Two types of tunnelling state in fast-neutron irradiated bulk silicon?

2000 J. Phys.: Condens. Matter 12 8135

(http://iopscience.iop.org/0953-8984/12/37/312)

J. Phys.: Condens. Matter **12** (2000) 8135–8143. Printed in the UK PII: S0953-8984(00)14837-4

Two types of tunnelling state in fast-neutron irradiated bulk silicon?

M Coeck† and C Laermans‡

† SCK–CEN, Boeretang 200, B-2400 Mol, Belgium

‡ KULeuven, Department of Physics, Celestijnenlaan 200D, B-3000 Leuven, Belgium

Received 20 June 2000, in final form 4 August 2000

Abstract. Ultrasonic attenuation measurements were performed on fast-neutron irradiated bulk silicon. The data are analysed in the framework of the tunnelling model. Good agreement was found with the results obtained from earlier measurements of the changes in ultrasonic velocity, performed on the same samples, and the presence of tunnelling states in this material was confirmed. More detailed analysis however gives an indication of the presence of two different types of tunnelling state.

1. Introduction

At low temperatures, amorphous and partly disordered solids show thermal [1], dielectric [2] and acoustic [3] properties that are different from those in crystals. These anomalies are universal: experiments carried out in a wide range of non-crystalline solids showed similar properties which turned out to be only slightly sensitive to structure, chemical composition and impurity content of the material.

To describe these anomalies several theoretical models were suggested. The first model that was able to give a correct description of all dynamic properties at low temperatures was the tunnelling model, developed in 1972 simultaneously by Anderson *et al* [4] and Phillips [5]. This model is based on the presence of low-energy excitations—tunnelling states (TSs)—which are characterized by a broad distribution of energies and relaxation times. It involves atoms or groups of atoms which can have two equilibrium positions and can tunnel in a double asymmetric potential well. In spite of its success, the tunnelling model is purely phenomenological, giving no indication on the microscopic origin of the tunnelling states.

The existence of tunnelling defects has been discovered in many different kinds of material such as glasses, polymers and a-Se. Also in neutron- and electron-irradiated single-crystalline SiO_2, tunnelling states were observed.

In this model, an ‘open structure’ (e.g. a wide range of bond angles) is required to host tunnelling states. As put forward by Phillips [5] highly coordinated networks exhibit very high potential barriers that inhibit tunnelling motions and reduce the number of tunnelling states. Therefore it was believed that tunnelling states could only occur in amorphous solids with a low average coordination of the individual atoms. The question of whether low-energy excitations can also appear in higher coordinated networks such as fourfold coordinated amorphous silicon or germanium is of great importance with respect to the physical nature of the low-temperature tunnelling process.

In order to contribute to this discussion concerning the presence of tunnelling states in high-coordinated materials, we started a study on partly disordered silicon. To avoid the consequences of sputtered amorphous films [6, 7], we used *bulk* silicon for our experiments. From previous studies performed on neutron-irradiated quartz [8, 9] it is clear that the use of fast-neutron irradiation is an appropriate method to induce TSs in bulk material. Since bulk amorphous silicon is not available, we used the same approach and exposed our bulk single-crystalline starting material to high fast-neutron doses.

In spite of its high coordination it is possible to obtain partly disordered silicon by means of fast-neutron irradiation [10]. From earlier measurement of the changes of the ultrasonic velocity in neutron-irradiated silicon, evidence was found for the introduction of TSs by means of fast-neutron irradiation in silicon [11].

2. Tunnelling model

The tunnelling model was developed in 1972, simultaneously by Anderson *et al* [4] and Phillips [5], in order to describe the anomalous dynamical properties of amorphous solids at low temperatures. Despite its success, this model gives no indication whatsoever of the microscopic origin of the TSs. The basic idea of this model is that in an amorphous solid, the structural disorder allows atoms or groups of atoms to have two equilibrium positions. The entities can tunnel in a double asymmetric potential well and are therefore called tunnelling states (TSs).

In a single well, the vibrational states of each particle are separated by an energy $\hbar\Omega$. To describe the low-temperature properties, only the ground state of each well has to be taken into account. The overlap of the wavefunctions is represented by λ:

$$\lambda = d\sqrt{2mV/\hbar^2} \tag{1}$$

where V represents the height of the potential barrier between the wells, d is the distance between the two wells and m is the mass of the particle. Because of this coupling, tunnelling becomes possible. In this case the ground state will not only be split due to the asymmetry parameter Δ which represents the energy difference between the two minima of the wells, but a tunnel splitting $\Delta_0 = \hbar\Omega\exp(-\lambda)$ occurs. The total level splitting of the ground state can then be written as

$$E = \sqrt{\Delta^2 + \Delta_0^2}.$$

One of the basic assumptions of the tunnelling model is that Δ and λ are independent of each other and are distributed uniformly: $P(\Delta, \lambda)\,\mathrm{d}\Delta\,\mathrm{d}\lambda = \bar{P}\,\mathrm{d}\Delta\,\mathrm{d}\lambda$, with $\bar{P}$ a constant representing the density of states of the tunnelling states. Since λ depends on different quantities such as m, V and d, a uniform distribution of λ seems to be rather unlikely, however, this assumption leads to a surprisingly good agreement between theory and experiment, and this for a wide range of amorphous materials.

When an elastic field is introduced in an amorphous solid containing TSs, the double well will be modified. This results in a change in the asymmetry parameter Δ and the energy overlap Δ_0. The tunnelling model assumes that possible variations of Δ_0 are of minor importance compared to changes in Δ, which are written as

$$\delta(\Delta) = \frac{\partial\Delta}{\partial e}e = 2\gamma e \qquad \text{where } \gamma = \frac{1}{2}\frac{\partial\Delta}{\partial e}.$$

Here, e is the strain field and γ represents the coupling parameter, describing the coupling between the elastic field and the tunnelling states.

Due to the interaction between the elastic field and the TSs, transitions between the two lowest levels become possible through absorption or emission of phonons. Two processes have to be taken into account here: the resonant and the relaxation process. The resonant process results from the disturbance of the equilibrium distribution of the thermal phonons by an acoustic wave with energy $\hbar\omega$. Relaxation to equilibrium is established through resonant absorption or emission of phonons by those tunnelling states with an energy difference $E = \hbar\omega$. Because of the wide distribution of the energy splitting, this process takes place at all frequencies. It leads to an attenuation [12, 13]

$$\alpha_{res} = \frac{C}{v_l}\omega\pi(1 + I/I_c)^{-1/2}\tanh\left(\frac{\hbar\omega}{2kT}\right) \qquad \text{with } C = \frac{\bar{P}\gamma_l^2}{\rho v_l^2}$$

where v_l is the longitudinal velocity, I and ω represent the intensity and the angular frequency of the ultrasonic wave, ρ is the mass density and γ_l describes the coupling of the tunnelling states with the longitudinal phonons. It is clear that, sufficiently below a critical intensity I_c, the attenuation will be independent of the intensity I. If I increases, the population of the levels will gradually be equalized and the absorption will decrease. This results in a negligible attenuation for high intensities: the so-called 'saturation of the acoustic attenuation'.

The relaxation process results from changes in the occupation of the tunnelling states themselves. When an elastic wave is applied, the asymmetry parameter Δ and thus the energy splitting E of the tunnelling states will be modified. In this way, the thermal equilibrium distribution of the tunnelling states is disturbed. Relaxation to equilibrium is established through interaction with thermal phonons. At low temperatures, the one-phonon process dominates, giving rise to a relaxation rate

$$\tau^{-1} = K_3\left(\frac{\Delta_0}{E}\right)^2\left(\frac{E}{2k}\right)^3\coth\left(\frac{E}{2kT}\right)$$

with

$$K_3 = \frac{4k^3}{\rho\pi\hbar^4}\sum_i\frac{\gamma_i^2}{v_i^5}.$$

This summation covers all polarizations. Hence, the parameter K_3 describes an average coupling, but can be simplified for isotropic solids to

$$K_3 = \frac{4k^3}{\rho\pi\eta^4}\left(\frac{\gamma_l^2}{v_l^5} + \frac{2\gamma_t^2}{v_t^5}\right)$$

where the indices l and t refer to the longitudinal and transverse modes respectively.

Taking into account the distribution of the relaxation times, the relaxational attenuation can be expressed as [14].

$$\alpha_{rel} = \frac{\gamma_l^2}{\rho v_l^3 kT}\int_{E_{\min}}^{E_{\max}} \mathrm{d}E\int_{u_{\min}}^{l}\frac{\omega^2\tau}{1+\omega^2\tau^2}\frac{\bar{P}}{u(1-u^2)^{1/2}}\left(\frac{\Delta}{E}\right)^2\operatorname{sech}^2(E/2kT)\,\mathrm{d}u.$$

This equation can be analytically solved in the case of $\omega\tau_m \ll 1$ and $\omega\tau_m \gg 1$, with τ_m the minimal relaxation time [14]. In the $\omega\tau_m \gg 1$ regime the relaxational attenuation can than be written as

$$\alpha_{rel} = \frac{\pi^4}{96}C\frac{K_3}{vl}T^3 = \frac{\pi^3k^3\bar{P}\gamma_l^2}{24\rho^2\hbar^4 v_l^3}\left(\frac{\gamma_l^2}{v_l^5} + \frac{2\gamma_t^2}{v_t^5}\right)T^3.$$

The $\omega\tau_m \ll 1$ condition holds at higher temperatures. In this range, the attenuation can be expressed as

$$\alpha_{rel} = \frac{\pi\omega}{2v_l}C = \frac{\pi}{2}\frac{\bar{P}\gamma_l^2}{\rho v_l^3}\omega.$$

At still higher temperatures Raman processes [14] and thermal activation have to be taken into account.

3. Samples and experimental details

We used bulk pure single-crystalline CZ silicon samples, unirradiated (Si-0) or irradiated with fast-neutron doses up to 1.7×10^{21} n cm^{-2} (Si-2) and 3.2×10^{21} n cm^{-2} (Si-4). The samples are cylindrically shaped, with a diameter of 3 mm and a length of 15 mm. In agreement with the requirements for hypersonic studies, the faces of the samples are polished to a flatness of $\lambda/10$ and are parallel within $2''$. The rod axis is parallel to the crystallographic [100] axis within $2'$. Using a hydrostatic method, the mass density was measured. For the unirradiated material a density of 2.333 ± 0.004 g cm^{-3} was measured and for the irradiated samples we obtained values of 2.326 ± 0.001 and 2.327 ± 0.002 g cm^{-3} for Si-2 and Si-4 respectively. These very small changes are in agreement with an expansion of 0.3%.

For the performance of the ultrasonic measurements, a piezoelectric transducer ($LiNbO_3$) was attached to one end of the samples, to transform the applied electromagnetic pulse into an acoustic wave.

4. Qualitative analysis

Ultrasonic attenuation measurements on Si-0 [15] show that below 28 K no attenuation change is detected within the accuracy of our measurement. The sensitivity is, for this measurement, better than 0.003 dB cm^{-1} and therefore, below 28 K, the attenuation change is below this value. For higher temperatures a very steep rise is observed, which levels off beyond approximately 100 K. The behaviour of the attenuation in the unirradiated silicon is similar to the response found for the hypersonic attenuation in many dielectric crystals. This result confirms that the unirradiated starting material used for this experiment is single crystalline and that it contains no defects that lead to a measurable contribution to the ultrasonic attenuation at very low temperatures.

Figure 1 presents the influence of fast-neutron irradiation on the behaviour of the ultrasonic attenuation as a function of temperature. While for the unirradiated sample no changes in attenuation are measurable below 28 K, the irradiated sample shows a steep increase from 0.3 K to approximately 10 K, after which a temperature-independent part is observed.

The influence of the frequency of the ultrasonic wave is shown in figure 2. It represents a double-logarithmic plot of the results of ultrasonic attenuation measurements, performed at 155 and 280 MHz. A temperature-independent background attenuation α_0 of 0.175 and 0.189 dB cm^{-1} respectively was subtracted. Both measurements show the same qualitative behaviour: a T^3-dependence is observed from 0.3 K to about 1.5 K, after which a levelling off to a temperature-independent part is detected. The T^3-dependence is independent of the frequency, in agreement with the predictions by the tunnelling model in the $\omega\tau_m \gg 1$ regime. Above 1.5 K the attenuation becomes dependent on the frequency. This is the transition region between the $\omega\tau_m \gg 1$ and the $\omega\tau_m \ll 1$ regime. The attenuation at the temperature-independent 'plateau' increases linearly with the frequency, which is also in agreement with the predictions made by the tunnelling model for the $\omega\tau_m \ll 1$ regime.

To obtain information concerning the influence of the neutron dose on the amount of TS present in the material, additional measurements were performed on sample Si-2. This sample was irradiated up to a dose of 1.7×10^{21} n cm^{-2}, which is approximately half of that of Si-4. Figure 3 shows the data obtained from attenuation measurements performed on Si-2 and Si-4 at

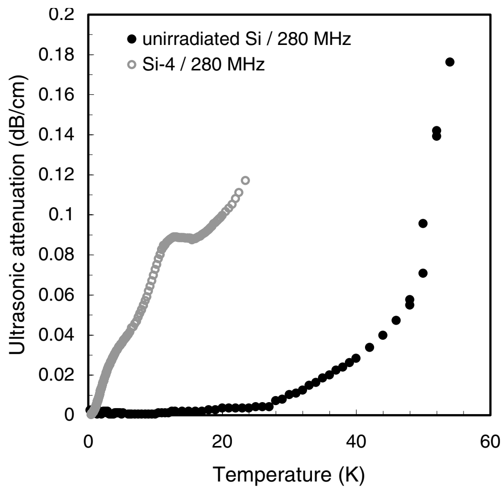

Figure 1. Ultrasonic attenuation as a function of temperature for pure and neutron-irradiated silicon.

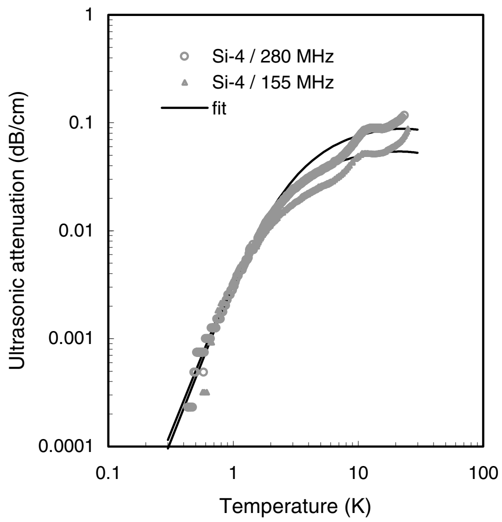

Figure 2. Ultrasonic attenuation as a function of temperature for different frequencies. The fit based on the TM equations using one type of TS is added.

frequencies of 165 and 155 MHz respectively. The background attenuation subtracted is 0.520 and 0.175 dB cm^{-1}. The qualitative behaviour of Si-2 is the same as that of Si-4. However, for the lower dose only a slight shoulder is observed at higher temperatures, whereas for the higher dose a plateau can clearly be seen. This is due to the very small attenuation exhibited by Si-2. The fact that the attenuation is higher for a higher neutron dose indicates that the density of states of the tunnelling states increases with increasing neutron dose.

This outcome, i.e. the similarity with the predictions of the tunnelling model, suggests the presence of tunnelling states in neutron-irradiated silicon. It is in agreement with the results obtained from earlier reported ultrasonic velocity measurements performed on the same samples [11].

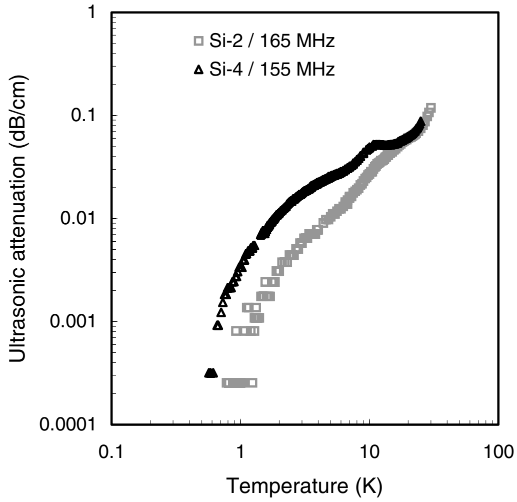

Figure 3. Behaviour of the ultrasonic attenuation as a function of temperature for two different irradiation doses.

5. Quantitative analysis

Since the measurements performed on Si-4 are the most accurate ones, our quantitative analysis will be performed on Si-4 data. As already seen in figure 2 the attenuation curves show a T^3-behaviour at the lowest temperatures, levelling off to a T-independent plateau at higher temperatures. These two characteristics can be well fitted. The height of the plateau, here equal to 0.09 and 0.05 dB cm^{-1} for the highest and lowest frequency respectively, determines the parameter C. K_3 is derived from the position of T^3. The calculated tunnelling parameters, from numerical fits to the tunnelling model, are given in table 1. Independent of the used frequency the parameters appear to be equal within the given accuracy. This indicates the internal consistency of the analysis of the performed attenuation measurements.

Table 1. Tunnelling parameters obtained from numerical fits on attenuation curves. The accuracy for C and $\bar{P}\gamma_l^2$ is 10%, for K_3, $\bar{P}$ and γ_l 30%.

Attenuation measurements performed on sample:	Si-4	Si-4
Neutron dose: (n cm^{-2}) ($E > 0.1$ MeV)	3.2×10^{21}	3.2×10^{21}
Frequency (MHz)	155	280
Height of plateau (dB cm^{-1})	0.05	0.09
C ($\times 10^{-6}$)	7.5	6.9
K_3 ($\times 10^7$ K^{-3} s^{-1})	11	10
$\bar{P}\gamma_l^2$ ($\times 10^6$ g cm^{-1} s^{-2})	12	11
γ_l (eV)	1.5	1.4
$\bar{P}$ ($\times 10^{29}$ erg^{-1} cm^{-3})	22	22

Comparing the absolute values determined from the attenuation data and those obtained from the velocity data [11], a discrepancy can be seen. This dissimilarity has been observed for most amorphous solids and also previously obtained values from fits performed on neutron-irradiated quartz data show these differences. This difference in fit parameters is one of the

Table 2. Parameters of two types of TS of which the effect is represented in figure 4.

	C ($\times 10^{-6}$)	K_3 ($\times 10^7$ K^{-3} s^{-1})	$\bar{P}\gamma_l^2$ ($\times 10^6$ g cm^{-1} s^{-2})	γ_l (eV)	$\bar{P}$ ($\times 10^{29}$ erg^{-1} cm^{-3})
TS 1	4.1	18	7	1.9	7
TS 2	2.8	0.01	5	0.05	6×10^3

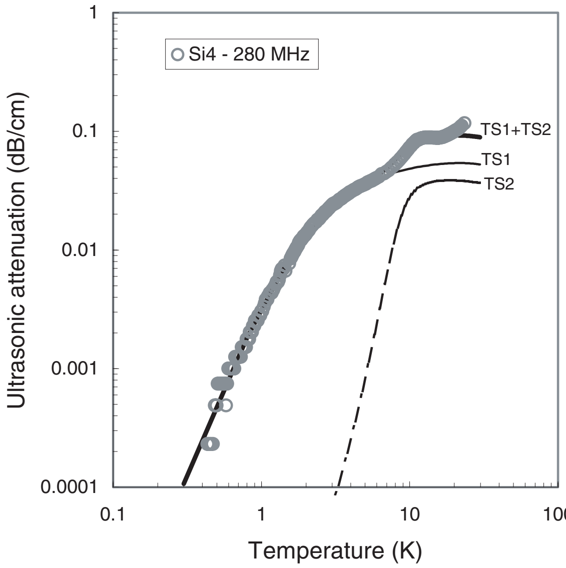

Figure 4. Fit to the experimental data of the ultrasonic attenuation using two different types of tunnelling state.

shortcomings of the tunnelling model. It is related to the wide distribution of relaxation times [16]. It is explained by the fact that tunnelling states with different relaxation times are involved: low relaxation times for attenuation measurements and higher ones for velocity measurements.

It should also be noted here that from these fits a relatively high value for the coupling parameter is found compared to the values obtained in amorphous solids. This observation is also discussed in [17].

Although the T^3 dependence at the lowest temperatures and the temperature-independent plateau at higher temperatures can be well fitted, the fit curves show a substantial deviation from the experimental data around 7 K. Around this temperature our data show an additional dip, which is not predicted by the tunnelling model and which is consequently not fitted well by the method described above.

A first possible explanation for the dip is related to the higher order phonon processes such as the Raman process, of which it can be assumed that they set in at approximately 7 K. Since, in the attenuation of silicon, a levelling off sets in at already 1.5 K, the effect of the higher order phonon processes becomes more pronounced around 7 K than in for example neutron-irradiated quartz, where the levelling off is observed at higher T. Furthermore this explanation can also be used to clarify the rather broad maximum observed in the velocity data of neutron-irradiated silicon [11]. When it is assumed that the one phonon processes (leading to a broad maximum) dominates the behaviour until approximately 7 K and beyond this temperature the Raman processes (making the maximum sharper and the decrease after it

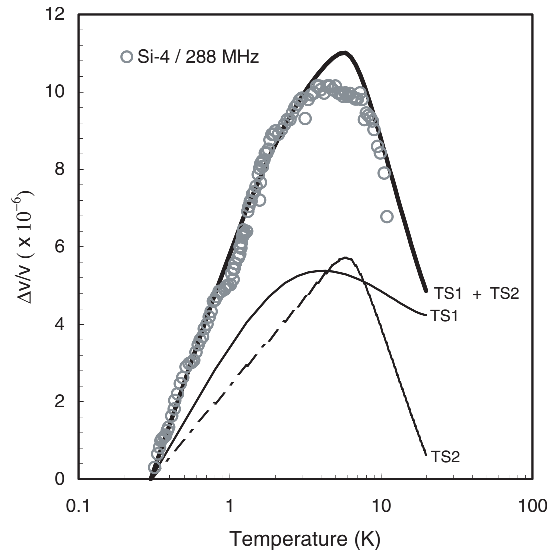

Figure 5. Fit of the ultrasonic velocity measurements using two different types of TS.

steeper) set in, a behaviour such as the one presented in [11] can be obtained.

A second explanation assumes that there are two different kinds of tunnelling state present in the material. Figure 4 shows the data obtained on Si-4 at a frequency of 280 MHz as well as the sum of two theoretically obtained curves, each representing the effect of one kind of tunnelling state on the ultrasonic attenuation. It is clear from this figure that, assuming the presence of two types of TS, a similar feature can be obtained in the behaviour of α. The typical parameters for both types of tunnelling state are given in table 2. For the curve associated with the second TS, we did take into account high-order Raman processes which 'sharpen' the levelling off to the plateau.

The parameters associated with TS1 are of the same order as the ones obtained from a fit that assumes that only one type of TS is present. From this it can be concluded that the main contribution comes from this type of TS. TS2 represents a totally different type with a very small coupling constant and a large density of states. This DOS is of the order of 10^{16} to 10^{17} cm^{-3}, which is comparable to the concentration of P atoms due to neutron transmutation ($\sim 3 \times 10^{17}$ cm^{-3}) or impurities such as C ($\sim 10^{16}$ cm^{-3}). Therefore the second type of TS might be associated with impurities or point defects.

It should also be mentioned here that taking into account two types of TS with the parameters of table 2, together with the discrepancy between tunnelling parameters obtained from attenuation and velocity measurements as discussed previously, the behaviour of the ultrasonic velocity measured for Si-4 at 288 MHz can also be very well simulated. The results of these calculations are presented in figure 5.

6. Summary and conclusions

From ultrasonic attenuation data obtained from an unirradiated bulk single-crystalline silicon sample it was clear that no indications were seen for the presence of tunnelling states. Comparing these results with the ones obtained from irradiated silicon, it could be concluded that due to fast-neutron irradiation a large additional effect is introduced in both attenuation and changes in velocity. Studying the temperature and frequency dependence, it was found that its behaviour at low temperatures is in agreement with the predictions of the tunnelling model that is put forward for amorphous solids. Numerical fits based on this tunnelling model were carried out. The qualitative behaviour of the ultrasonic attenuation and velocity at low temperatures together with the consistency of our fits (and the fact that our samples are partly amorphous as concluded from Raman data [10]) gave clear evidence for the fact that due to fast-neutron irradiation, tunnelling states are introduced in silicon.

A new feature, never observed before, is the dip in the attenuation data that is seen around 7 K. It is not a typical feature observed in the low-temperature behaviour of amorphous solids and is not described by any theoretical model. We explained the presence of this dip giving two possible explanations. The presence of two types of TS in the material under study is put forward as most likely being the cause of the dip.

References

[1] Zeller R C and Pohl R O 1971 *Phys. Rev.* B **4** 2029
[2] von Schickfus M, Hunklinger S and Piché L 1975 *Phys. Rev. Lett.* **35** 876
[3] Piché L, Maynard R, Hunklinger S and Jäckle J 1974 *Phys. Rev. Lett.* **32** 1426
[4] Anderson P W, Halperin B I and Varma C M 1972 *Phil. Mag.* **25** 1
[5] Phillips W A 1972 *J. Low Temp. Phys.* **7** 351
[6] Graebner J E and Allen L C 1984 *Phys. Rev.* B **29** 5626
[7] von Haumeder M, Strom V and Hunklinger S 1980 *Phys. Rev. Lett.* **44** 84
[8] Vanelstraete A and Laermans C 1990 *Phys. Rev.* B **42** 5842
[9] Keppens V and Laermans C 1995 *Phys. Rev.* B **51** 8158
[10] Coeck M, Laermans C, Provoost R and Silverans R E 1997 *Mater. Sci. Forum* **258–263** 623
[11] Coeck M and Laermans C 1998 *Phys. Rev.* B **58** 6708
[12] Hunklinger S and Arnold W 1976 *Physical Acoustics* vol 12, ed W P Mason and R N Thurston (New York: Academic) p 155
[13] Jäckle J 1972 *Z. Phys.* B **257** 212
[14] Doussineau P, Frénois C, Leisure R G, Levelut A and Prieur J Y 1980 *J. Physique* **41** 1193
[15] Laermans C and Coeck M 1996 *Czech J. Phys.* **46** 2225
[16] Raychaudhuri A K and Hunklinger S 1984 *Z. Phys.* B **57** 113
[17] Coeck M, Laermans C and Peeters E 1998 *Nucl. Instrum. Methods* B **141** 585