P. Serra, *J. Chem.Phys.* **135**, 044504 (2011).
- [46] N.N. Zholonko, *Fizika Nizkikh Temperatur (Low Temp. Phys.)* **33**, 676 (2007).
- [47] P. Stachowiak, E. Pisarska, A. Jezowski and A. I. Krivchikov, *Europhys.Lett.* **74**, 96 (2006).