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Abstract

Pulsed Nuclear Quadrupole Resonance (NQR) measurements, at room temperature, and 77 K have been performed on arsenolite in commercial powder and polycrystalline sample obtained from commercial As_2O_3 by recrystallization. As expected, from scanning electron micro graphs, three kinds of layers are present in commercial powder. The differences in line shape and line intensity between two samples are discussed and a theory is presented to explain the experimental results.

Date: July 19, 1993

Running title:
NQR in crystalline and glassy phases

1   Introduction

Arsenic compounds are common in different materials like crystals, amorphous semiconductors, glasses, super lattices, etc. Despite the importance of and the ease in observing the Nuclear Quadrupole Resonance (NQR) of ^{75}As, very few NQR studies of this element can be found in the literature. In the late seventies and early eighties some articles were presented discussing the structure of As_2O_3 in crystalline and vitreous state[1,2,3,4,5]. Few others were presented studying this material by means of the NQR, demonstrating the power of this technique to analyze short range order properties[6,7]. 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[8]. Crystals containing NQR sensitive nuclei were used as filler material in polymers, to study the internal stress induced by the polymerization of copolymers[9]. A theoretical work with some experimental data in uniaxial-stress dependence of the NQR frequency was done by Zamar et.al[10]. Arsenolite (As_2O_3) and senarmontite (Sb_2O_3) are good candidates to be used as probes for local stress distribution. Arsenolite, the high temperature stable phase of As_2O_3 has been used to test the NQR imaging in the rotating frame method[11,12,13]. In these works commercial samples were used. 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. In this paper we present a comprehensive NQR study of arsenolite in commercial material and in polycrystalline samples obtained from the commercial powder by a recrystallization process. The reduction of the line width and the increase of the line intensity is explained.

2   Experimental

The measurements were performed using an automatized home made NQR spectrometer which was built using the following equipment: a Matec gating modulator (Mod. 5100), a Matec broad band receiver (Mod. 625) and a Phillips Frequency Synthesizer (Mod. PM5390S). The data acquisition system is composed of a Tektronix digital oscilloscope (Mod. 2430A), and IBM compatible AT 286 microcomputer and a Hewlett-Packard measurement plotting system (Mod. 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 were not determined. The polycrystalline sample (PL) was prepared by slow evaporation at 50 ^{o}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 ^{o}C during 20 hours. 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 handling of samples. The NQR spectra was obtained from spin echo by Fast Fourier Transform (FFT) algorithm. The scanning electron micro graphs of the powder samples were obtained by stereoscan 180 (Cambridge) and those of polycrystalline samples by Jeol JEM 840-A.

3   Results

3.1   NQR line shape

Some typical NQR spectra of PW, FP and PL samples with and without annealing are presented in this section. Fig. 1 shows the NQR absorption line of polycrystalline sample (PL), at room and liquid nitrogen temperature. The full width at half maximum (FWHM) are 5.37 KHz and 6.25 KHz respectively.

INSERT FIGURE 1

Fig. 2 depicts the same as Fig. 1 for commercial powder (PW). In this sample the experimental data cannot be fitted with a single gaussian. The FWHM of two gaussians are 8.02 KHz and 15.67 KHz at room temperature (Fig 2a) and 9.63 KHz and 18.22 KHz at 77 K (Fig 2b).

INSERT FIGURE 2

The corresponding NQR spectrum of FP sample at room temperature with the line widths of 10.18 KHz and 22.16 KHz is shown in Fig. 3a.

INSERT FIGURE 3

The broadening of the NQR line in respect to the PW sample is due to the internal stress induced during the mechanical treatment. After annealing process the NQR line of the FP sample can be fitted by two gaussians with 4.95 KHz and 14.79 KHz FWHM, which shows the stress relaxation during the heat treatment (Figure 3b). The NQR line of annealed PW sample is composed of two gaussians with FWHM of 5.01 KHz and 14.90 KHz. while heat treatment does not have any considerable influence on PL sample. The influence of annealing process in NQR line width of different samples is summarized in table I.

INSERT TABLE I

3.2   Scanning electron micro graph

The scanning electron micro graphs of PW sample with amplification factors of 132, 792 and 2500 are shown in Fig. 4a, b and c respectively. As

overview of PW sample (Fig. 4a) reveals the granulate material is composed of about 100 μm almost spherical grains. One of the unbroken grains is shown in Fig. 4b. Fig. 4c 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.

INSERT FIGURE 4

The micro graphs corresponding to the PL sample with amplification factors of 44, 125 and 1250 are presented in Figs. 5a, b and c respectively.

INSERT FIGURE 5

3.3 Integrated spin-echo intensity

In order to compute the fraction of material in PW sample with arsenolite structure, we compared the area covered by the spin echo of 200 mgr of 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 changing the sample without any change in spectrometer adjustment. No appreciable change on the signals of each sample was observed in the sequence. The Area PW/Area PL ratio was .55, in other words, only 55% of commercial powder is composed of As_2O_3 with arsenolite structure. It is reasonable to assume that the arsenolite crystals in PW sample are located in the core of the grains.

4 Theory

We consider the evolution of the electric field gradient (EFG) from the center of the specimen to the surface as a random walk problem. The degrees of freedom responsible for the disorder in EFG are taken to generate random fluctuations in the position of the central frequency of the NQR. The line shape, up to a given distance from the center, is determined from that at the center (where a long range ordered phase is present) by an average over the random variable that specifies the peak position.

The peak position, $\nu_Q(\Delta q)$ is written as

$$\nu_Q(\Delta \nu) = \nu_Q^0 + \Delta \nu \tag{1}$$

where $\Delta \nu = a \Delta q$, Δq is the measure of the random fluctuation of the EFG, ν_Q^0 is the peak position at the center, a is a constant, and Δq is taken to be random. Considering a gaussian shape for the intensity

$$I_{\Delta \nu}(\nu) = I_0 e^{\left[-\frac{(\nu - \nu_Q(\Delta \nu))^2}{\Delta \nu^2} \right]} \tag{2}$$

We then write for the intensity at a given radius R the following average

$$\overline{I}(\nu) \equiv \int d(\Delta \nu) P(\Delta \nu) I_{\Delta \nu}(\nu) \tag{3}$$

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The distribution P($\Delta \nu$) is obtained from the maximum entropy principle stated as follows

$$\delta[S' - \lambda < 1 > -\alpha < (\Delta \nu)^2 >] = 0 \qquad (4)$$

Where

$$S' = -\int d(\Delta q) ln P(\Delta \nu) P(\Delta q)$$

$$< 1 > \equiv \int d(\Delta q) P(\Delta q) = 1$$

$$< (\Delta q)^2 > \equiv \int d(\Delta q)(\Delta q)^2 P(\Delta q) = \frac{1}{\alpha}$$

Performing the variation in Equation (4) we find

$$P(\Delta q) = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-(\Delta q)^2 \alpha} = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-(\Delta \nu)^2 \frac{\alpha}{a^2}} \qquad (5)$$

With P(Δq) above, the integral in Equation (3) can be easily evaluated to yield

$$\bar{I}(\nu) = \left[\sqrt{\frac{\alpha}{\alpha + a^2}}\right] I_0 exp \left[-\frac{(\nu - \nu_Q^0)^2}{\Delta_\nu^2(\bar{q})\left(\frac{\alpha + a^2}{a^2}\right)} \right] \qquad (6)$$

We see from Equation (6) that random fluctuations which apparently set in as one moves out of the center of the grain, cause the broadening of the NQR line. The new width, which specifies the line shape up to a layer or the surface (amorphous), is

$$\Delta_\nu^2(R) = \Delta_\nu^2(0)\frac{\alpha(R) + a^2}{a^2} \qquad (7)$$

Where R refers to the radius of the layer, that we take to influence the value of $\alpha(R)$.

Equation (7) is the fundamental result of this section. It shows how the line shape is widened as one goes away from the center of the grain. In the analysis of the data, presented in the next section, we apply Equations (6) and (7) to obtain $\alpha(R)$ at the boundary of the sample in terms of the basic distribution width, $a \equiv \frac{\Delta \nu}{\Delta q}$, at the center of the specimen, considered here as an ordered phase.

5 Discussion

A careful search was carried out from 90 MHz to 117 MHz within the temperature range of 77 K to 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 Figure 1a and 1b 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 line width of 5 KHz approximately. The NQR lines corresponding to PW and FP are composed of two gaussians, figure 2 and 3. The line widths of all the

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gaussians are considerably larger than 5 KHz. However, after the annealing process, the narrower gaussian in both samples has a line width of 5 KHz approximately, as it can be observed in Figures 2 and 3 and table I. In PW sample the narrower gaussian represents 40 % of total area while in FP sample it represents only 15 % of total area. Again, after the annealing process the contribution of narrower gaussian increases to 40 % of the total area, which shows that the broadening of the remaining 60 % of sample is due to disorder and not due to the stress. From these results and the ones previously described, we conclude that the grains in the commercial powdered As_2O_3 present three concentric regions with inequivalent structures, each region contributing in a different way to the NQR parameters. The outer shell, representing 45 % of the sample, made of amorphous As_2O_3, does not contribute to the observed NQR signal. The inner core, representing 22 % of the sample, with a polycrystalline structure, contributes with a narrow line. Finally, there is a polycrystalline intermediate shell, with some distortions, connecting the internal (ordered) and the external (disordered) structures. The density of distortions increases continuously towards the outer shell, ultimately assuming an amorphous form. The distortions induce a dispersion on the Electric Field Gradient at the ^{75}As nuclei sites, broadening in consequence the NQR line. Such a dispersion depends on the distance from the center of the grain. 33 % of sample is located in this intermediate region having an approximately 15 KHz wide gaussian lineshape. Using polycrys-

talline As_2O_3 instead of the commercial powder in the imaging techniques, one can increase the sensitivity by a factor two and the resolution by a factor three.

From the theoretical consideration of section 4 one may reach a general conclusion that summarizes, to a reasonable extent, the above discussion. Roughly speaking, the $\Delta_\nu^2(R)$ is found to be three times larger than $\Delta_\nu^2(0)$. This implies from Equation (7) that $\alpha(R) = 2a^2 = 2\langle \frac{\Delta \nu^2}{\Delta q^2} \rangle$.

6 Acknowledgements

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Table I – Influence of annealing on NQR line width (room temperature)

| Sample	Line width(kHz)			
	Annealed		Without annealing	
	1^{st}Gauss.	2^{nd}Gauss.	1^{st}Gauss.	2^{nd}Gauss.
Polycrystalline(PL)	5.37	-	5.37	-
Comm. powder(PW)	5.01	14.90	8.01	15.67
Fine powder(FP)	4.95	14.70	10.18	22.16

Fig. 1 NQR absorption line of polycrystalline sample (PL) at a) 300 K and b) 77 K.

Fig. 2 NQR absorption line of commercial powder (PW) at a) 300 K and b) 77 K.

Fig. 3 NQR absorption line of fine powder (FP) a) without annealing at 300 K and b) annealed one at 77 K.

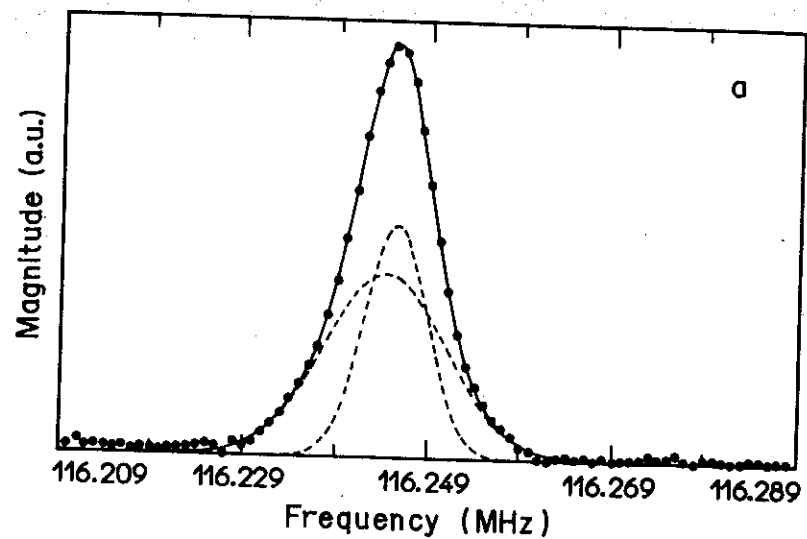Fig. 4 The scanning electron micro graphs of PW sample with amplification factors of a) 132, b) 792 and c) 2500.

Fig. 5 The scanning electron micro graphs of PL sample with amplification factors of a) 44, b) 125 and c) 1250.

Fig. 1
Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."
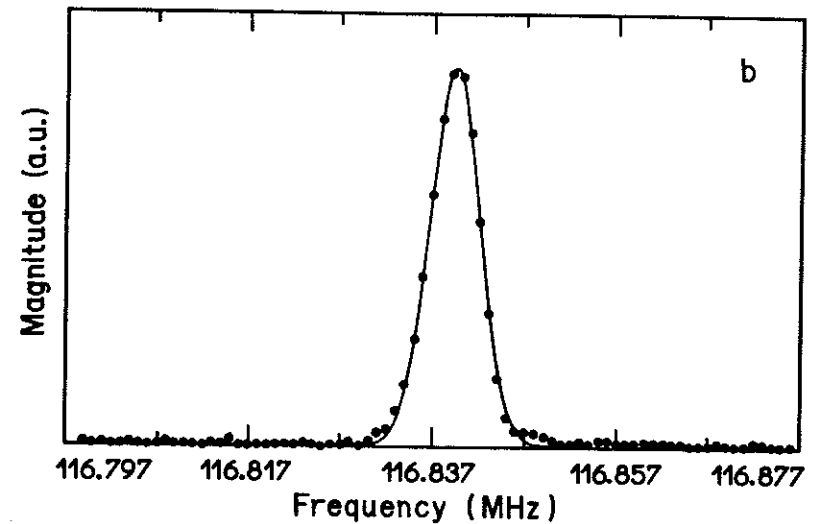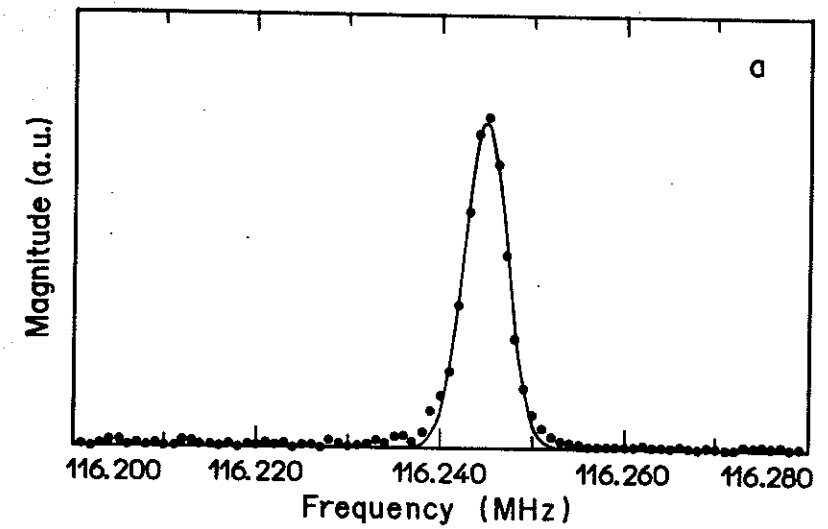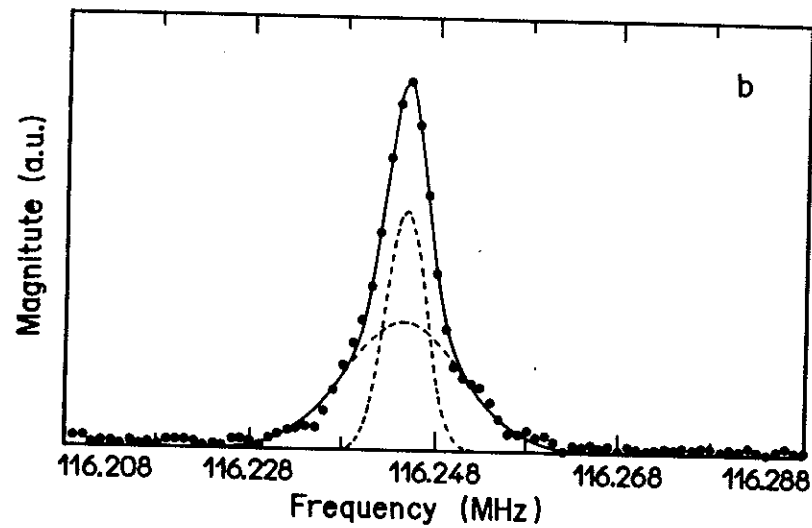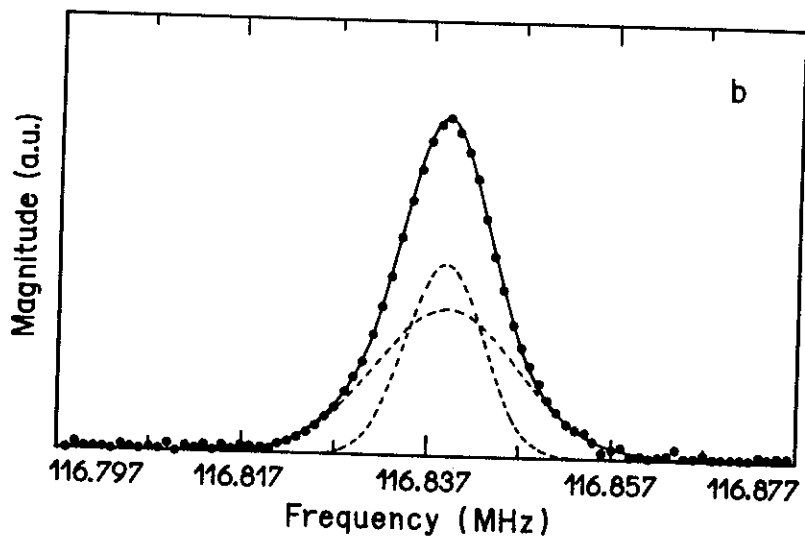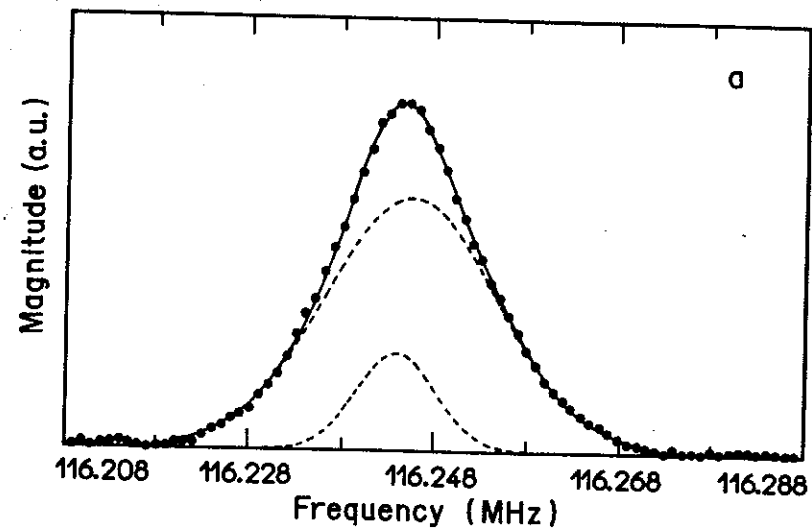
Fig. 2
Saïd R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 3
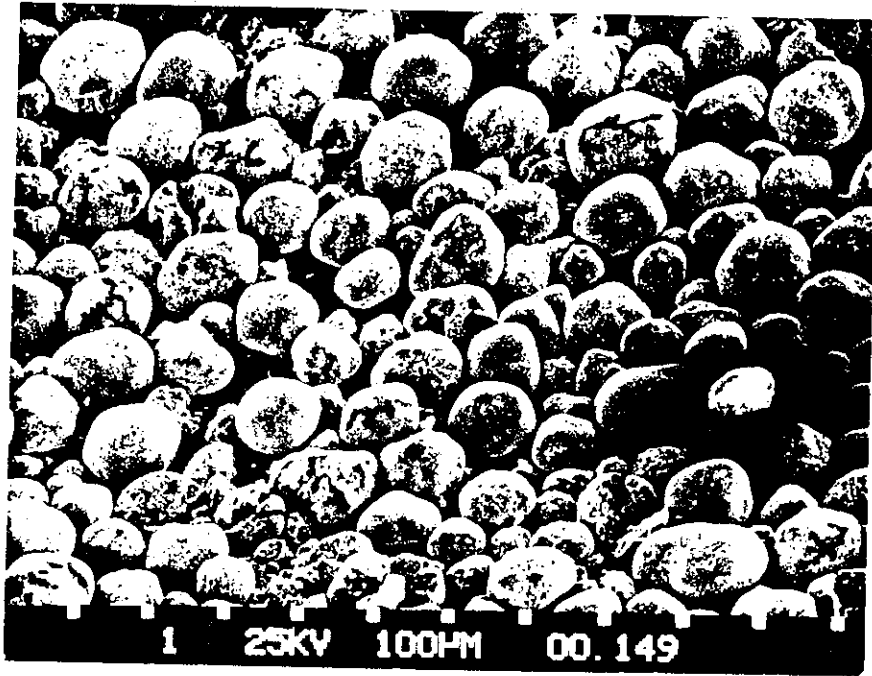Saïd R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 4a
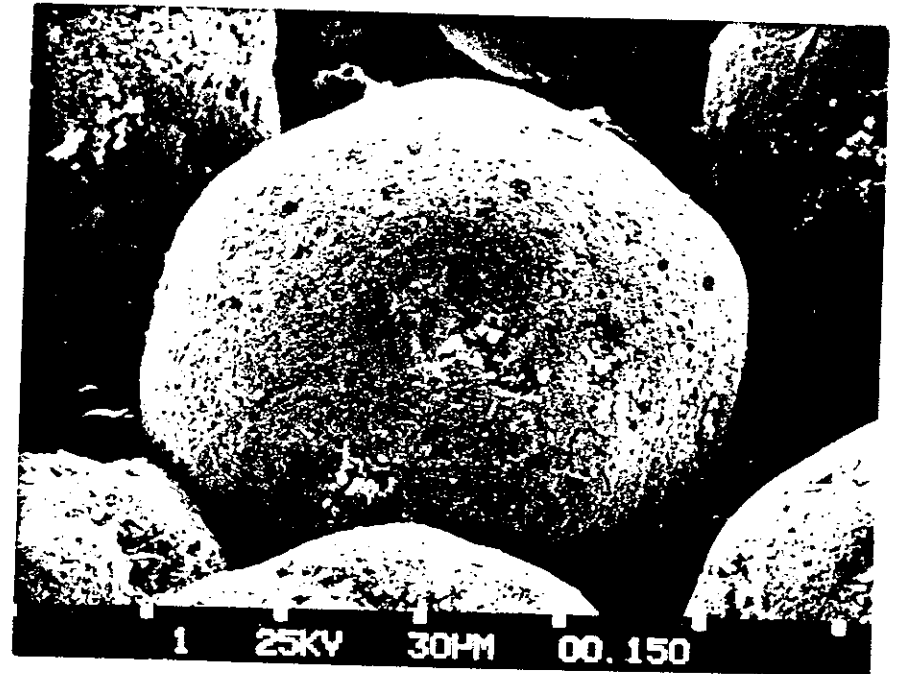Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 4b
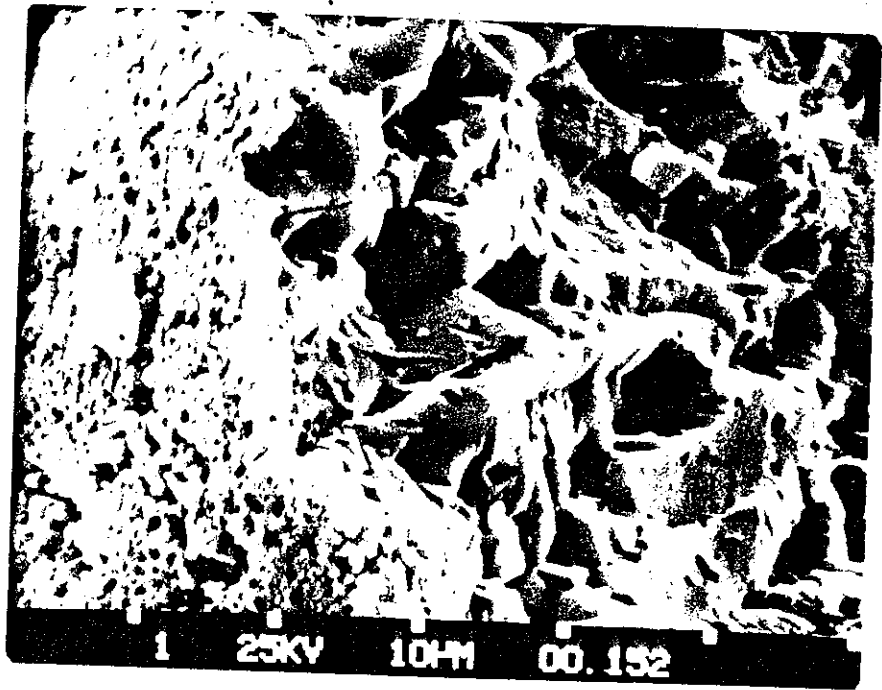Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 4c
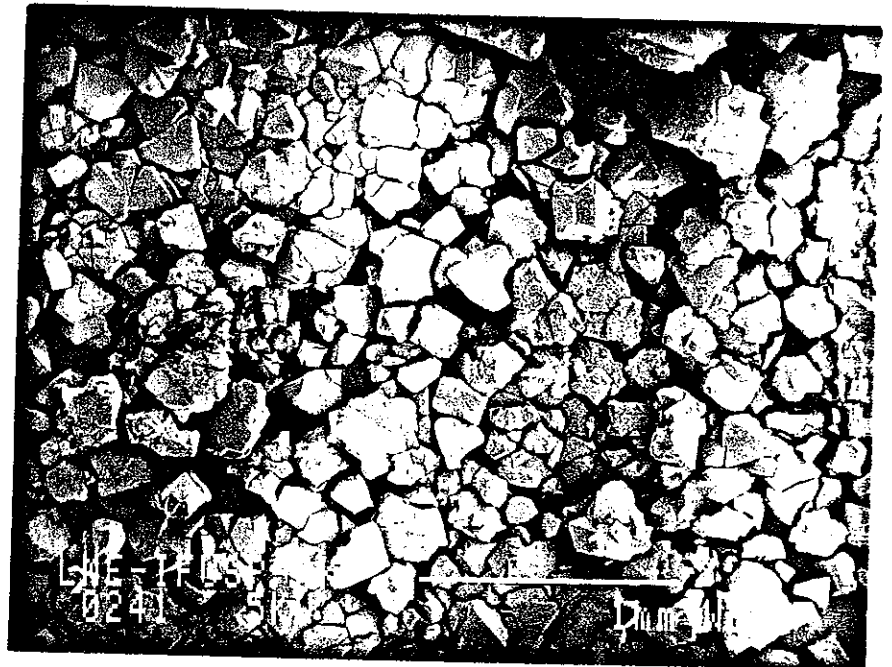Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 5a
Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 5b
Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."

Fig. 5c
Said R. Rabbani et.al. "Pure Nuclear Quadrupole ..."