

Specific-heat study of the phonon-fracton crossover in glassy ionic conductors

A. Avogadro, S. Aldrovandi, and F. Borsa

Dipartimento di Fisica "Alessandro Volta," Università degli Studi di Pavia, I-27100 Pavia, Italy

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Specific-heat measurements as a function of temperature in the range 1.2–40 K are reported for the ternary glassy ionic conductors $(\text{AgI})_x (\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3)_{1-x}$ for $x=0, 0.2, 0.5,$ and 0.65 . A pronounced maximum in C/T^3 vs T is observed in the above temperature range. This anomaly and the anomalous temperature dependence observed previously at higher temperature are interpreted in terms of an energy spectrum typical of localized modes of fractal nature, which dominate over the long-wavelength elastic modes.

I. INTRODUCTION

The study of the shape of the energy density of states and of the nature of the excitations is of paramount importance in understanding the glassy state. In glassy ionic conductors the knowledge of the energy spectrum of the excitations has important implications also regarding the dynamics of the very mobile ions responsible for the high conductivity. The ternary $\text{AgI}\text{-Ag}_2\text{O}\text{-B}_2\text{O}_3$ system offers a very good example of ionic conductors which can be prepared easily and reproducibly in the glassy state over a wide range of composition and displays a wide range of electric ionic conductivity.^{1,2} This system has already been investigated by a number of experimental techniques mostly aimed at the understanding of the mechanisms responsible for its high ionic conductivity.¹⁻⁵ From a structural point of view the vitreous matrix appears formed by a network of $\text{BO}_3\text{-BO}_4$ groups showing short-range order. This order is not substantially affected by AgI addition as also proved by Raman⁶ results and by specific heat, C , measurements reported previously from 15 K up to room temperature.³ These measurements had already indicated an anomalous temperature dependence of C such as the one normally found in polymeric material.⁷ We present, in the following, measurements of specific heat performed in four samples of $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3)_{1-x}$ with different AgI content, in the temperature range 1.2–40 K. Our aim is to investigate the nature of the excitations in the light of the models proposed for the glassy systems.⁸⁻¹⁰ The specific-heat measurements presented here show, when plotted as C/T^3 versus T a maximum around 5–8 K. This behavior is a well-known feature of most glass-type materials¹¹ and also of ferroelectric crystals and other crystals displaying soft-phonon modes.¹² The maximum observed in our samples is very pronounced, and its position and size depends on the AgI content. Below 1.5 K there is also indication of the presence of a term in the specific heat which varies linearly with temperature and which is commonly ascribed to two-level-type excitations.¹³ In this work we focus our analysis on the temperature region above 1.5 K, and we will show that the data can be interpreted in terms of a combination of an energy spectrum typical of long-wavelength elastic modes

and one typical of localized excitations in clusters of low effective or fractal dimensionality,^{14,15} whereby the second is dominant in the temperature interval investigated.

II. EXPERIMENTAL

The compounds were prepared from certified reagent-grade AgI , AgNO_3 , and B_2O_3 , as described elsewhere.^{1,2} Ingots of about 3 g were prepared in cylindrical shape and mounted directly on a sample holder between two copper plates. The measurements were performed with a standard-type heat-pulse adiabatic calorimeter with a mechanical switch.¹⁶ The temperature measurements were performed with a germanium calibrated resistance thermometer. The heat capacity of the addenda is of the order of 5–20 % of the total heat capacity depending on the temperature. The sample was first cooled by thermal contact with a liquid-helium bath (pumped on to achieve 1.2 K) and the measurements were performed on heating. The sample temperature was monitored on a chart recorder for several minutes before and after the application of heat pulse (typical duration 10–30 sec). At the end of the heat pulse an overshoot lasting 5–10 sec is observed after which the drift becomes constant. By adjusting the temperature of the radiation shield the drift can be made to be practically zero. However, we found it more convenient to perform most of the measurements by allowing for a small temperature drift (less than 0.013 K/min) and correcting the readings accordingly. The resolution of the measurements is typically of the order of 0.01 K. The performance of the calorimeter was checked against a high-purity Cu standard yielding results within $\pm 0.5\%$ of the calibration curve. The low-temperature measurements (1.5–10 K) in the sample with $x=0$ and $x=0.5$ were repeated at the Ames Laboratory by using similar adiabatic calorimeter.¹⁶ The results were found to agree with ours within 1%. (See Fig. 1.)

III. RESULTS AND DISCUSSION

The measurements of specific heat as a function of temperature are shown in Figs. 1 and 2 for samples of different content of AgI . The results in the temperature range 1–40 K are plotted in Fig. 1 as C/T^3 versus T to

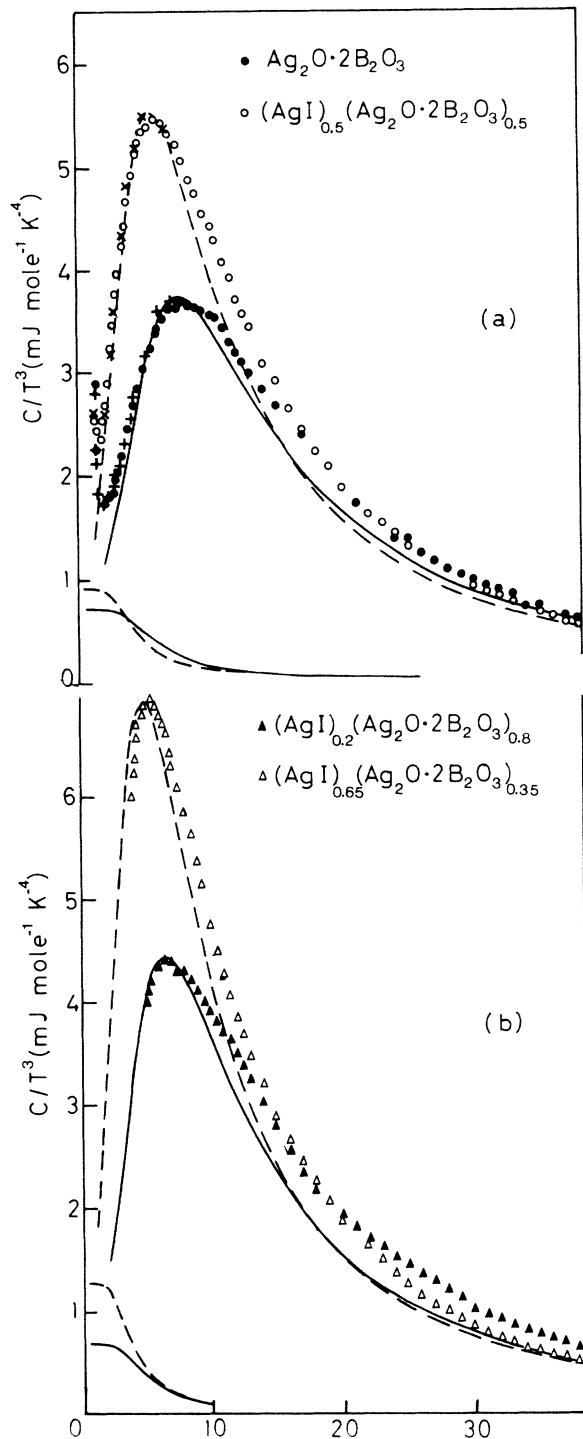


FIG. 1. Specific heat (divided by the cube of the temperature) of $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3)_{1-x}$ as a function of temperature for four samples with different AgI content. The continuous and dashed lines are theoretical curves deduced from Eq. (2) with the values for the parameters as listed in Tables I and II. In the lower part of both (a) and (b) we show the Debye elastic contribution corresponding to the first term in Eq. (2). The crosses in (a) are representative experimental points corresponding to measurements performed at the Ames Laboratory

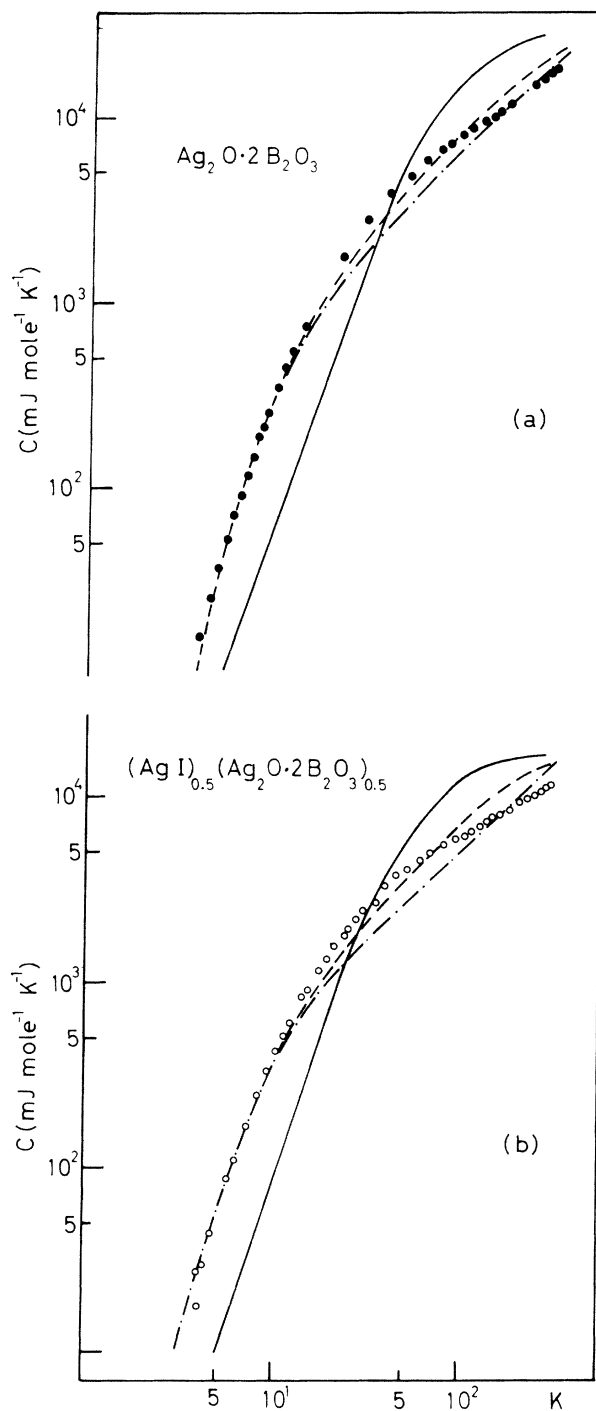


FIG. 2. Specific heat of $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot 2\text{B}_2\text{O}_3)_{1-x}$ versus T . The experimental points $T > 40$ K are from Ref. 3. (—) indicates Debye behavior. (---) indicates phonon-fracton behavior obtained from Eq. (2), the parameters in Tables I and II, and the density of states depicted in Fig. 3 by the continuous line. (-·-·-) indicates phonon-fracton behavior as above but with the modified density of states according to the dashed curve in Fig. 3.

emphasize the departure of the experimental behavior from the Debye predictions. It should be noticed that the linear term in the specific heat present in all glassy materials may be appearing below ~ 2 K. In general, a hump in C/T^3 versus T of the type observed here could be interpreted in terms of low-energy optical modes with almost no dispersion (Einstein modes), giving a contribution to be added to the usual Debye contribution, as was done successfully in a number of ferroelectric crystals displaying soft modes.¹² However, this scheme of interpretation does not appear acceptable in our case since the existence of these modes is not proved by other experimental techniques and not even supported by microscopic models. Furthermore, the presence of low-frequency optical modes does not explain the results of specific heat at higher temperature (40–300 K), which display an almost linear temperature dependence and lie well below the Debye prediction (see Fig. 2).

An alternative scheme of interpretation for the spectrum of excitations of glassy materials which is recently gaining support is the one based on the concept of fractals.¹⁷ In this approach^{10,14,15} the density of states goes as ω^2 only up to a frequency ω_{co} corresponding to a wavelength for the Debye-type elastic modes comparable to the characteristic size of structural units in the disordered systems (or regions of short-range order). For $\omega > \omega_{co}$ the density of states crosses over to a regime corresponding to modes localized on clusters of low effective dimensionality of fractal dimensionality. A first theoretical treatment assumed a crossover in the dispersion spectra of phonons and fractons leading to the prediction of a sudden drop in the density of vibrational states at the crossover frequency.¹⁰ More recent analysis¹⁸ based on the assumption of an overlap of parts of the phonon and fracton spectra predicts instead a discontinuous increase at ω_{co} . Further work based on a scaling approach seems to suggest that the ratio of the fracton to phonon density at crossover is noncritical and depends on normalization requirements.¹⁹

In keeping with the above considerations we chose to fit the data in Fig. 1 by using the density of states sketched in Fig. 3 where the cutoff of the spectrum at high frequencies, ω_M , is determined by the normalization condition

$$\int_0^{\omega_M} D(\omega) d\omega = 3N_0\nu \quad (1)$$

(ν is the number of atoms per formula unit and N_0 is Avogadro's number.)

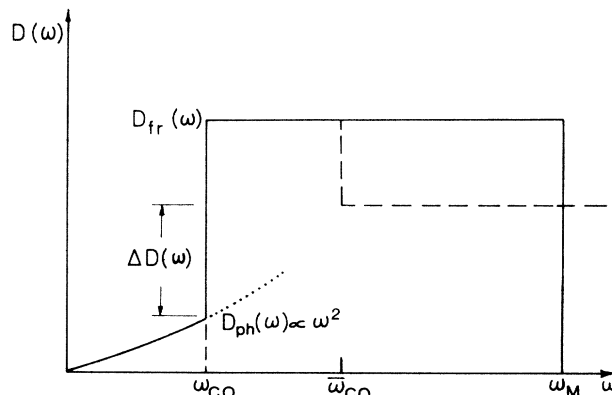


FIG. 3. Sketch of the density of states used in fitting the data in Figs. 1 and 2. The parameters referring to the continuous line are listed in Tables I and II) and were obtained by fitting the experimental data below 40 K. The dashed curve was obtained by adding the condition of fitting the experimental data at 150 K for $x=0$ and 0.5. In this case we find a reduction of the fracton density of states $D_{fr}(\omega)$ of 1.39 at $\Theta_{co}=94$ K for $x=0$ and of 1.63 at $\Theta_{co}=69.5$ K for $x=0.5$.

Therefore,

$$\frac{C}{R} = 9\nu \left[\frac{T}{\Theta_D} \right]^3 \int_0^{\Theta_{co}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + 9\nu \frac{T}{\Theta_D} Q \int_{\Theta_{co}/T}^{\Theta_M/T} \frac{x^2 e^x}{(e^x - 1)^2} dx, \quad (2)$$

where the first term is the Debye elastic contribution and

$$\Theta_D = \left[\frac{6\pi^2 N_0 d \nu}{P_M} \right]^{1/3} \frac{\hbar}{K \bar{v}} \quad (3)$$

(P_M is the molecular weight and d is the absolute density) is the Debye temperature of the long-wavelength elastic modes. The Debye temperature calculated from Eq. (3) and the measured sound velocity \bar{v} is summarized in Table I. The second term in Eq. (2) is the fracton contribution with the upper limit of integration given by the normalization condition Eq. (1) and $K\Theta_{co} = \hbar\omega_{co}$. The only parameters to be determined to fit the experimental data are Θ_{co} and the dimensionless constant Q which is related to the value of the fracton density of states $D_{fr}(\omega)$ (see Fig. 3): $Q = D_{fr}(\omega)K\Theta_D/9N_0\nu$. The values of the parameters

TABLE I. Values of physical quantities of interest in $(AgI)_x(Ag_2O \cdot 2B_2O_3)_{1-x}$. The sound velocities \bar{v} are low-temperature values. The densities are room-temperature values; the thermal expansion coefficient is negligibly small in our case.

x	ν	P_M	d (g/cm ³) ^a	\bar{v} (cm/s) ^b	Θ_D (K)
0	13	370.98	4.03	2.65×10^5	334
0.2	10.8	343.74	4.38	2.42×10^5	313
0.5	7.5	302.88	4.75	2.08×10^5	255
0.65	5.85	282.85	4.94	1.77×10^5	207

^aReference 2.

^bReference 5.

TABLE II. Summary of the parameters obtained from the experimental results as explained in the text.

x	Θ_{co} (K)	Q	L (Å)	Θ_M (K)	a (Å)
0	27.3	0.11	28	1035	2.27
0.2	23.1	0.10	31	993	2.39
0.5	20.1	0.12	31	722	2.41
0.65	17.5	0.11	30	613	2.53

obtained from fitting the position and the height of the maximum in C/T^3 versus T (Fig. 1) are summarized in Table II and the corresponding theoretical curves are shown in Fig. 1. As one can see from Fig. 1, the specific heat is dominated above about 2–3 K by the fracton contribution [second term in Eq. (2)]. The presence of the additional contribution linear in T at very low temperatures prevents one from observing the pure elastic Debye contribution [first term in Eq. (2)].

By using the same values for the parameters one obtains the correct, almost linear temperature dependence at high temperature but with a value too large by about 30% (see Fig. 2). It should be noted that the fit of the hump in C/T^3 versus T is sensitive mainly to the value of ω_{co} and to the discontinuous increase of the density of states at ω_{co} . Therefore, a better agreement with the high-temperature data can be obtained by lowering the value of the constant Q and thus of the fracton density of states for $T > \Theta_{co}$. To demonstrate this point we have also plotted in Fig. 2 the theoretical curve obtained from the density of states by the dashed curve in Fig. 3. As one can see, this modified behavior of the vibrational density of states at crossover, even though it is only a drastic schematization, agrees well with the behavior suggested in Ref. 19.

IV. CONCLUSIONS

The use of a spectrum made up of phonons at low frequency and fractons at higher frequencies promises to offer a unifying scheme of interpretation of the excitations in percolating networks and in disordered glassy materials.

One can relate the value of the frequency ω_{co} to the structural characteristic length¹⁰ L of the glass by writing $L = (\Theta_D/\Theta_{co})a$ where a is an atomic distance which sets the shortest length scale in the problem. By using for Θ_D and Θ_{co} , the data in Tables I and II, and for a , the average interatomic distance, one obtains the values of L summarized in Table II. By the order of magnitude of the data it does not appear evident that a correlation exists between the AgI content and the structural characteristic length as suggested in Ref. 5.

From the density of states in Fig. 3 (dashed line) and the values of the parameters in Table II for the samples

with $x=0$ and 0.5 one can try to verify some predictions¹⁹ about the nature of the crossover region. It should be noticed that for simplicity our results have been fitted by using a fractal coefficient $p=1$ [defined by $D_{fr}(\omega) \propto \omega^{p-1}$] which, however, does not lead to a completely satisfactory agreement with the experiments (see Fig. 2). The ratio $D_{fr}(\omega_{co})/D_{ph}(\omega_{co})$ is 11.8 and 11.7 for $x=0$ and $x=0.5$, respectively. This result is consistent, within the limits of uncertainty of the present experiment, with the predictions of the scaling approach¹⁹ of a noncritical ratio, i.e., independent of ω_{co} . The difference $D_{fr}(\omega) - D_{ph}(\omega)$ in the crossover region is also practically independent of ω_{co} again in agreement with the scaling approach which predicts the power-law relationship $\Delta D \sim \omega_{co}^{p-1}$ ($p=1$ in our case).

It should be pointed out, moreover, that microscopic approaches of different nature have reproduced curves for the density of states similar to the one schematized in Fig. 3. For example, a frequency-independent density of states at high temperature was invoked to explain the specific heat in polymeric materials.⁷ Furthermore, the idea of localized vibrations in structural units of limited coherence is contained in the cellular approach⁹ that also allows for a nonzero density of states at $\omega=0$ which offers an explanation for the linear term in temperature in the very-low-temperature specific heat, a term not included, yet explicit in the phonon-fracton approach.

We conclude that the glassy superionic conductors investigated here offer a good example of a system in which the excitation spectrum can be schematized as made up of long-wavelength (low-frequency) phonons at low temperature and of short-wavelength localized vibrations (fractons) at higher temperature.

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