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Pulsed nuclear-quadrupole resonance in nonuniformly disordered systems

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Pulsed nuclear-quadrupole resonance (NQR) measurements at room temperature and 77 K have been performed on distinct specimen of arsenolite in (a) a polycrystalline sample and (b) a specimen with a varying degree of disorder, ranging from amorphous to crystalline order. The NQR absorption line in these specimen, obtained by the fast-Fourier-transform (FFT) method, has different intensity and line shape. A theoretical model is proposed that explains the experimental results very well. The model is based on the assumption that the electric field gradient (EFG) due to the intermolecular interaction changes randomly from site to site characterized by a distribution. In sample (b) this distribution is approximately constant in regions of mesoscopic dimensions (i.e., large enough to be a few hundred interatomic distances but small enough compared to the bulk dimensions of the sample) but changes throughout the sample. The scanning electron micrographs of these samples are presented, which support our assumption.

I. INTRODUCTION

Arsenic compounds are common in different materials like crystals, amorphous semiconductors, glasses, superlattices, etc. Due to the importance of and the ease in observing the nuclear-quadrupole resonance (NQR) of ^{75}As, NQR studies of this nucleus has been reported in a variety of compounds like elemental arsenic, arsenic sulfide, arsenic telluride, and arsenic selenide in crystalline and vitreous forms.[1–3] In the late 1970s and early 1980s some articles were presented discussing the structure of As_2O_3 in crystalline and vitreous states.[4–8] A few others were presented studying this material by means of NQR, demonstrating the power of this technique to analyze short-range-order properties.[9–12] NQR of different nuclei has been used to study glasses and the theoretical model has been presented to describe the NQR line shape of organic glasses.[13] A common feature in these NQR works is that the samples used are either polycrystalline or amorphous, where the disorder is uniform throughout the sample. This work deals with a specimen where the electric field gradient (EFG) due to the intermolecular interaction changes randomly from site to site, characterized by a distribution which varies in different regions of the sample.

Crystals containing NQR-sensitive nuclei were used as filler material in polymers, to study the internal stress induced by the polymerization of copolymers.[14] A theoretical work with some experimental data of the uniaxial-stress dependence of the NQR frequency was done by Zamar and Brunetti.[15] Arsenolite (As_2O_3) and senarmontite (Sb_2O_3) are good candidates to be used as probes for the local stress distribution. A commercial powder of arsenolite, the high-temperature stable phase of As_2O_3, has been used to test the NQR imaging by using the rotating frame method.[16–18] The spatial resolution of the image and the sensitivity of the technique strongly depend on the NQR line shape and intensity, respectively. The narrower the lines are, the higher is the spatial resolution, and the more intense the lines are, the higher is the sensitivity of the method. The results presented in this paper show that the polycrystalline samples obtained from the commercial powder by a recrystallization process are much more suitable for these studies.

II. EXPERIMENT

The measurements were performed using an automatized home-made NQR spectrometer which was built using the following equipment: a Matec gating modulator (model 5100), a Matec broadband receiver (model 625), and a Phillips frequency synthesizer (model PM5390S). The data acquisition system is composed of a Tektronix digital oscilloscope (model 2430A), an IBM-compatible AT 286 microcomputer, and a Hewlett-Packard measurement plotting system (model 7090A). A commercial Asyst program, specially configured for this experiment, was used for transferring and analyzing the data. The powder samples of As_2O_3 (PW), with grains of approximately 10–100 μm, were obtained from Merck Company and used without further purification. The finer powder (FP) of material was obtained by grinding the commercial powder; however, the size of the grains was not determined. The polycrystalline sample (PL) was prepared by slow evaporation at 50 °C in an oven from a saturated and filtered aqueous solution of As_2O_3. An additional set of samples was prepared and annealed at 250 °C for 20 h. In the NQR spectra of these material no line due to claudetite was present, which shows that during the annealing process no arsenolite to claudetite phase transition had happened. Due to the toxic nature of As_2O_3, extra care should be taken during the preparation and

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handling of samples. The NQR spectra were obtained by spin echo by a fast Fourier transform (FFT) algorithm. The scanning electron micrographs of the powder samples were obtained by stereoscan 180 (Cambridge) and those of polycrystalline samples by Jeol JEM 840-A.

III. RESULTS

A. NQR line shape

Some typical NQR spectra of PW, FP, and PL samples with and without annealing are presented in this section. Figure 1 shows the NQR absorption line of the polycrystalline sample (PL), at room and liquid nitrogen temperatures. In both cases the espectral line can be fitted to a single Gaussian with a full width at half maximum (FWHM) of 5.37 kHz and 6.25 kHz, respectively. This is a clear indication that the sample is polycrystalline. (This fact is confirmed by the micrographs presented in Fig. 5.)

Figure 2 depicts the same as Fig. 1 for commercial powder (PW). In this sample the NQR line is broader and cannot be fitted with a single Gaussian or Lorentzian, demonstrating that the spread in the EFG is not constant throughout the sample.

The corresponding NQR spectrum of the FP sample at room temperature is shown in Fig. 3(a). Again the NQR line in this sample is broader than that of the PL and PW samples and cannot be fitted either by a single Gaussian or Lorentzian.

The broadening of the NQR line in respect to the PW sample is due to the internal stress induced during the mechanical treatment. After the annealing process the NQR line of the FP sample has a similar linewidth to the PW sample, which shows the stress relaxation during the heat treatment Fig. 3(b). The heat treatment does not have any considerable influence on the PL and PW samples.

B. Scanning electron micrograph

The scanning electron micrographs of the PW sample with amplification factors of 132, 792, and 2500 are shown in Figs. 4(a), 4(b), and 4(c), respectively. As an overview of PW sample reveals [Fig. 4(a)], the granulate material is composed of about 100 μm almost spheri-

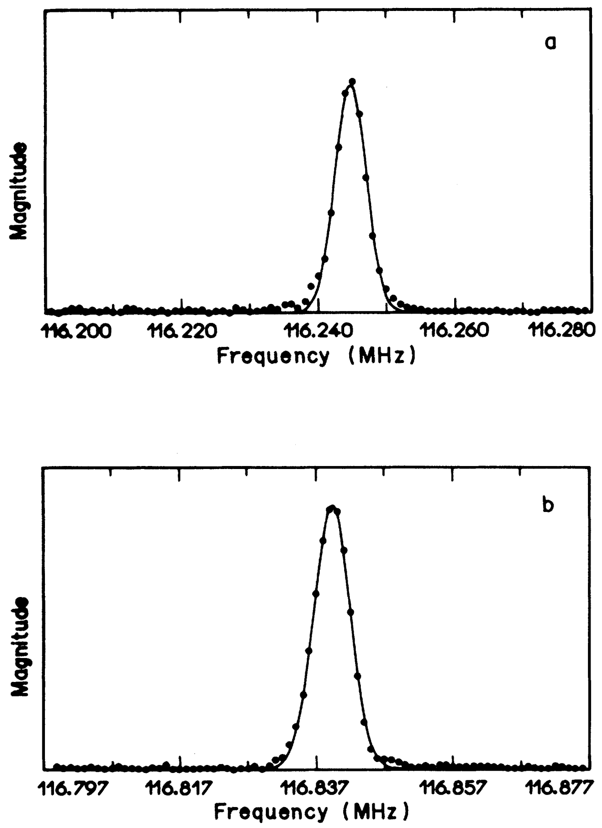

FIG. 1. NQR absorption line of the polycrystalline sample (PL) at (a) 300 K and (b) 77 K. The experimental data (solid circles) are superimposed with a single Gaussian line (solid line).

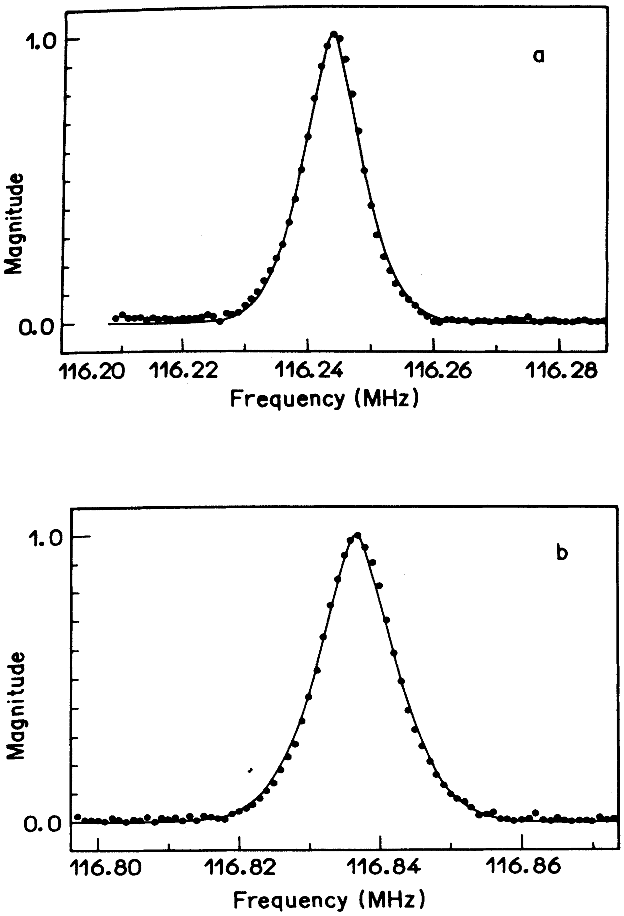

FIG. 2. NQR absorption line of commercial powder (PW) at (a) 300 K and (b) 77 K. The experimental data (solid circles) are superimposed with a theoretical curve (solid line) generated using Eq. (8).

cal grains. One of the unbroken grains is shown in Fig. 4(b). Figure 4(c) presents the detail of a broken grain. A polycrystalline structure is observed in the inner part of the grain, resembling the arsenolite crystalline structure; however, the shell material seems to be amorphous.

The micrographs corresponding to the PL sample with amplification factors of 44, 125, and 1250 are presented in Figs. 5(a), 5(b), and 5(c), respectively. As can be seen, this material is made of different size moncrystals and there is no evidence of amorphous parts.

C. Integrated spin-echo intensity

It is well known that amorphous arsenolite has a much broader NQR absorption line than the polycrystalline one.[10] Therefore, in order to compute the fraction of material in the PW sample which is narrow enough to be detected, we compared the area covered by the spin echo of 200 mg of the PW and PL samples. The experimental condition was checked by measuring the PW and PL spin-echo intensity in a PW, PL, PW sequence by

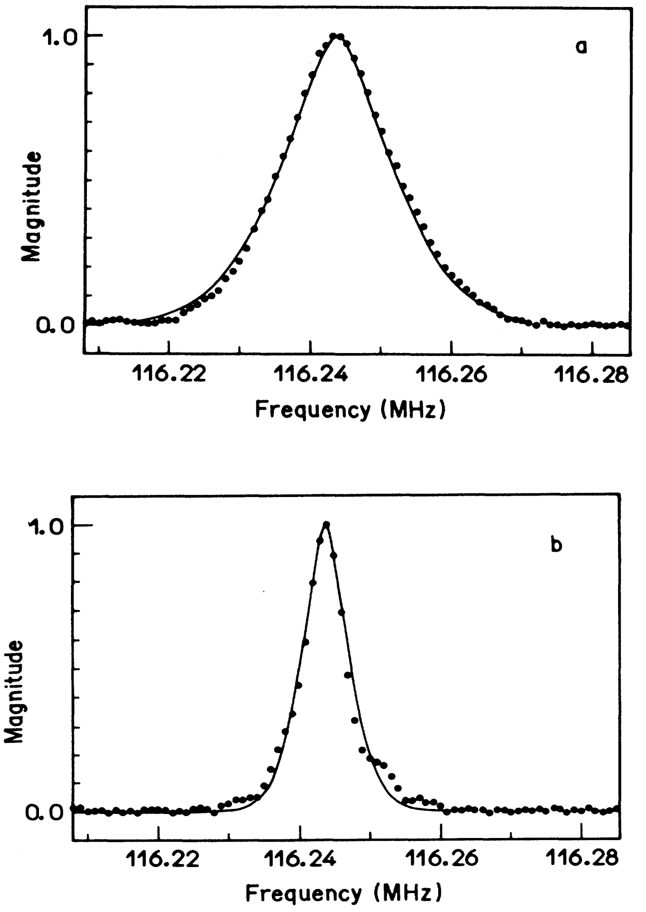

FIG. 3. NQR absorption line of fine powder (FP) (a) without annealing at 300 K and (b) annealed one at 77 K. The experimental data (solid circles) are superimposed with a theoretical curve (solid line) generated using Eq. (8).

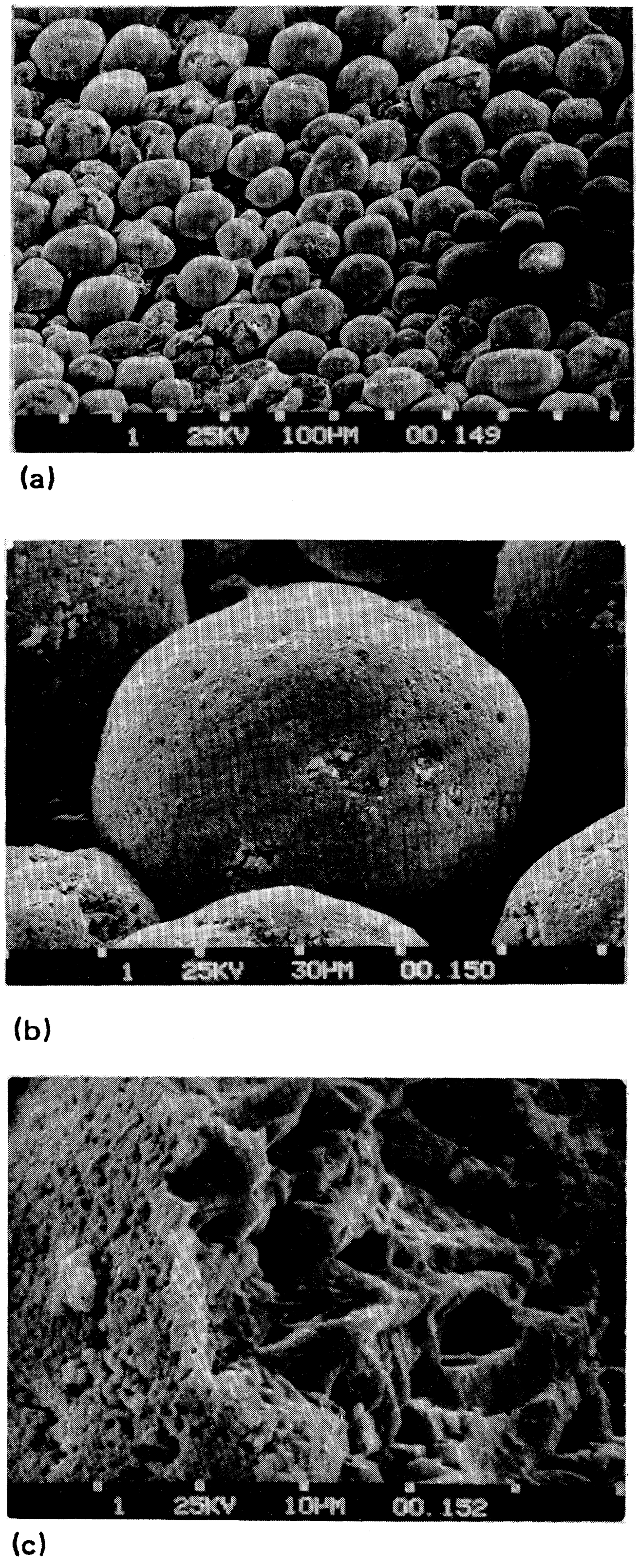

FIG. 4. The scanning electron micrographs of the PW sample with amplification factors of (a) 132, (b) 792, and (c) 2500.

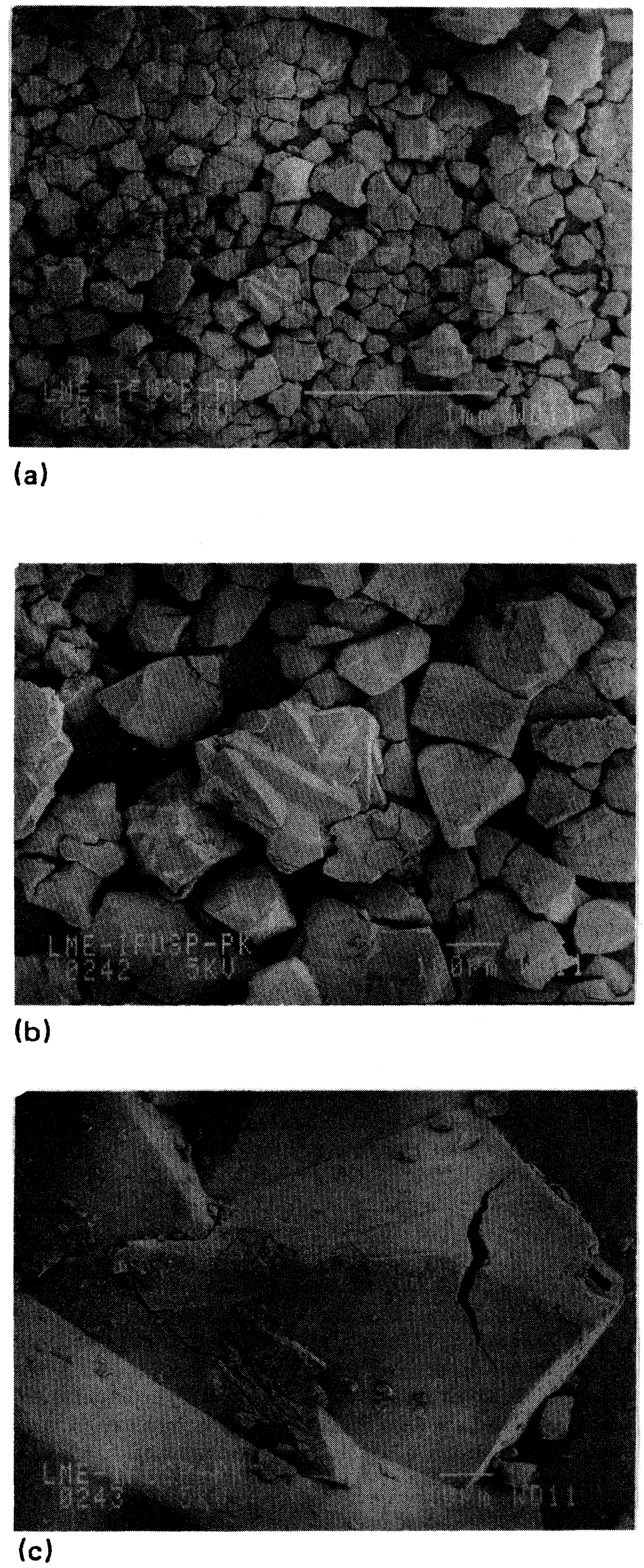

FIG. 5. The scanning electron micrographs of the PL sample with amplification factors of (a) 44, (b) 125, and (c) 1250.

changing the sample without any change in spectrometer adjustment. No appreciable change in the signals of each sample was observed in the sequence. The (area PW)/(area PL) ratio was 0.55; in other words, only 55% of commercial powder is detectable. Another 45% is too broad to be detected. It is reasonable to assume that the NQR line in the PW sample is progressively broadened from center to the border of the grains and eventually becomes so broadened that it is not detectable any more.

IV. THEORY

The effect of disorder on the line shape of the NQR spectrum has been the subject of previous studies.[13] The aim of this work is to study both theoretically and experimentally this effect in a more general setting, where the disorder is not uniform, but varies throughout the sample.

Due to the dependence of the resonance frequency on the EFG, the disorder will influence the resonance frequency in a manner which reflects the local distribution of disorder. Consider a generalized random diplacement field u. The resonance frequency in a region can be thought, barring extreme cases, as an analytical function of u and can thus be expanded in a Taylor series

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

The actual value of the derivatives of ν with respect to u is not known, for its theoretical calculation is beyond present approximation schemes. As has been done before,[13] this lack of knowledge leads to the treatment of a_i as fitting parameters.

The model of the disorder we have in mind is as follows. On an intermolecular scale, u varies randomly from site to site, characterized by a distribution. This distribution is the same inside a certain region of mesoscopic dimensions $(\Delta r)^3$, i.e., large enough to have a few hundred interatomic distances but small compared to the bulk dimensions of the sample.

It is natural to assume that u is described by $f_r(u)$, a Gaussian distribution which we take to be

$$f_r(u) = \frac{1}{\sqrt{2\pi}\sigma_r} e^{-\frac{u^2}{2\sigma_r^2}}, \tag{2}$$

and the width of the distribution may vary on a mesoscopic length scale.

Due to Eq. (2), it can be seen that the contribution of a given region $(\Delta r)^3$ will be

$$\rho_r(\nu) d\nu = f(u_r) du_r; \tag{3}$$

thus

$$\rho_r(\nu) = \frac{f(u_r)}{\mid \frac{d\nu}{du_r} \mid}, \tag{4}$$

the total spectral density, will be the incoherent sum of all such contributions from the sample:

$$\rho(\nu) = \int_{\text{sample}} \rho_r(\nu) \frac{d^3 r}{V}, \tag{5}$$

where the integral is over a sample of volume V. This is quite general and we now look at the particular case where the material, as described in Sec. III, is a powder which, according to the experimental data, has a crystalline order at the center and is rather amorphous at the surface of almost spherical powder particles.

The basic point of the following analysis is to argue that the width of $f_r(u)$ grows as one goes from the center to the surface of the sphere. For the polycrystalline sample this is not true and the crystallization is more or less constant throughout the sample, as can be seen in the electron micrographs of Fig. 5 and the Gaussian shape of the NQR line of Fig. 1. We model the width $\sigma(r)$ of the distribution by a homogeneous function of r. The important feature is its growth and not the specific details of its variation. For simplicity and because it is not necessary to put more details than necessary to explain the experimental data, we take $\sigma(r)$ to be linear in r and assume spherical symmetry,

$$\sigma(r) = br. \tag{6}$$

The value of b is not known and it will turn out not to be important. With this simpification the spectral density is given by

$$\rho(\nu) = \frac{3}{\sqrt{2\pi}R_0^3 \mid \frac{d\nu}{du} \mid} \int_0^{R_0} \left(e^{-\frac{1}{2}\frac{u^2}{b^2 r^2}}\right) \frac{r dr}{b}, \tag{7}$$

where R_0 is the radius of the sphere. By defining a new rescaled integration variable $\frac{br}{u} = x$ and calling $\frac{bR_0}{u} = \frac{1}{y}$, we have

$$\rho(\nu) = \frac{3}{\sqrt{2\pi} \mid \frac{d\nu}{dy} \mid} y^2 \int_0^{\frac{1}{y}} e^{-\frac{1}{2x^2}} x dx. \tag{8}$$

In this form we have rescaled the generalized displacement field u and substituted by y. Equation (1) can be rewritten as

$$\nu = \nu_0 + \tilde{a}_1 y + \frac{\tilde{a}_2}{2} y^2 + \cdots , \tag{9}$$

where $\tilde{a}_1$ and $\tilde{a}_2$ are related to the previously unknown a_1 and a_2 by

$$\tilde{a}_1 = a_1 b R_0 \quad , \quad \tilde{a}_2 = a_2 (bR_0)^2. \tag{10}$$

Notice the important fact that all new unknown parameters that were introduced in the modeling process have not been implied in a larger number of fitting parameters. The line shape is thus described by a prefactor, which carries basic quadrupolar influences, times a universal function $F(y)$ given by

$$F(y) = y^2 \int_0^{\frac{1}{y}} e^{-\frac{1}{2x^2}} x dx. \tag{11}$$

The only parameters to be fitted are $\tilde{a}_1$, $\tilde{a}_2$ and the ordered state resonance frequency ν_0.

As reported in Ref. 13 the effect of a nonzero $\tilde{a}_2$ is to introduce asymmetry with respect to ν_0. In the case of the material we study, the symmetrical line shape strongly indicates that the effect of $\tilde{a}_2$ is negligible and thus can be taken as zero. We are left with a one-parameter fit. The excellent agreement with the experimental data is discussed in the next section.

V. DISCUSSION

Before attempting to compare Eq. (8) with the experimental results we should mention several points.

(a) As can be seen in Fig. 4 the grains of the powder are neither spherical nor uniform in size, varying almost an order of magnitude in diameter.

(b) In developing the theory it was assumed that the disorder starts at the center and goes all the way to the surface. However, it is perfectly possible that there is a central part of the grains which maintains the crystalline order and contributes to the line shape with a Gaussian of constant linewidth. This would change slightly the line shape.

With the above considerations it is clear that the theory presented is an order of magnitude calculation and the general shape of the spectrum is the best test for the theory rather than the values of the parameters derived from it. However, it should be mentioned that the theory can be used for a more quantitative analysis when the disorder profile is known.

A careful search was carried out from 90 to 117 MHz within the temperature range of 77 – 300 K. The only absorption line detected was the one corresponding to arsenolite around 116 MHz. In particular, no signal from claudetite was found. The experimental data of Figs. 1(a) and 1(b) can be well fitted to a single Gaussian. Therefore, it is reasonable to assume that the polycrystalline arsenolite has a Gaussian shape NQR line with a linewidth of approximately 5 kHz. The NQR lines corresponding to the PW and FP samples are neither a pure Gaussian nor Lorentzian and are broadened compared to the PL sample, Figs. 2 and 3. In the case of the FP sample the NQR line is broader than the PW line; however, after the annealing process its linewidth is comparable to the PW linewidth and the annealing process does not have any appreciable effect on the PL and PW samples.

Since we could not find any extra lines in the PW sample, it is clear that the 45% reduction in the NQR signal in this sample is due to the broadening of the NQR line in some region of the sample, making the signal from this region undetectable. Furthermore, the annealing process does not show any appreciable effect on the NQR line of the PW sample which indicates that the broadening is due to structural disorder and not to any mechanical stress. Therefore, it is justified to use Eq. (8) to fit our experimental data. As can be seen in Figs. 2 and 3, the theoretical curves (solid line) fit very well the experimental data (solid circles). These confirm our assumption that the linewidth of NQR line changes from region to region of the sample.

A series of works[16,19,17,20] has been done using As_2O_3 as a probe to measure the stress effect in polymers and for imaging porposes. In these works a commercial powder of As_2O_3 was used; however, our results show that a recrystallized material would render much better results, increasing the sensitivity and the resolution of these techniques.

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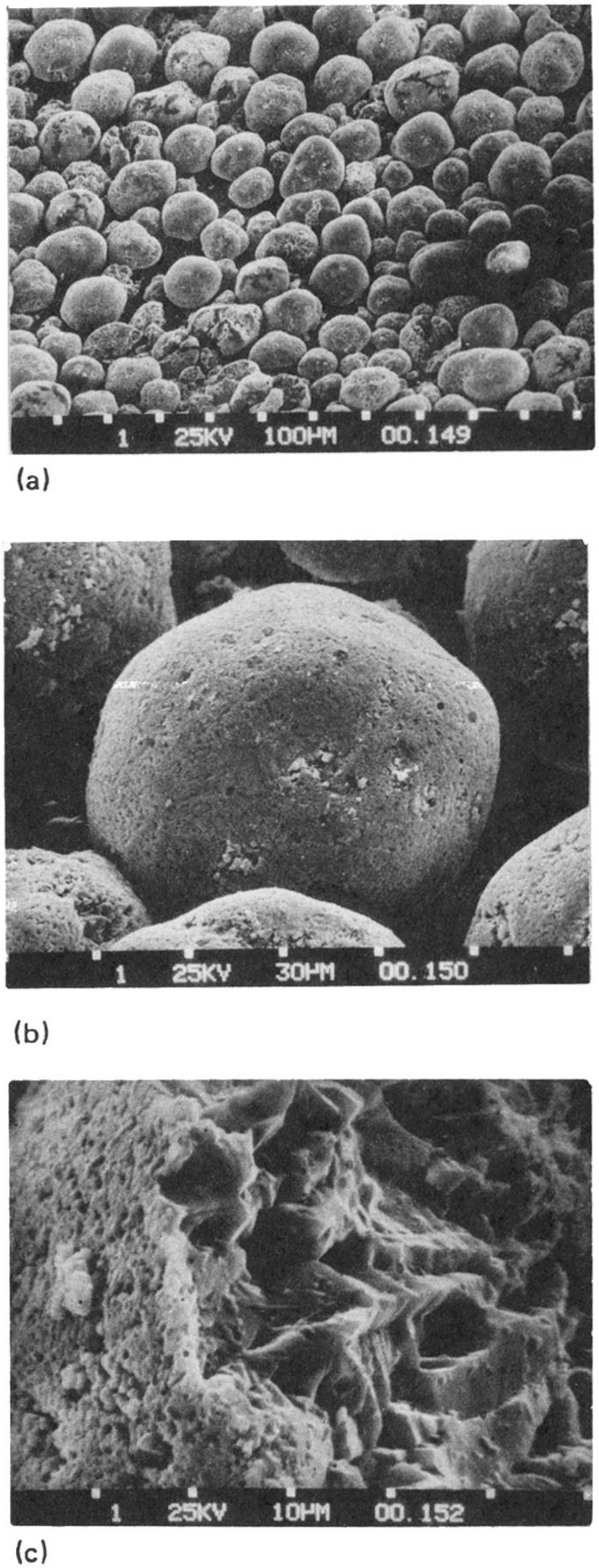

FIG. 4. The scanning electron micrographs of the PW sample with amplification factors of (a) 132, (b) 792, and (c) 2500.

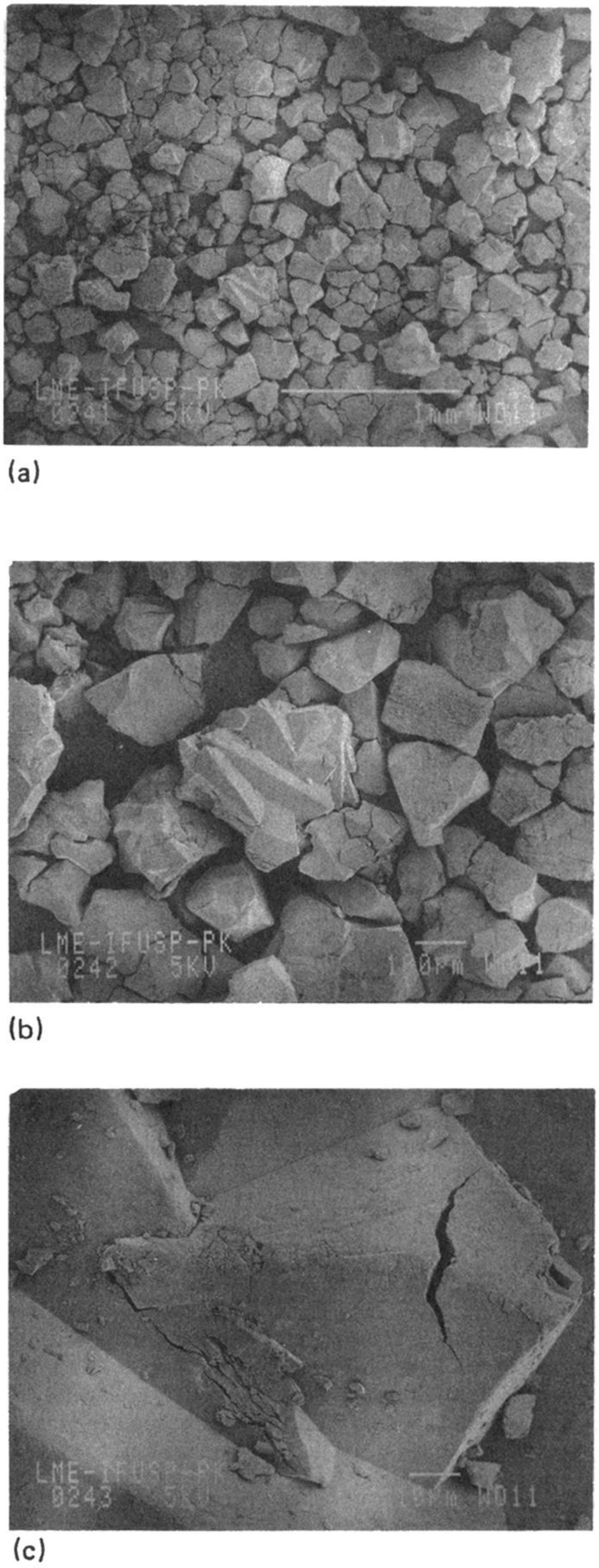

FIG. 5. The scanning electron micrographs of the PL sample with amplification factors of (a) 44, (b) 125, and (c) 1250.