

## Temperature and concentration dependences of the LA[110] Brillouin shift in the structural glass $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$

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Temperature studies of the LA[110] Brillouin shift have been conducted on the mixed ferroelectric-antiferroelectric system,  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  for two ammonium concentrations ( $x=0.28$  and  $0.42$ ). The shift undergoes a softening around 100 K, followed by a hardening of the mode below 50 K. This is due to both a linear (piezoelectric) and a quadratic coupling of this acoustic mode to the polarization fluctuations. The quadratic coupling results from the large electrostriction in these materials and becomes the dominant mechanism at low temperature. This is related to the frustration of the ammonium ions below 100 K. This temperature behavior is consistent with the results previously reported by Courten *et al.* on other concentrations of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  system.

Crystals consisting of a mixture of ferroelectric  $\text{RbH}_2\text{PO}_4$  (RDP) and antiferroelectric  $\text{NH}_4\text{PO}_4$  (ADP) have recently been shown to constitute a unique series of structural glass compounds,  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  (RADP).<sup>1-3</sup> The glassy nature of these materials appears at low temperatures over a specific range of  $x$  and is believed to result from the competition between the characteristic ordering of the acid protons in the ferroelectric phase of RDP and that of the antiferroelectric phase of ADP. The well-known parent crystals RDP and ADP, the ease to grow high-quality mixed crystals over the entire range of the ammonium concentration  $x$ , the high degree of randomness of the mixtures, and the diversity of the experiments that can be performed have resulted in a considerable amount of interest in these structural glasses.

Several experiments, including birefringence,<sup>1,2</sup> x-ray<sup>4-6</sup> and dielectric<sup>1,2,7,8</sup> measurements, have been performed on these materials resulting in a temperature-concentration phase diagram.<sup>3</sup> In this diagram, the paraelectric phase exists at temperatures above 150 K for all concentrations. As the temperature is lowered, a ferroelectric phase occurs for  $x < 0.22$  while an antiferroelectric phase results for  $x > 0.75$ . In the region,  $0.22 < x < 0.75$ , there is an onset of freezing of the polarization around  $T = 100$  K. This freezing is believed to be due to the  $\text{NH}_4^+$  ions forming hydrogen bonds with nearby  $\text{PO}_4$  tetrahedra, occupying oxygen sites, preventing the ferroelectric ordering from occurring.

Recently, some extensive temperature-dependent Brillouin scattering studies<sup>9-11</sup> have been conducted for the concentrations  $x = 0.25$ ,  $0.35$ , and  $0.72$ . Using the strong electrostrictive coupling of the local polarization to the acoustic phonons, these measurements were used to confirm the existence of an Edwards-Anderson order parameter.<sup>12</sup> Such a parameter is used as an indication of a system forming slow, long-range polarization fluctuations as it progresses to a glasslike state.

In this study, Brillouin scattering measurements are re-

ported on RADP crystals at new ammonium concentrations. In particular, the temperature dependence of the LA [110] Brillouin shift for two of these concentrations ( $x = 0.28$  and  $0.42$ ) will be compared with the results of concentrations previously studied.

The Brillouin scattering experiments were conducted using a right-angle scattering configuration. A Spectra Physics argon-ion laser was used to produce a single mode output of the 514.5-nm line at a power of  $\approx 250$  mW. The incident and scattered light beams were parallel to the crystallographic  $x$  and  $y$  directions, respectively, and were horizontally polarized. This  $x(y,x)y$  scattering geometry allows the observation of the LA[110] acoustic phonon. This configuration is similar to the one commonly used in Raman scattering experiments to observe the soft optical  $B_2$  mode in KDP.<sup>13</sup>

The temperature studies were performed with the samples mounted inside a custom-made Janis "Supervari-temp" helium Dewar. A calibrated silicon diode sensor was mounted right behind the sample and was used in conjunction with a Lake Shore temperature controller. Good thermal contact with the sample was achieved through a layer of thermal compound consisting of Crycon Copper Oxide and Apiezon *N*-grease. This allowed for a temperature accuracy of better than  $\pm 0.5$  K and a control capability of  $\pm 0.1$  K.

The scattered light was frequency analyzed using a piezoelectrically scanned Burleigh Fabry-Perot interferometer operating in the triple pass mode with a free spectral range of  $1.359 \text{ cm}^{-1}$ . The output from the Fabry-Perot was filtered and focused onto a cooled ITT FW-130 photomultiplier tube (PMT). The output signal of the PMT was amplified and sent to a multichannel analyzer (MCA) for data acquisition. An IBM-XT computer was then interfaced to the MCA for data storage and analysis.

The room-temperature indices of refraction were measured at 514.5 nm using a slight variation of the minimum angle of deviation technique normally used for

a 60° angle cut sample. The advantage of this variation is that it uses a 90° edge of the sample.<sup>14</sup> The densities of the samples were determined by an Archimedean technique where spectroscopic grade cyclohexane ( $\rho=0.7726$  g/cm<sup>3</sup>) was used as the working fluid.

All samples used in these investigations were grown by slow evaporation from a saturated aqueous solution. This method is commonly used in growing water-soluble crystals.<sup>15</sup> RADP crystals were grown from a mixture of saturated solutions of pure RDP and ADP. The exact ammonium concentrations were determined according to the method which compares the density of the RADP sample with the known densities of RDP and ADP.<sup>16</sup> Samples with ammonium concentrations  $x=0.28$  and  $x=0.42$  were selected for the temperature-dependent studies since these concentrations have not been explored previously. The samples were carefully polished using different diamond paste polishing grits and lubricating fluid. These crystals were of rather good optical quality with typical sizes of  $1.5 \times 0.5 \times 0.3$  cm<sup>3</sup>.

The temperature studies were conducted from room temperature down to 5 K. A Brillouin spectrum was taken every 5° as the temperature was lowered. The data

were analyzed using a fitting program to extract the Brillouin frequency shift.<sup>17</sup> The accumulated data for the two concentrations  $x=0.28$  and  $x=0.42$  are shown in Figs. 1(a) and 1(b), respectively. The open circles represent the data taken using liquid helium and the inverted triangles represent the data taken using liquid nitrogen. It is important to note that the data obtained from the two different cryogenics match quite well at the common temperatures. The data indicate that some phonon softening occurs starting at 100 K, reaching a maximum at 50 K for both concentrations. The phonon mode then starts to harden again as the temperature is lowered below 50 K.

Actual spectra of the anti-Stokes Brillouin components are shown in Figs. 2(a) and 2(b) for  $x=0.28$  and  $x=0.42$ , respectively. The data shown here are for several temperatures between 81 and 5 K. Comparing the results for these two concentrations we notice a relatively high background for the case of  $x=0.28$ . This is due to large polarization fluctuations which can be associated with the high Rb<sup>-</sup>-ion concentration.<sup>11</sup> This background becomes negligible below 20 K indicating a possible ordering of these polarizations.

The phonon frequency in a nonpiezoelectric material is a very useful quantity and is defined as<sup>10</sup>

$$\omega_a = q\sqrt{C/\rho} . \quad (1)$$

This is called the bare or uncoupled phonon frequency. The wave vector  $q$  and the effective elastic constant  $C$  for the LA[110] acoustic mode are given as  $q=(4\pi/\lambda)n_0\sin 45^\circ$  and  $C \equiv (C_{11} + C_{12})/2 + C_{66}$  where  $\rho$  is the density and  $n_0$  is the ordinary index of refraction. The temperature dependence of this quantity can be described by a Debye anharmonic approximation as follows:

$$\omega_a(T, x) = \omega_a(0, x) [1 - A \Theta(x) F(\Theta(x)/T)] , \quad (2)$$

where  $\Theta(x)$  is the concentration dependent Debye temperature and  $F(x)$  is the Debye integral given by

$$F(x) = \frac{3}{x^4} \int_0^x \frac{u^3}{e^u - 1} du . \quad (3)$$

The measured Brillouin frequencies  $\omega_B$  can be related to the uncoupled phonon frequencies through an inverse coupling coefficient  $Q^{10}$ ;

$$\omega_B \approx \omega_a \sqrt{(Q-1)/Q} \quad (4)$$

$Q$  can be obtained from dielectric measurements. At high temperatures ( $> 200$  K) the polarization coupling is small and nearly constant. Hence,  $Q$  is relatively constant at these temperatures.

Since we are not equipped to perform the dielectric measurements, we used the results from Ref. 11 for the concentrations  $x=0.25$  and  $x=0.72$  to interpolate good estimates for the room-temperature values of  $Q$  for  $x=0.28$  and  $x=0.42$ .<sup>18</sup> The values obtained for  $Q^{-1}$  are

$$Q^{-1}(x=0.28) = 0.0057 ,$$

$$Q^{-1}(x=0.42) = 0.0108 .$$

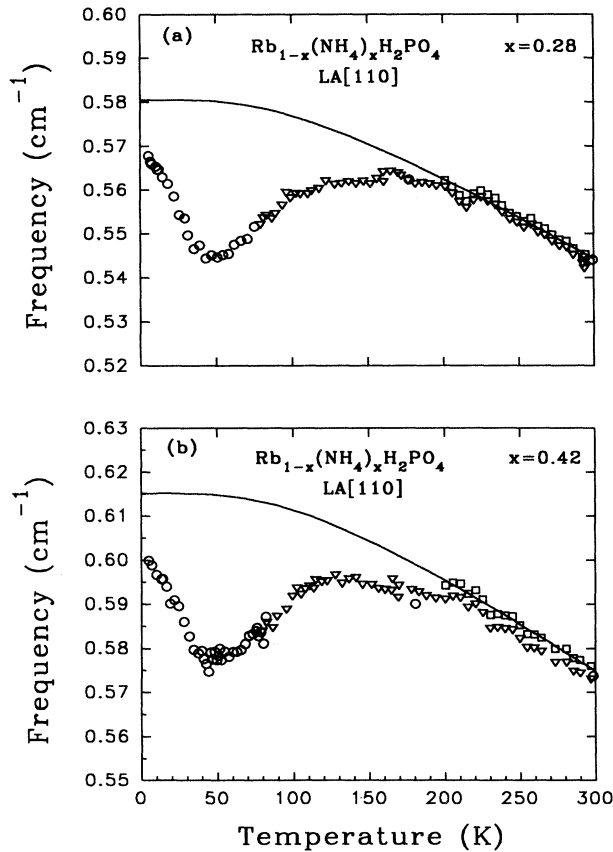


FIG. 1. Frequency shift versus temperature of the LA[110] phonon for (a)  $x=0.28$  and (b)  $x=0.42$ . The circles and triangles are the measured frequencies ( $\omega_B$ ) while the squares are the calculated bare phonon frequencies ( $\omega_a$ ). The solid line is the theoretical Debye curve explained in the text.

The corresponding values of  $Q$  were then inserted in Eq. (4) and the bare phonon frequencies  $\omega_a$  were obtained. The uncoupled phonon frequencies are denoted by the squares in Fig. 2.

We have also used Table I of Ref. 11 to interpolate the Debye temperatures for our concentrations and obtained the following:

$$\Theta(x=0.28)=409 \text{ K} ,$$

$$\Theta(x=0.42)=427 \text{ K} .$$

The calculated high temperature bare phonon frequencies were then fit to the Debye curve given by Eq. (2) using the above Debye temperatures. From the fitting we obtained an extrapolation of the bare phonon frequency at  $T=0 \text{ K}$  [ $\omega_a(0,x)$ ] and the coefficient  $A$  representing a weighting factor for the amount of anharmonicity. We obtained different values of  $A$  for the two concentrations of interest. These values are

$$A(x=0.28)=3.59 \times 10^{-4} ,$$

$$A(x=0.42)=3.86 \times 10^{-4} .$$

The above result for  $x=0.28$  is in good agreement with Ref. 11 where  $A$  was taken as a constant equal to

$3.42 \times 10^{-4}$ , independent of concentration. But the value of  $A$  given above for  $x=0.42$  is considerably larger which cannot be accounted for by experimental uncertainties alone. We believe that the amount of anharmonicity expressed through  $A$  increases with higher ammonium concentrations. However, complimentary experiments, such as dielectric and birefringence measurements, are needed to further confirm this result.

A plot of the Debye curve obtained from Eq. (2) is shown as a solid line in Figs. 1(a) and 1(b). At very low temperature,  $\omega_B$  data (open circles) tend toward  $\omega_a(0,x)$  but never reach it. This suggests that the phonon coupling to the polarization is not only a linear piezoelectric coupling due to linear polarization fluctuations which vanish at  $T=0 \text{ K}$ , but also contains a quadratic component due to electrostriction. We can then claim that at  $T=0 \text{ K}$ ,  $\Delta\omega=\omega_a-\omega_B$  is mainly due to frozen polarization fluctuations associated with the Edwards-Anderson order parameter similar to a glass. This is consistent with the previous theoretical treatment used to explain the  $x=0.35$  Brillouin data.<sup>10</sup>

Finally, by comparing Figs. 1(a) and 1(b) we can clearly see that  $\Delta\omega(T=0)$  is about 18% larger for  $x=0.42$  than for  $x=0.28$ . From this we conclude that the electrostriction coupling must increase with increasing  $\text{NH}_4$  concen-

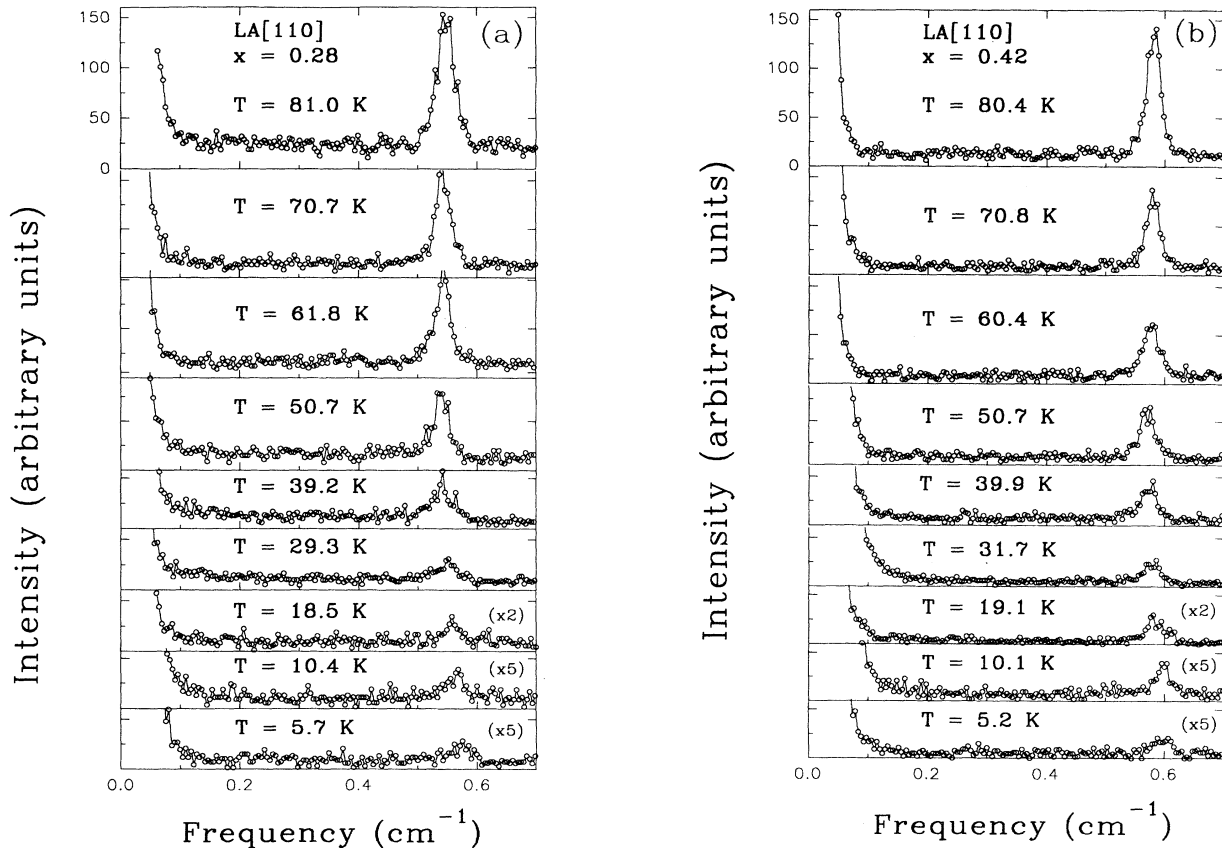


FIG. 2. Anti-Stokes components of the LA[110] Brillouin shift for temperatures between 5 and 81 K for (a)  $x=0.28$  and (b)  $x=0.42$ . The circles are the measured data while the solid line is a guide to the eye.

tration. In addition, we note that the depth of the minima around 50 K is about the same for both concentrations. This is all in good agreement with the previous study for  $x=0.25$  and  $x=0.72$ .<sup>11</sup>

In summary, we have performed a systematic study of the LA[110] phonon mode as a function of temperature from 300 to 5 K for two RADP crystals with ammonium concentrations of  $x=0.28$  and  $x=0.42$ . We observed a softening of this mode starting at  $\approx 100$  K followed by a hardening below 50 K. Using an analysis similar to Courtens *et al.*,<sup>10,11</sup> we found consistent results regarding the origins of this low-temperature behavior. Both a linear and a quadratic coupling of this mode to the polarization fluctuations are necessary to explain our results. The quadratic coupling is due to the large electrostriction which is characteristic of these materials.<sup>9</sup> At low tem-

perature, the electrostriction becomes the dominant coupling mechanism and is seen to increase as the ammonium concentration of the RADP crystals increases. This is related to the frustration of the  $\text{NH}_4^+$  ions which already start to freeze below 100 K resulting in slow and static polarization fluctuations. This is also consistent with the system developing an Edwards-Anderson order parameter similar to a glass.

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<sup>18</sup>These estimates are obtained via linear interpolation of  $\omega_a(x=0.28)$  and  $\omega_a(x=0.42)$  at room temperature from Fig. 8 of Ref. 11 and using Eq. (4) with our measured values of  $\omega_B$ .