

## Low-energy excitations in the mixed crystal $Ba_{1-x}La_xF_{2+x}$

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We have studied the evolution of a glasslike distribution and density of low-energy excitations in the mixed crystal  $Ba_{1-x}La_xF_{2+x}$ . Increase in the concentration  $x$  from 0 to 0.46 gradually changes the behavior of the low-temperature thermal conductivity, specific heat, and internal friction from those of a pure crystal to the characteristic properties of an amorphous solid.

A distribution of low-energy excitations governs the low-temperature properties of amorphous solids.<sup>1</sup> A phenomenological tunneling model<sup>2</sup> accurately describes the consequences of these excitations for the low-temperature thermal and elastic properties but a microscopic basis for the nearly universal density of low-energy excitations observed in all amorphous solids is still lacking. Recently, disordered crystals that have glasslike low-temperature properties<sup>3</sup> have been the focus of many studies. The study of crystals with controlled disorder should facilitate the search for a microscopic basis of the tunneling model. Here, we present a new example of such a disordered crystal.

The most thoroughly studied<sup>4</sup> of the disordered crystals that display glasslike properties is  $(KBr)_{1-x}(KCN)_x$ . Since crystals can be prepared for any value of  $x$ , experiments can be performed over a wide range of disorder. Unfortunately, the glasslike excitations in  $(KBr)_{1-x}(KCN)_x$  cannot be studied near the end points  $x=0$  or  $x=1$ , since for  $x < 0.2$  the tunneling excitations of isolated impurities obscure the beginning of glasslike properties. Furthermore, for  $x > 0.7$  the cubic structure is unstable at low temperatures and internal boundaries obscure the results of many measurements.

In this Rapid Communication we describe the evolution of glasslike properties in another mixed crystal,  $Ba_{1-x}La_xF_{2+x}$ , that can also be prepared with a wide range of disorder. We show that, unlike  $(KBr)_{1-x}(KCN)_x$ , the low-energy excitations have a distribution characteristic of amorphous solids even at low concentrations ( $x=0.045$ ). For  $x \geq 0.33$ , the density of low-energy excitations saturates at the level typical of amorphous solids.

$Ba_{1-x}La_xF_{2+x}$  is a member of a large class of mixed crystals of the form  $M_{1-x}R_xF_{2+x}$ , where  $M$  is Pb, Cd, Ca, Sr, or Ba and  $R$  is Bi, Y, La, or any rare earth that forms a  $3+$  ion.<sup>5</sup> Kazanskii<sup>6</sup> was the first to show through dielectric loss at GHz frequencies that crystals of this type have glasslike properties at low temperatures. Many of these crystals maintain the cubic fluorite structure up to large concentrations  $x$  of dopant, often approaching<sup>7</sup>  $x=0.5$ . The defect structures have been studied extensively;<sup>8</sup> the dominant defect, at least for values of  $x < 0.01$  in  $Ba_{1-x}La_xF_{2+x}$ , is an interstitial  $F^{-1}$  neighboring a  $La^{3+}$  that substitutes for a  $Ba^{2+}$  (see Fig. 1). The relaxation rate of the interstitials is consistent with thermal activation over a barrier of  $\sim 0.5$  eV.<sup>5</sup> This large

barrier is consistent with our observation (see below) that the isolated defects are immobile at low temperatures. At higher concentrations, complex defects composed of clusters of substitutional La and interstitial F have been invoked to explain the dielectric loss<sup>9</sup> and diffuse neutron scattering.<sup>10</sup>

The  $Ba_{1-x}La_xF_{2+x}$  crystals (cylinders 1 cm in diam and 5 cm long) were grown by Optovac<sup>11</sup> using the Stockbarger method in graphite crucibles and with 1%  $PbF_2$  added as a scavenger for oxygen containing impurities. The concentrations of La in the crystals were determined by x-ray fluorescence; crystals with  $x=4.5 \times 10^{-3}$ , 0.03, 0.10, 0.30, and 0.45 in the melt were found to have  $x=8 \times 10^{-3}$ , 0.045, 0.12, 0.33, and 0.46 in the crystal. The values of  $x$  we refer to in this paper are the values determined by the x-ray fluorescence. X-ray diffraction on crystals with  $x=0.33$  and  $x=0.46$  confirmed the cubic fluorite structure.

Since we use the tunneling model for comparing the distribution of low-energy excitations as seen by different experiments, we briefly review the important assumptions.<sup>2</sup> The low-energy excitations arise from the motion of an atom or group of atoms in a double-well potential. The double well is parametrized by an asymmetry  $\Delta$  and a tunneling parameter  $\lambda$  that determines the tunneling matrix

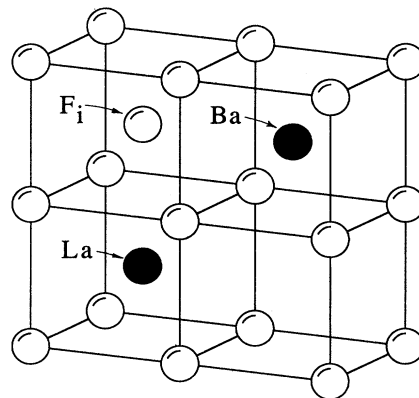


FIG. 1. Structure of an isolated defect in  $Ba_{1-x}La_xF_{2+x}$ . The  $La^{3+}$  ion substitutes on a  $Ba^{2+}$  site. The charge-balancing fluorine interstitial, marked  $F_i$  is shown in a nearest-neighbor position.

element  $\Delta_0 = \hbar \omega_0 e^{-\lambda}$ , where  $\omega_0$  is on the order of the Debye frequency. Due to disorder, a distribution of double wells is expected and the distribution is assumed to be flat  $P(\lambda, \Delta) = \bar{P} = \text{const}$ . The coupling of the tunneling state to strain is given by  $\gamma = \frac{1}{2} \partial \Delta / \partial e$ , where  $e$  is a dimensionless strain. Here, we are mostly concerned with the coupling  $\gamma_i$  to shear or transverse strains. We then have two parameters,  $\bar{P}$  and  $\gamma_i$ , to describe the data. The model has been very successful in explaining a wide range of experiments on amorphous solids and disordered crystals.<sup>2</sup>

The low-temperature specific heat at temperature  $T$  is dominated by tunneling states that have energy splittings  $E = (\Delta_0^2 + \Delta^2)^{1/2} \sim 2.4 k_B T$  and can reach thermal equilibrium within the time scale of the measurement  $t$ . In Fig. 2(a) we plot the specific heat taken by a standard heat-pulse technique<sup>12</sup> on a time scale of  $t \sim 10$  sec. Within the accuracy of our technique, the specific heat for  $x = 8 \times 10^{-3}$  is indistinguishable from the expected Debye  $T^3$  behavior of pure  $\text{BaF}_2$  based on measurements of the speed of sound. Clearly, isolated defects introduced by La doping do not result in low-energy excitations that have a

relaxation time less than 10 sec. However, as  $x$  is increased a term approximately linear in temperature becomes visible. While for  $x \leq 0.12$  the linear term does approximately scale with the concentration of F interstitials (this will be demonstrated later, in Fig. 4) the total entropy calculated from the specific heat below 1 K is at most only  $\sim 10^{-4} k_B$  per interstitial atom. At  $x \geq 0.33$  the linear term saturates at a magnitude typical of amorphous solids [Fig. 2(a)].

Within the tunneling model, the specific heat is given by<sup>2</sup>

$$C_p = \frac{1}{\rho} \frac{\pi^2 k_B^2}{12} \bar{P} T \ln \left( \frac{4t}{\tau_{\min}(T)} \right) + c_D T^3. \quad (1)$$

We have added the term  $c_D T^3$  to account for the Debye specific heat of the lattice vibrations. The minimum relaxation time  $\tau_{\min}(T)$  is that of the fastest relaxing tunneling states that can contribute to the specific heat at a temperature  $T$ . The tunneling model predicts  $\tau_{\min}(T) \sim T^{-3}$  and  $\tau_{\min}$  can be calculated if  $\gamma_i$  is known; we use  $\gamma_i = 0.33$  eV estimated from the combination of specific heat and internal friction data (see below). The calculated Debye term  $c_D$  varies little with  $x$ ; at  $x = 0.33$ , the speeds of sound are only 3% larger than the pure crystal.<sup>13</sup> We ignore changes in the measuring time  $t$  as a function of temperature since these are small compared to the strong temperature dependence of  $\tau_{\min}$ . The solid lines in Fig. 2(a) are fits using Eq. (1) to determine the one remaining parameter  $\bar{P}$ . The agreement between Eq. (1) and the data is very good; in particular, there is no evidence for a  $T^3$  term in excess of  $c_D$  that is present in many amorphous solids.<sup>12</sup>

The low-temperature thermal conductivity is sensitive to symmetric tunneling states ( $\Delta_0 > \Delta$ ) that can resonantly scatter the dominant phonons for heat transport. At a temperature  $T$ , the dominant scatterers have  $\Delta_0 \sim 4 k_B T$ . Low-energy excitations are not observed in thermal conductivity for  $x = 8 \times 10^{-3}$ ; the thermal conductivity is boundary limited and proportional to  $T^3$  [see Fig. 2(b)]. As  $x$  is increased and the specific-heat anomaly increases, the thermal conductivity decreases, becomes proportional to  $T^2$ , and at  $x = 0.33$  has a magnitude similar to amorphous solids.

To analyze the thermal conductivity data, we make the reasonable approximation that  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  is isotropic since the speeds of sound in  $\text{BaF}_2$  vary by only a few percent in different crystal directions.<sup>14</sup> We also assume that  $\gamma^2 = 2.5 \gamma_i^2$  as found for amorphous solids.<sup>15</sup> The tunneling model can then be used<sup>2</sup> to find  $\bar{P} \gamma_i^2$  from the thermal conductivity  $\Lambda$ ,

$$\Lambda = \frac{\rho k_B^3}{6\pi \hbar^2} (\bar{P} \gamma_i^2)^{-1} T^2 \left[ 2v_t + \frac{1}{2.5} v_l \right]. \quad (2)$$

Internal friction measured with mechanical oscillators provides another probe of the distribution of tunneling states<sup>16</sup> and a means of studying the relationship between the low-temperature properties and thermally activated relaxations at higher temperatures.<sup>17</sup> Internal friction at

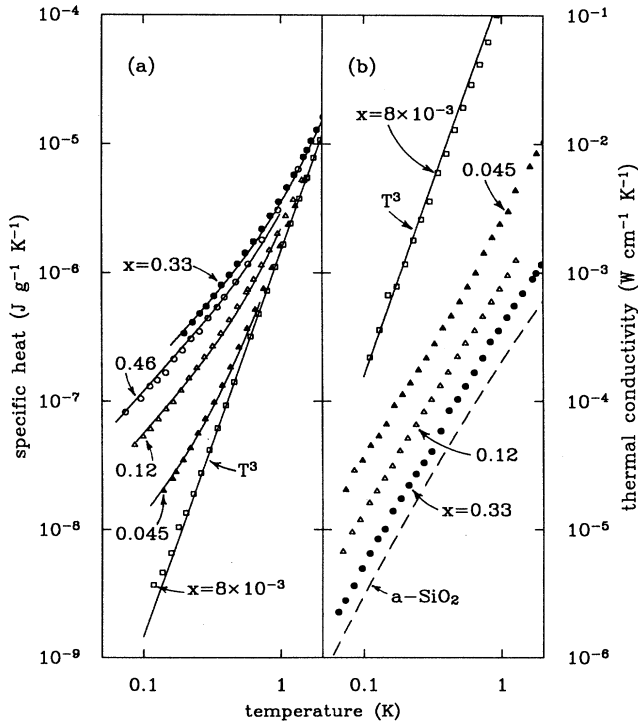


FIG. 2. (a) Specific heat of  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ . Typical sample mass was 10 g; the addenda heat capacity has been subtracted (see Ref. 12). The line marked  $T^3$  is the Debye specific heat for  $\text{BaF}_2$ . At 4 K,  $\rho = 4.94 \text{ g cm}^{-3}$ ,  $v_{l(\text{III})} = 2.30$ ,  $v_{t(\text{III})} = 4.44 \text{ km sec}^{-1}$ ,  $c_D = 14.5 \text{ erg g}^{-1} \text{ K}^{-4}$ . Solid lines are fits using Eq. (1) to determine the one free parameter  $\bar{P}$ . The linear specific heat of  $a\text{-SiO}_2$  is  $\sim 10^{-7} \text{ J g}^{-1} \text{ K}^{-1}$  at 0.1 K (see Ref. 2). (b) Thermal conductivity of  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  measured using a steady-state technique (see Ref. 12). The line marked  $T^3$  is the boundary-limited conductivity calculated for the  $x = 8 \times 10^{-3}$  sample using a mean free path equal to the sample width:  $l = 2.5 \text{ mm}$ . Dashed line is  $a\text{-SiO}_2$  data following  $T^{1.9}$  (see Ref. 2).

temperature  $T$  is sensitive to asymmetric tunneling states  $\Delta > \Delta_0$  with  $\Delta < 3k_B T$ . The internal friction peaks when the relaxation rate of the tunneling state is equal to the angular frequency of the oscillator. We measured the mechanical loss in torsion at 90 kHz using a composite oscillator technique,<sup>18,19</sup> with a bar-shaped sample,  $3 \times 3 \times 12$  mm<sup>3</sup>, epoxied (Stycast 2850 FT) to a cylindrical quartz transducer. Data for pure BaF<sub>2</sub> (solid line marked  $x=0$  in Fig. 3) should be taken as the value of the background losses from the epoxy.

At low temperature, the relaxation of tunneling states in dielectric solids is due to one-phonon processes. This is observed at  $T < 5$  K in Ba<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub>. (Above 5 K, the speed of sound decreases rapidly with increasing temperature, marking the onset of multiphonon processes.<sup>13,16</sup>) The internal friction in torsion is then<sup>16</sup>

$$Q^{-1} = \frac{\pi}{2} \frac{\bar{P}\gamma_i^2}{\rho v_i^2} \quad (3)$$

Below 5 K, the data in Fig. 3 show only small deviations from the temperature-independent internal friction predicted by the tunneling model. In this temperature range, the internal friction of most amorphous solids falls within the narrow range<sup>13</sup>  $10^{-4} < Q^{-1} < 6 \times 10^{-4}$ ; data for *a*-SiO<sub>2</sub> (dashed line in Fig. 3) are typical. For  $x \geq 0.12$  the internal friction of Ba<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub> also lies within this interval.

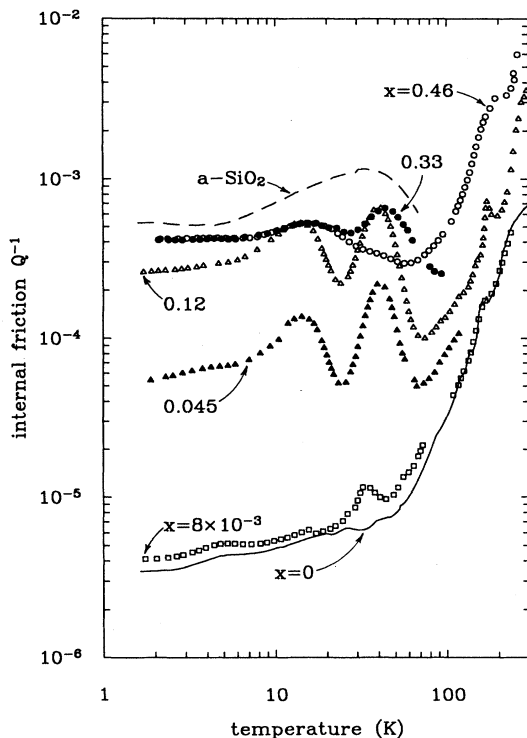


FIG. 3. Internal friction measured using a compound oscillator in torsion at 90 kHz. The strain amplitude was held constant at  $\sim 10^{-7}$ . Below 20 K, data for  $x=0.33$  and  $x=0.46$  are nearly identical. The dashed line is our *a*-SiO<sub>2</sub> data (Suprasil 2) for comparison.

Above 5 K, the data show two peaks, one at  $T \approx 14$  K and one at  $T \approx 40$  K, and a rapidly increasing loss above 150 K that is probably due to the motion of F<sup>-</sup> interstitials. The peaks become larger and broader as  $x$  increases (with the exception of the 40-K peak for  $x=0.46$  which is much smaller than at  $x=0.33$ ) but the peak temperatures do not change significantly. Both peaks are also present in dielectric loss data,<sup>20</sup> the 40-K peak is probably related to a peak at 21 K seen by thermal depolarization.<sup>21</sup> Complex defect clusters have been suggested as the origin of the dielectric losses in doped fluorite crystals<sup>9</sup> and these may be important for describing the mechanical loss in Ba<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub>. However, the glasslike density and distribution of these states at low temperatures suggests that a common explanation might exist for amorphous solids and the many disordered crystals that have glasslike properties.

Using the tunneling model with the parameters  $\bar{P}$  and  $\gamma_i$  defined above, we now compare the results of our experiments (see Fig. 4).  $\bar{P}\gamma_i^2$  determined from thermal conductivity and internal friction are in good agreement. Since each experiment probes a different part of the distribution of tunneling states, the agreement indicates that the distribution of low-energy excitations closely matches the tunneling model for  $x \geq 0.045$ .  $\bar{P}$  measured by the specific heat has the same dependence on  $x$  and gives further evidence of a glasslike distribution even at small levels of disorder.

In conclusion, we note how Ba<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub> and (KBr)<sub>1-x</sub>(KCN)<sub>x</sub> are complementary for the study of low-energy excitations in disordered solids. The glasslike properties of (KBr)<sub>1-x</sub>(KCN)<sub>x</sub> have been suggested to arise through the elastic interaction between CN mole-

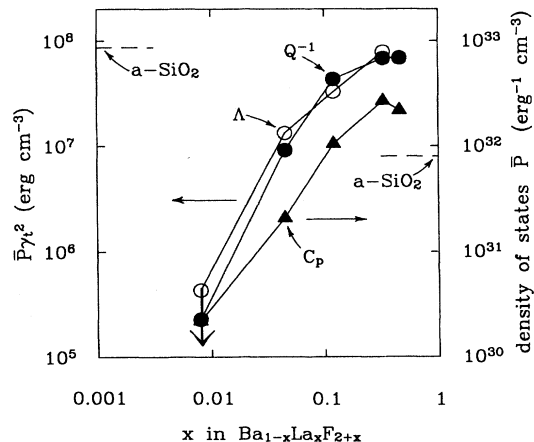


FIG. 4. Comparison of the tunneling model parameters extracted from the experiments as a function of  $x$ . The specific-heat data and Eq. (1) give the density of states  $\bar{P}$  (solid triangles) plotted using the right axis.  $\bar{P}\gamma_i^2$  from thermal conductivity at 0.2 K using Eq. (2) (open circles) and internal friction at 2 K using Eq. (3) (solid circles) are plotted using the left axis. Dashed lines are the values of  $\bar{P}$  and  $\bar{P}\gamma_i^2$  for *a*-SiO<sub>2</sub> (see Ref. 15). Points for  $x=8 \times 10^{-3}$  are only upper limits; the experiments were not sensitive enough to determine the values of the parameters at this small value of  $x$ .

cules;<sup>17</sup> as  $x$  is increased the interactions become strong enough to greatly reduce the number of CN molecules that determine the low-temperature properties. In  $Ba_{1-x}La_xF_{2+x}$ , we have shown how the excitations develop gradually as  $x$  is increased. The remarkable result is that for both systems near  $x=0.50$ , the density of low-energy excitations becomes essentially identical to what is observed in amorphous solids.

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