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Nuclear quadrupole resonance of ^{35}Cl nuclei in glassy solution of chlorobenzene in pyridine

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Pulsed nuclear quadrupole resonance (NQR) measurements of ^{35}Cl nuclei were performed on 43.5 mol % chlorobenzene solution in pyridine (a) in glassy state ($T_g = 131$ K) after quenching in liquid nitrogen and (b) in crystalline precipitate under slow cooling starting from liquid phase. In both cases the NQR line shape, obtained by the fast Fourier transform (FFT) method, consisted of a structure of two peaks, interpreted as contributions of two nonequivalent ^{35}Cl-nucleus sites. A theoretical model is proposed for the line-shape analysis and the best-fit parameters yield excellent agreement with experimental spectra. It is suggested that the nonequivalent sites consist of nearly parallel and antiparallel alignment of chlorobenzene and pyridine molecules and that the line-broadening mechanism is due to a random distribution of angular displacements from these positions. Our data are in agreement with Goldstein studies of molecular-relaxation processes related to the changes observed on physical properties of amorphous materials at T_g.

I. INTRODUCTION

Since the early experiments of pulsed nuclear quadrupole resonance (NQR) in amorphous solids first carried out by Rubinstein and Taylor,[1,2] subsequent work in this area has received the effort of relatively few workers.[3–11] Although the NQR linewidth of the spectra obtained from amorphous materials is too broad to be readily analyzed by the current techniques of Fourier transforms, the pulsed methods and spin-echo experiments have been extremely useful to describe the structural and dynamical properties of several amorphous semiconductors.

The local order could be evaluated in many opportunities with the aid of comparative studies of crystalline solids with similar chemical compositions. In addition, some universal properties of amorphous materials, such as the elementary excitations at low temperatures,[12,13] have been successfully studied using NQR.

The purpose of this work is to study the pulsed Fourier-transform NQR (FT-NQR) of glasses having glass transition temperature T_g in the range easily accessible at the spectrometer in order to obtain complementary informations of the study of dielectric properties of chlorobenzene-pyridine solution by Johari and Goldstein.[14]

Goldstein and co-workers[14–20] developed thermodynamic and dielectric studies on several glassy solutions in the range near T_g and arrived at the conclusion that the changes observed in specific heat and thermal-expansion coefficient are better explained by molecular dynamics than by thermodynamic transitions. As NQR is very sensitive to molecular vibrations,[21] it is expected to obtain local and sensitive description of the behavior of the glass when the temperature is scanned throughout the glass transition-temperature range.

Another observation concerning NQR of amorphous materials is the lack of detailed models and theories explaining the $\rho(\nu)$ shape, although some important characteristics such as the dihedral angle distribution in three-coordinate amorphous arsenic[7] could be satisfactorily explained. It is our purpose to present a model based on the theory of Blinc[22] about the incommensurate systems.

As in the crystals, several amorphous systems have a finite number of topologically nonequivalent nuclear sites. The difference resides in the random distribution of local deformations always present in the amorphous matrix. As the nuclear quadrupole frequencies are directly sensitive to the distribution of electric field gradients produced by the nearest neighbors, it is expected, for each allowed transition, the observance of a spectral line for each site, broadened by the effect of local deformations. The line shape will be governed by the statistical distribution law of the local "deformations" (e.g., bonding distances and angles), which can be either symmetric or asymmetric.

II. MODEL OF THE LINE SHAPE

The NQR spectrum, arising from distributed electric field gradients, reflects the distribution law of distortions at the sites of the observed nuclei, as a consequence of the proportionality between the resonance frequency and the maximum component of electric field gradient (EFG) q.

Defining the local deformation (which is generally small) as a displacement field u, the resonance frequency at a given site can be expanded in powers of u:

$$\nu = \nu_0 + a_1 u + \tfrac{1}{2} a_2 u^2 + \cdots , \tag{1}$$

where ν_0 is the resonant frequency at a nuclear site of deformations. The displacements field u is a function of the deformation law, which depends on a general parameter θ:

$$u = u(\theta) , \tag{2}$$

where θ equals the deformation of distance, angle, etc. As long as $f(u)$ describes the statistical distribution of the distortion field, we can write the density of the spectral line $\rho(\nu)$ as

$$\rho(\nu)d\nu = f(u)du , \tag{3}$$

then

$$\rho(\nu) = \frac{f(u)}{|d\nu/du|} . \tag{4}$$

If a single line corresponding to a given site has the line shape $L(\nu-\nu_c)$, the inhomogeneous line shape of the composite spectrum is

$$F(\nu) = \int L(\nu-\nu_c)\rho(\nu_c)d\nu_c . \tag{5}$$

Writing the resonance frequency in powers of the distortion field as in Eq. (1), and assuming that

$$f(u) = e^{-u^2/2\sigma^2} , \tag{6}$$

where σ is the Gaussian half-width, we can deduce an explicit expression of $\rho(\nu)$ for a few simple cases as follows.

(i) If the linear term in Eq. (1) is dominant,

$$\nu \simeq \nu_0 + a_1 u \tag{7}$$

and the frequency distribution is

$$\rho(\nu) \propto \frac{e^{-u^2/2\sigma^2}}{|a_1|} = \frac{e^{-(\nu-\nu_0)^2/2a_1^2\sigma^2}}{|a_1|} , \tag{8}$$

which corresponds to a symmetrical line. The density of states has a maximum at $\nu=\nu_0$ [Fig. 1(a)]. This is an agreement with the experimental NQR line shape for a-As_2S_3.[6]

(ii) When the quadratic term is dominant the resonance frequency is

$$\nu \simeq \nu_0 + \tfrac{1}{2} a_2 u^2 \tag{9}$$

and

$$\rho(\nu) \propto \frac{e^{-|\nu-\nu_0|/|a_2|\sigma^2}}{[2a_2(\nu-\nu_0)]^{1/2}} \quad \text{for } a_2(\nu-\nu_0) > 0 , \tag{10a}$$

$$\rho(\nu) = 0 \quad \text{for } a_2(\nu-\nu_0) \le 0 . \tag{10b}$$

The resultant line shape is asymmetric with a maximum at $\nu=\nu_0$.

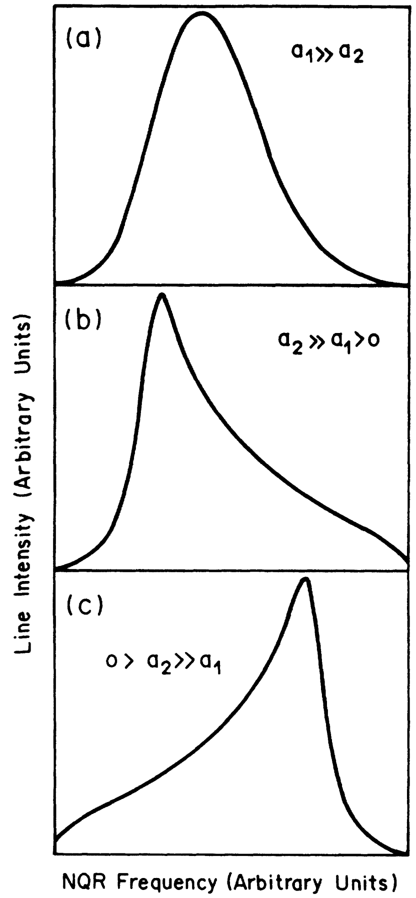

FIG. 1. Examples of computer simulation of NQR line shapes calculated after the model described in the text. (a) Symmetrical line, obtained when the linear term in Eq. (1) is dominant; (b) asymmetric line, when the second term dominates, with $a_2 > 0$ and (c) with $a_2 < 0$.

(iii) If both linear and quadratic terms are to be taken into account, the density of the spectral lines corresponds to an asymmetric line shape which depends on the coefficient a_2. Then, if $a_2 > 0$,

$$\rho(\nu) \propto g(\nu) \quad \text{for } \nu > \nu_0 - (a_1^2/2a_2) , \tag{11a}$$

$$\rho(\nu) = 0 \quad \text{for } \nu \le \nu_0 - (a_1^2/2a_2) , \tag{11b}$$

[see Fig. 1(b)], and for $a_2 < 0$

$$\rho(\nu) \propto g(\nu) \quad \text{for } \nu \le \nu_0 - (a_1^2/2a_2) , \tag{12a}$$

$$\rho(\nu) = 0 \quad \text{for } \nu > \nu_0 - (a_1^2/2a_2) , \tag{12b}$$

where

$$g(\nu) = \frac{\exp\left[-\left\{-\frac{a_1}{a_2} + \left[\left[\frac{a_1}{a_2}\right]^2 + \frac{2}{a_2}(\nu-\nu_0)\right]^{1/2}\right\}^2 / 2\sigma^2\right] + \exp\left[-\left\{\frac{a_1}{a_2} + \left[\left[\frac{a_1}{a_2}\right]^2 + \frac{2}{a_2}(\nu-\nu_0)\right]^{1/2}\right\}^2 / 2\sigma^2\right]}{(a_1/a_2)^2 + (2/a_2)(\nu-\nu_0)} . \tag{13}$$

This line shape has the maximum at $\nu=\nu_0-a_1^2/2a_2^2$.

III. EXPERIMENTAL

The sample (43.5CB-P) of 43.5 mol % chlorobenzene-pyridine solution was prepared as suggested by Johari and Goldstein.[1] Subsequently, it was sealed in a Pyrex glass tube, with elementary and important safety cautions taken during the sealing procedure because the compound is highly flammable. The glass was obtained by quenching the chlorobenzene-pyridine solution directly in liquid nitrogen. The obtained glassy state was confirmed by visual inspection as a transparent material.

The pulsed NQR measurements were carried out with a conventional spectrometer equipped with a Hewlett Packard Model No. 86668 Synthesizer, Amplifier Research Model No. 200L transmitter, Matec Model No. 254 preamplifier, Matec Model No. 625 receiver, and a Nicolet Model No. 4094B data acquisition and fast Fourier transform (FFT) system. The temperature controller was homemade, allowing the stabilization of the sample temperature within 0.1 K in the range of 77–300 K. The line shape in the crystalline phase (obtained with slow cooling rate) was determined using FFT facilities, directly from the free-induction decay following a $\pi/2$ radio-frequency pulse. The corresponding line shape of the glassy state was recorded using the signal intensity, point by point, as suggested by Taylor and co-workers.[7]

IV. DESCRIPTION OF THE RESULTS

The power spectrum measured at the temperature of 88.4 K was obtained immediately after quenching the solution (Fig. 2). A line structure consisting of two peaks shifted by 250 kHz was observed. The low-frequency peak is slightly narrower and, consequently, higher.

In order to observe the annealing effects, the liquid solution was quenched at 77 K and stored in liquid nitrogen over 24 h. The spectra obtained at increasing temperatures [(a) $T=80.6$ K; (b) $T=98.5$ K; (c) $T=130.3$ K] are shown in Fig. 3. At temperatures similar to those of Fig. 2, the spectra exhibit noticeable sharpening, but the splitting observed between both peaks remained unchanged.

Figures 3(a) and 3(b) present similar line shapes. The half width of the low-frequency peak is approximately 75 kHz and that corresponding to the high frequency is of the order of 150 kHz. In contrast, Fig. 2(c) shows a noticeable line broadening of the high-frequency peak at the expense of the low-frequency peak. The linewidth of the low-frequency peak is now nearly 120 kHz and the corresponding high-frequency peak is approximately 200 kHz. The spectrum shown in Fig. 2(c) was obtained near the glass transition temperature ($T_g \simeq 131$ K). The observed spectra do not show a significant frequency shift at relatively low temperatures ($T \ll T_g$). In contrast, at $T \simeq T_g$, a dramatical shift towards low frequencies was observed.

A third set of measurements started from the liquid phase being cooled slowly (~ 5 K/h). At the temperature of 150 K, a first signal appeared at a frequency around 34.900 MHz. Figure 4 denotes the power spectrum at $T=141.8$ K. Two peaks were also observed with half linewidths equal to 5 kHz (lower frequency) and 10 kHz (higher frequency), consistent with linewidths usually observed in molecular crystals. The line frequencies are about 300 kHz higher than the corresponding ^{35}Cl NQR of pure dichlorobenzene ($\sim 8Q=34.480$ MHz), and approximately 900 kHz lower than those observed in the glassy solution. Obviously the spectrum corresponds to a crystalline chlorobenzene-pyridine alloy. The two peaks reflect two nonequivalent ^{35}Cl nuclei sites. A reasonable picture could be proposed as a layered structure of alternate chlorobenzene and pyridine planar molecules with parallel and antiparallel orientations. Some detailed specific models could be proposed in order to explain the broadening and structure of this spectrum as compared with pure crystal, but this is beyond the scope of this work.

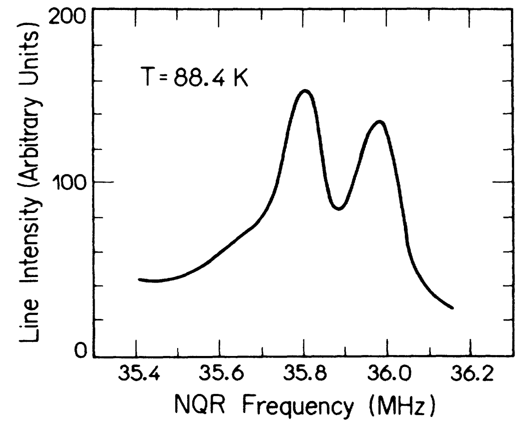

FIG. 2. FT-NQR power spectrum of ^{35}Cl in glassy solution of 43.5 mol % chlorobenzene in pyridine measured at $T=88.4$ K immediately after quenching in liquid nitrogen.

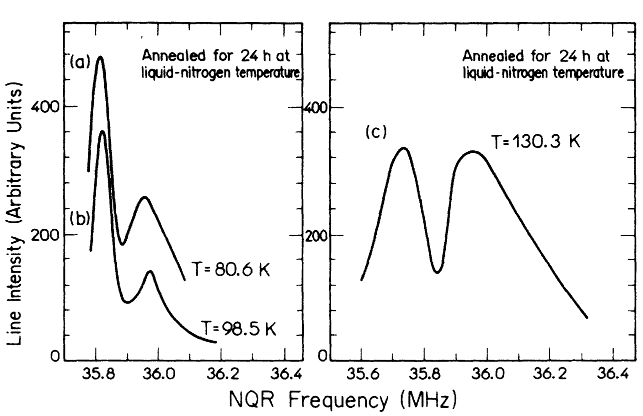

FIG. 3. FT-NQR power spectrum of the same sample, shown in Fig. 2, after storage for 24 h at liquid-nitrogen temperature and measured at the temperatures (a) 80.6 K, (b) 98.5 K, and (c) 130.3 K.

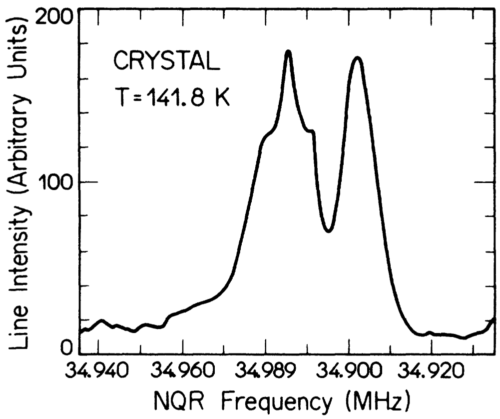

FIG. 4. FT-NQR spectrum of 43.5 mol % chlorobenzene-pyridine solution measured at the temperature of 141.8 K after a slow cooling (~5 K/h) starting from the liquid phase.

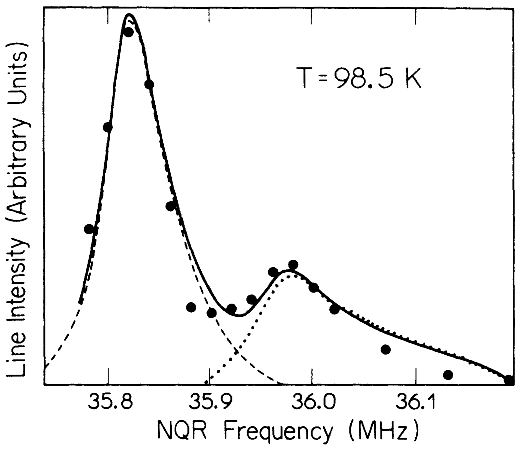

FIG. 5. Computer simulation (solid line) of the experimental NQR line shape obtained at 98.5 K (solid circles). The best fit was obtained as a sum of separate simulations for each of the two peaks (dashed and dotted lines).

V. DISCUSSION

The two peaks observed in the NQR spectrum of the glassy solution could be interpreted on the basis of similarities with the power spectrum of the crystallized alloy. The two peaks in the crystal are ascribed to the parallel-antiparallel orientations in the layered structure (as mentioned previously). Consequently, a nearly similar, but distorted, structure, without long-range order, is expected to remain in the glass. In this model the random distribution of angular distortions θ over parallel or antiparallel positions is a source of random distribution of the electric field gradient at each ^{35}Cl nucleus site. Consequently, an inhomogeneous line broadening is observed. The theoretical model proposed could account for the experimental line shape by assuming the superposition of two spectra, each one arising either from parallel, or from both parallel and antiparallel, randomly distorted angular positions. As an example, Fig. 5 illustrates the fit of the line shape at $T=98.5$ K. As can be seen, the obtained agreement is fairly good. Table I exhibits the most significant best-fit parameters obtained from the measurements. The fitting parameters behave nearly constant at the lower temperatures. However, a sudden change is observed at $T=130.3$ K ($\sim T_g$). Two features are therefore remarkable: (i) the central frequencies of both peaks shifted towards lower values as a consequence of a more effective EFG averaging due to the increase of molecular mobility, and (ii) the increase of the root mean square of the distortive field half width σ suggests an increment in both the static and dynamic contributions of the mean amplitude of the randomly distributed angular distortion θ; the dynamic contribution could be explained in a similar fashion of that described in proton pseudospin glasses in the linear approximation.[23] However, a more detailed experimental study is still necessary to develop a more complete description of dynamical processes near T_g. This behavior could be interpreted as an unfreezing of the molecular modes in such a way that more freedom of the relative orientation of the molecules is allowed and the overall behavior approaches to that of a viscous liquid.

The relatively broad spectrum obtained at $T=98.5$ K in a sample, immediately after the liquid solution was quenched at 77 K, is related to internal strains producing a concomitant increase in the mean amplitude of the angular distortions. After annealing the sample at the same temperature (which is not too far from T_g) during a 24 h period, the internal strains have been considerably relaxed in addition to the observed sharpening of the resonance spectrum (the mean angular distortion has diminished).

In summary, this work has supported the basic ideas developed by Taylor and co-workers[7,21] using NQR as a very sensitive probe in the study of static and dynamic properties of amorphous materials. This method was

TABLE I. NQR line breath and frequencies of the glassy solution 43.5 mol % chlorobenzene-pyridine.

Temperature line	Low-frequency line		High-frequency	
(K)	(MHz)	σ(MHz)	(MHz)	σ(MHz)
80.6	35.794	0.053	35.945	0.4
98.5	35.804	0.045	35.955	0.3
130.5	35.660	0.150	35.800	0.6

now applied to an organic glassy material with T_g in a convenient range, so that the complete thermal treatment of the sample could be done into the spectrometer, rendering, accessible, the studies near the transition temperature. Our results are in complete agreement with Johari and Goldstein's theory of the molecular relaxation process which is directly responsible for the physical properties near T_g.

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