

## Mössbauer-effect studies of the lattice dynamics of granular tin\*

S. Akselrod and M. Pasternak

*Physics Department, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel  
and Soreq Nuclear Research Centre, Yavne, Israel*

S. Bukshpan

*Soreq Nuclear Research Centre, Yavne, Israel*

(Received 28 May 1974)

The atomic mean-square displacement (MSD) of granular tin was studied by the Mössbauer effect. Tin grains with a 45-Å average size embedded in an oxide matrix were produced by evaporating the metal in the presence of O<sub>2</sub>. The lattice parameters and grain-size distribution were measured by electron microscopy. From the temperature variation of the MSD of the granular material, it was found that the  $\langle\omega^{-2}\rangle$  moment of the phonon spectrum increases by  $(8 \pm 3)\%$  with respect to the bulk. These results, combined with data of the hyperfine constants and electron microscopy suggest a quasi-isolated grain whose vibration frequency and electronic structure are barely altered and whose interaction with the surrounding oxide is negligible.

### I. INTRODUCTION

The lattice dynamics of microcrystals having a substantially high surface-to-volume ratio has become the subject of many theoretical and experimental investigations. The purpose of these studies was to predict and test the effects of the relatively large surface on the frequency distribution of the phonons of the microcrystal. Several investigations involving interactions of phonons with electrons, such as superconductivity<sup>1-3</sup> and tunneling experiments,<sup>4</sup> have suggested that modifications of the phonon spectrum, in its lower portion, had to be assumed in order to account for the results obtained for granular materials. Recently, low-temperature specific-heat measurements of lead grains in porous glass were reported by Novotny *et al.*<sup>5</sup> They observed a significant enhancement of the specific heat in samples with pore diameters of 22 and 37 Å. This phenomenon was attributed to the large surface-to-volume ratio of the grains.

A complementary quantity that probes the phonon spectrum is the atomic mean-square displacement. This probe differs from the specific heat in that it measures different moments of the phonon spectrum, and it is more sensitive to local microscopic variations.

Values of the mean-square displacement, (MSD)  $\langle x^2 \rangle$ , or of Debye-Waller factors, can be readily obtained from the Mössbauer effect (ME) through the recoil-free fraction of the nuclear  $\gamma$  resonance. In fact, since the early days of this relatively new spectroscopy technique, various measurements taken on microcrystals and amorphous materials have produced only controversial and inconclusive results.<sup>6</sup> With particles smaller than 100 Å, where the surface-to-volume ratio (S/V) begins to be significant, measurements done with gold<sup>7</sup> suggested a decrease in the MSD while a later work on tung-

sten particles<sup>8</sup> indicated an increase in the MSD. Very recently, Bogomolov and Klushin<sup>9</sup> reported measurements on Sn embedded in glass pores of 70 Å. Very strange results were obtained for the absolute value of the recoil-free fraction  $f$  at 80 °K and its variation at higher temperatures. As suggested by the authors, these results could be due to condensation of low-dimensional grains.<sup>10</sup>

In the present work we performed Mössbauer-effect (ME) measurements in both Sn grains of 45 Å average size and bulk Sn. Simultaneous measurement of the lattice parameters and grain-size distribution were carefully made and the results were correlated with the ME parameters. Experiments were performed in the "high-temperature" range of the MSD, namely, for  $T > \frac{1}{2}\Theta$ . The value of the  $(-2)$  moment of the phonon spectrum,  $\langle\omega^{-2}\rangle$ , was determined from the slope of  $\langle x^2(T) \rangle$  and compared with that obtained for bulk Sn. As will be shown, the combined experimental results provide evidence for the existence of quasifree  $\beta$ -Sn grains with lattice parameters equal, within the experimental errors, to the bulk parameters and with a slightly enhanced high-temperature mean-square displacement.

### II. EXPERIMENTAL PROCEDURES

#### A. Preparation of samples

The granular tin was prepared by condensing high-purity tin on an Al substrate at 85 °K. Tin was evaporated at a rate of 30 Å/sec in an O<sub>2</sub> atmosphere at a pressure of 10<sup>-4</sup> Torr. The presence of tin oxides inhibits the formation of large grains. In general, it was found that the above mentioned conditions were crucial for obtaining tin grains with diameters less than 70 Å. Under these conditions the granular material remained stable with respect to coalescence even for a period as

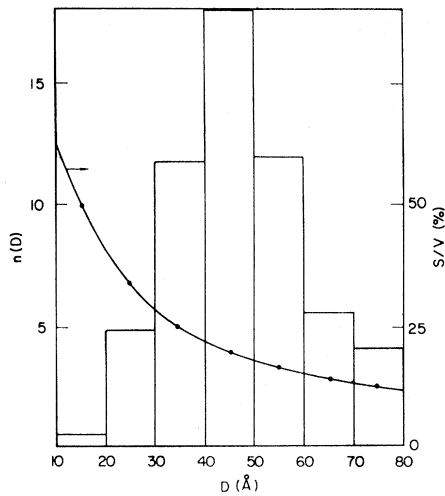


FIG. 1. Size-distribution histogram of a typical sample. The curve represents the surface-to-volume ratio dependence on grain size for Sn.

long as six months.

At each evaporation, three samples were *simultaneously* prepared: one for the ME measurements where the material was deposited over a large Al foil, the second for conductivity measurements will be discussed in a separate paper, and the third for electron microscopy measurements. The last two samples were rather thin films with 300-Å width and were formed under the same conditions as that for the ME measurements, by opening a special shutter for a short period of time during the evaporation. Altogether, three samples were used for each measurement.

#### B. Microstructure determination

Both the lattice parameters and the grain-size distribution were determined for the three samples. The lattice parameters were measured by recording several diffraction patterns with a JEM-7 electron microscope using a  $\text{TiCl}_3$  sample as a standard. The position of the lines were obtained by averaging over several patterns. It was found that the grains consist of  $\beta$ -Sn with lattice constants  $a = 5.82 \pm 0.01$  Å and  $c = 2.16 \pm 0.01$  Å which are the same within the experimental error as those for bulk Sn, as measured by Pearson<sup>11</sup> ( $a = 5.831$  Å and  $c = 3.176$  Å). The lines were substantially broadened which is characteristic of small microcrystals. The broadening established the uncertainty in the lattice-constant parameters. No lines indicating the presence of crystalline SnO and  $\text{SnO}_2$  could be found, suggesting that the oxides are in amorphous state. Recent diffraction measurements of granular Al (Ref. 3) also have shown that the lattice spacing is not affected by the grain size down to 35-Å diameter.

The grain-size distribution was obtained by means of dark-field microscopy using a JEM 100B electron microscope. Taking a random portion of the sample, 140 grains were checked on the photographic plate. The results were plotted in histogram form. A typical histogram (sample No. 15) is shown in Fig. 1. Very similar histograms were obtained for the other two samples.

#### C. Mössbauer measurements

The Mössbauer spectra were recorded with a conventional spectrometer using a  $\text{BaSnO}_3$  source. The absorbers containing 10  $\text{mg}/\text{cm}^2$  of material, were encapsulated in a lucite holder which was attached to an oven inside an evacuated chamber. Both the chamber and the source were immersed in liquid nitrogen. Measurements were performed at absorber temperatures above 78 °K.

### III. DISCUSSION AND CONCLUSIONS

When metallic Sn is evaporated in an oxygen atmosphere under the conditions described above, the size of the grains of Sn formed is limited by the presence of oxygen and oxides formed simultaneously as the matrix for Sn grains. The tin oxides, namely, SnO and  $\text{SnO}_2$  will show themselves in the absorption spectrum. Whereas Sn and  $\text{SnO}_2$  are characterized by single lines with different isomer shifts (i. s.), the SnO spectrum is composed of a doublet resulting from the quadrupole interaction at the  $^{119}\text{Sn}$  nucleus. Typical spectra for various temperatures (sample No. 19) are shown in Fig. 2. These composite spectra were analyzed by means of an appropriate least-squares-fit program with all the positions, linewidths, and intensity parameters allowed to vary freely. The only restrictions imposed were the requirements that the linewidths of both components of the SnO spectrum be the same and their intensities equal. The deduced parameters at 80 °K are given in Table I. The good quality of the fit suggests that no other oxidation states of Sn, apart from those mentioned, are present in the samples. It is interesting to note that despite the extremely small dimensions of the grains, with an average of 1300 atoms/grain, no significant differences are observed in the i. s. or the linewidth between the bulk and granular samples. The lack of appreciable broadening suggests that the symmetry around the Sn atoms is not altered as a result of possible penetration of surface defects. One might have expected that boundary conditions would affect the electronic structure of the grains. However we do not observe any change in the isomer shift, which is proportional to the s-electron density at the nucleus; we conclude that the electronic structure is unaffected by the smallness of the grains.

Another interesting observation concerns the

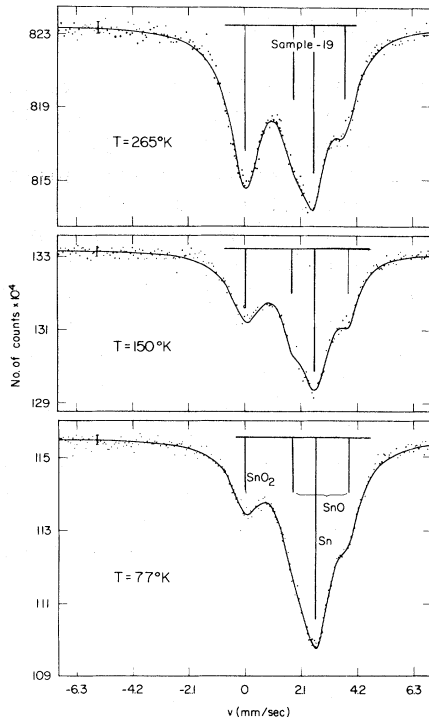


FIG. 2. Mössbauer absorption spectra of granular Sn (sample 19) at three different temperatures. The computer-fitted positions and relative intensities of the sample's constituents Sn, SnO, and SnO<sub>2</sub> are marked with vertical lines. The solid line through the experimental points is the least-squares-fitted spectrum.

magnitude of the quadrupole coupling constant of SnO. The layers of intergranular SnO are amorphous as is evident from the electron diffraction pattern and the micrographs. This suggests grain sizes of less than 20 Å. Nevertheless the quadrupole coupling constant and the i. s. remain the same as in the bulk. In fact, one may calculate the average number of oxide layers separating the grains. We assume from ionic-radii data that on the average the width of a layer is 2 Å. From the ME spectrum and knowledge of absolute  $f$  for the oxides and Sn metal we calculate, for sample 19,  $\text{Sn}/(\text{SnO} + \text{SnO}_2) = 3/2$ . Thus, for a 45-Å particle we find approximately six layers of oxides between grains.

The main objective of this work was to study the lattice dynamics of granular tin. This information is contained primarily in the recoil-free fraction  $f$  of the absorbing nucleus. In principle, it is possible to obtain the absolute value of  $f$  by measuring the area under the absorption peak. From the relation

$$f = e^{-k^2 \langle x^2 \rangle} \quad (1)$$

the absolute value of the mean-square displacement  $\langle x^2 \rangle$  is then obtained. However, in our case, since

TABLE I. The isomer shift (i. s.), quadrupole splitting (q. s.), and linewidth ( $\Gamma$ ) (in mm/sec) of the several constituents of sample 19 as well as of bulk Sn, at 80°K. The i. s. is with respect to a BaSnO<sub>3</sub> source at 80°K.

	Sn	SnO <sub>2</sub>	SnO	Sn(bulk)
i. s.	$2.69 \pm 0.03$	$0.025 \pm 0.02$	$2.82 \pm 0.03$	$2.59 \pm 0.01$
q. s.	...	...	$2.07 \pm 0.05$	...
$\Gamma$	$0.72 \pm 0.04$	$0.68 \pm 0.04$	$0.53 \pm 0.03$	$0.70 \pm 0.01$

the number of absorbing nuclei of each constituent is not known, this kind of information is unattainable. Nevertheless, one can measure the temperature dependence of the mean-square amplitude and within the high-temperature limit of the harmonic approximation one obtains from the slope of  $\langle x^2(T) \rangle$  the  $\langle \omega^{-2} \rangle$  moment of the phonon spectrum.

In the high-temperature region where  $kT > \frac{1}{2}h\omega_{\max}$  one can expand the expression for  $\langle x^2 \rangle$  in a series (Thirring expansion) where, to a good approximation, it will be linear with  $T$ , e. g.,

$$\langle x^2 \rangle = -2RkT \langle (\hbar\omega)^{-2} \rangle \quad (2)$$

or, in the Debye model,

$$\langle x^2 \rangle = -6RT/k\Theta^2, \quad (3)$$

where  $R$  is the recoil energy of the absorbing  $\gamma$  ray and  $\Theta$  is the Debye temperature. In fact, evidence for harmonic behavior of the grain will be the linear dependence of the effect on  $T$  on a logarithmic scale. In Fig. 3 we depict the temperature dependence of the area under the Sn absorption line. Within the error of measurements it is indeed linear. In Table II we give the average results of

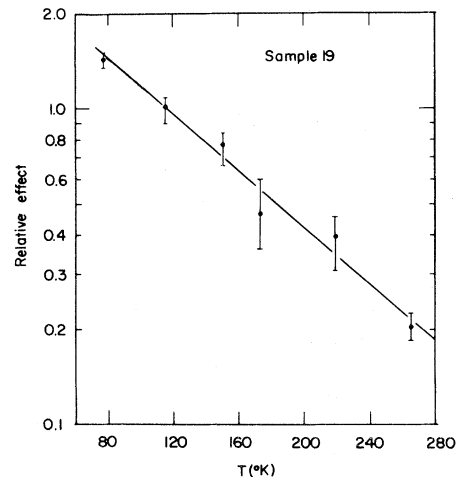


FIG. 3. Temperature dependence of the absorption peak of granular Sn. The straight line is a least-squares fit to the experimental points.

TABLE II. Values of  $\langle\omega^{-2}\rangle$  calculated from the slope of  $\langle x^2(T)\rangle$  using a least-squares-fit program. The values of the errors were obtained from the computer. The Debye temperature  $\Theta$  (see text) is proportional to  $(\langle\omega^{-2}\rangle)^{-1/2}$ .

Sample No.	$\langle\omega^{-2}\rangle(10^{-27} \text{ sec}^2)$	$\Theta$ ( $^{\circ}\text{K}$ )
15	$9.5 \pm 0.3$	$129 \pm 2$
18	$9.5 \pm 0.3$	$130 \pm 2$
19	$9.3 \pm 0.4$	$131 \pm 2$
bulk	$8.8 \pm 0.1$	$135 \pm 1$

$\langle\omega^{-2}\rangle$  and of  $\Theta$  for the granular samples and for bulk tin. These results were obtained by a least-squares fit of the linear curve. Our results for bulk tin agree very well with those obtained by Hohenemser.<sup>12</sup> One immediately sees that there is an increase in  $\langle\omega^{-2}\rangle$  with respect to the bulk, which is beyond the experimental error, and is the same in all three samples. This result shows that there is indeed a change in the phonon spectrum as detected by this high-temperature probe.

We consider the possibility of change in  $\Theta$  due to contraction or expansion of the grain's lattice. Within the uncertainty of our electron-diffraction measurements one can expect a deviation of 0.01 Å in the values of  $a$  and  $c$ . Making use of the Grüneisen relation, namely,  $\Delta\Theta/\Theta = -\gamma\Delta V/V$ , where  $\gamma$  is the Grüneisen constant, taken as 2 for Sn, and  $V$  is the grain's volume, we find that the change in  $\Theta$  is of the order of 1.5%. This is much smaller than our observed change in  $\Theta$ .

Let us assume that all the increase in  $\langle\omega^{-2}\rangle$  with respect to the bulk is due to surface effects only. Using a simple model we can then estimate values of the mean-square displacement at the surface. We assume each layer is characterized by its own  $\langle x^2 \rangle$  and to simplify it even more we assume that the major influence due to the boundary conditions affects only the first layer of the grain whereas the inner atoms behave as in the bulk. Consequently the measured  $f_G$  for the grains can be considered the result of a weighted average of  $f_B$  of the inner-bulk atoms and of  $f_S$  of the surface atoms, as follows:

$$f_G = \alpha f_B + (1 - \alpha) f_S, \quad (4)$$

where  $\alpha$  is the fractional number of atoms inside the grain. The value of  $\alpha$  can be estimated with the aid of the histogram as shown in Fig. 1. The surface to volume ratio  $S/V(D)$  is calculated for each grain diameter  $D$  and the average value is found according to

$$\langle S/V \rangle = \sum n(D)S/V(D), \quad (5)$$

where  $n(D)$ , the normalized size distribution values are taken from the histogram. We find for all three of our samples that  $\langle S/V \rangle = 0.2$  or that 20% of the atoms are at the surface. From expressions (1) and (2) we calculate the values of  $f_G$  and  $f_B$  by using the values of  $\langle\omega^{-2}\rangle$  from Table II. By inserting them in expression (4) we can obtain the value of  $f_S$  and from it the "surface Debye temperature"  $\Theta_S$ . These values were calculated for various temperatures; for 100  $^{\circ}\text{K}$ ,  $\Theta_S = 114$   $^{\circ}\text{K}$  and for 200  $^{\circ}\text{K}$ ,  $\Theta_S = 117$   $^{\circ}\text{K}$ . This result represents an increase on  $\langle\omega^{-2}\rangle$  of 37%, or  $\langle x^2 \rangle_S / \langle x^2 \rangle_B = 1.4$ . It should be emphasized that these calculations are based on the assumption of a perfect "bulk behavior" for layers beyond the first one. In reality, one might take into account the influence of the boundary effect in the second and probably the third layer. Unfortunately, there are no available calculations of mean-square displacements for grains. Nevertheless, it is interesting to compare our results with those obtained by Chen *et al.*<sup>13</sup> whose calculations were performed for a semi-infinite slab of NaCl, using a quasiharmonic approximation on 15 layers. The values of  $\langle x^2 \rangle_S / \langle x^2 \rangle_B$  at 100 and 200  $^{\circ}\text{K}$  were found to be 1.30 and 1.33, respectively, agreeing remarkably well with our results. One should bear in mind that for a grain, the surface-to-volume ratio is higher than in a thin slab, resulting in a further enhancement in the ratio of  $\langle x^2 \rangle$ . Another interesting calculation in Ref. 11 provides the values of the ratio of the second and third layer to bulk. At 300  $^{\circ}\text{K}$  they are found to be 1.1 and 1.03, respectively. These results confirm our assumption that beyond the first layer the surface effects decrease rapidly.

The substantial increase of the  $\langle x^2 \rangle_S$  as obtained from our experimental results suggests that the bonding of the grain to its surrounding matrix (trapped  $\text{O}_2$  and oxides) is fairly weak. This conclusion, combined with the previously discussed findings of the isomer shift and electron diffraction, is consistent with a picture of an isolated grain that, apart from its first layer, is barely different from bulk material in its interatomic distances, lattice symmetry, electron structure, and vibrational frequencies.

#### ACKNOWLEDGMENT

We are indebted to E. Grünbaum for his valuable assistance with the electron microscopy and fruitful discussions.

\*Research supported in part by grants of the International Atomic Energy Agency No. 1446/RB and Israel Academy of Science and Humanities.

<sup>13</sup>M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglas, and M. A. Jensen, Phys. Rev. Lett. 21, 1320 (1968).

- <sup>2</sup>J. J. Hauser, Phys. Rev. B 3, 1611 (1971).
- <sup>3</sup>G. Deutscher, H. Fenichel, M. Gershenson, E. Grünbaum, and Z. Ovadyahu, J. Low Temp. Phys. 10, 231 (1973).
- <sup>4</sup>M. Strongin, Physics 55, 155 (1971).
- <sup>5</sup>V. Novotny, P. P. Meincke, and J. H. P. Watson, Phys. Rev. Lett. 28, 901 (1972).
- <sup>6</sup>An extensive review on experimental and theoretical studies on this subject is given by D. Schroer, in *Mössbauer Effect Methodology*, edited by J. J. Gruverman (Plenum, New York, 1969), Vol. 5, p. 141.
- <sup>7</sup>S. W. Marshall and R. M. Wilenzick, Phys. Rev. Lett. 16, 219 (1966).
- <sup>8</sup>S. Roth and E. M. Hörli, Phys. Lett. A 25, 299 (1967).
- <sup>9</sup>V. N. Bogomolov and N. D. Klushin, Fiz. Tverd. Tela 15, 514 (1973) [Sov. Phys. -Solid State 15, 357 (1973)].
- <sup>10</sup>J. P. Suzdalev, M. Ya. Gen, V. I. Gol'danskii, and E. F. Makarov {Zh. Eksp. Teor. Fiz. 51, 118 (1966) [Sov. Phys. -JETP 24, 79 (1967)] reported a dramatic decrease in the absolute value of  $f$  for Sn microcrystals with 250-Å diameters. The corresponding decrease of 15% in  $\Theta$  as compared to bulk value is very unreasonable due to the fact that even for their smallest microcrystals (250 Å) only ~4% of the atoms are at the surface. Furthermore, the drastic decrease in the absolute value of  $f$  should have resulted in an increase in the slope of  $f(T)$  vs  $T$  which cannot be detected from the curves shown in this paper.
- <sup>11</sup>W. P. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, Oxford, 1964/67).
- <sup>12</sup>C. Hohenemser, Phys. Rev. A 139, 185 (1965).
- <sup>13</sup>T. S. Chen, G. P. Alldredge, F. W. de Wette, and R. E. Allen, Phys. Rev. B 6, 623 (1972).