Journal of Alloys and Compounds, *211/212* (1994) 349–351
JALCOM 023

Ultrasonic attenuation in α-quartz as a result of E′ defect centres

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Abstract

The ultrasonic attenuation (acoustic losses) in α-quartz as a result of relaxation processes at E′ series defect centres is calculated. For this purpose use is made of the theoretical temperature dependences of the E′ relaxation time, reported elsewhere, based on the pseudo-Jahn–Teller effect and the reaction rate method. A comparison is made of the temperature curve of the acoustic losses at 5 MHz with a literature experimental loss curve of an AT-cut quartz resonator measured following irradiation with neutrons.

1. Introduction

It is well known that point defects such as acoustic loss (AL)-associated and H-related defect centres lead to ultrasonic attenuation (acoustic losses) in natural and synthetic quartz [1, 2]. Oxygen vacancies (E′ defect centres) are also an important class of defects in quartz. Stable E′ defects are known to form upon irradiation with high energy particles in knock-on collisions [1]. From a fundamental point of view these structural defects should also bring about acoustic losses. The aim of this paper is to calculate the acoustic losses due to the relaxation behaviour of these defect centres.

2. E′ defect centres modelling

Figure 1 shows structural models for defects of the E′ series as well as the ideal lattice of α-quartz for comparison. An E′ centre obtaining as an O atom bridging two SiO_3 tetrahedra is removed and substituted for by one non-bonding electron. Otherwise the resulting oxygen vacancy is "atom empty" in E'_1 but hosts an off-centre H^- ion in E'_2 and E'_4.

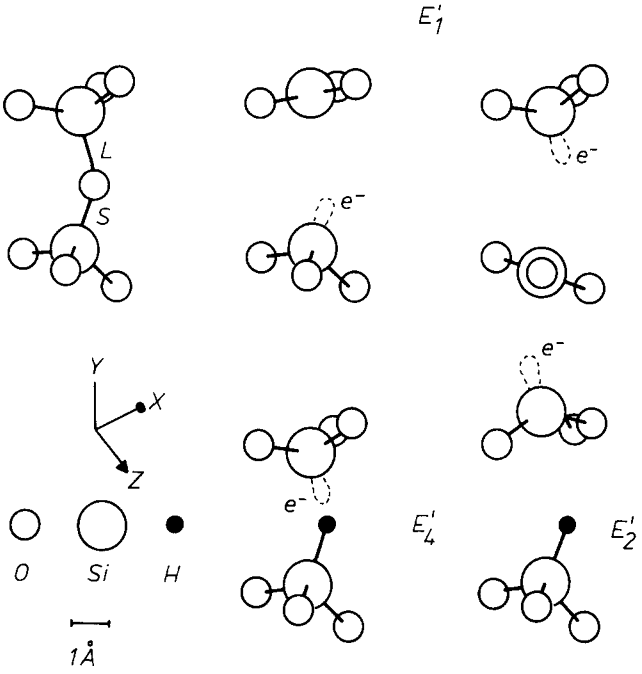

Fig. 1. Structural models for E′ series defect centres in α-quartz. Note the slight inequivalence of the bond lengths, short (S) and long (L), in the ideal lattice.

It is characteristic of the E′ series that the extra electron is trapped in a dangling orbital at one of the Si atoms, which is balanced by a gross asymmetric relaxation of both Si atoms. For instance, in E'_1 the Si atom with the trapped electron (the short (S)-bond partner) displaces slightly towards the vacancy, while the other Si atom (the long (L)-bond partner) relaxes in the plane of its O atoms, to which it remains bonded. The extra-electron sp^3 orbital extends towards the vacancy. In E'_4 the sp^3 orbital, also spreading towards the vacancy, is at the L-bond Si, but now the configurational distortions within the two neighbouring pyramids are less significant. E'_2 forms from E'_4 as the extra-electron orbital flips in the opposite direction away from the hydrogen-occupied vacancy. Now the orbital flip-flop brings about a larger structural transfigurement in which the vertex of the L-bond SiO_3 tetrahedron flips away from the impurity along with the electron orbital. There also is an accompanying asymmetric relaxation of the H^- ion in E'_4 which brings it into an off-centre position (H^- ion relaxation is not shown in Fig. 1).

SSDI 0925-8388(93)00023-R

Gross asymmetric relaxations such as those in Fig. 1, as well as the associated structural defect models, can be predicted by way of quantum chemical cluster calculations and electron paramagnetic (EPR) data [3–5]. An alternative approach to the problem is based on the pseudo-Jahn–Teller effect [6, 7]. Two pairs of equilibrium conformations believed to correspond to (E'_1, E'_1) and (E'_2, E'_4) defect types are shown in Fig. 1. From a fundamental point of view, switch-over transitions are conceivable between any two conformations within each pair. From a practical point of view, switch-overs of this type will definitely contribute to the dielectric or acoustic losses in the material.

3. Calculation

A basic quantity to be precalculated by the theory in order to forecast losses due to E′ centres is the switch-over relaxation time. We had earlier computed intrapair relaxation times for E′ defect centres in α-quartz by applying the reaction rate method [6, 8, 9] to the structural models depicted in Fig. 1. Our calculations had shown that E′ centres in α-quartz relaxed through thermally activated tunnelling within the temperature range where defect centre manifestation is observed [1]. This transition type involves both quantum mechanical tunnelling and classical jumps near the barrier top. Relaxation times of the incorporated hydrogen in E'_4 have also been computed [7].

Physically, the relaxational absorption of ultrasound in solids is based on the coupling of the relaxation process at defects in the crystalline lattice to the elastic strain by way of the deformation potential. In the cases under consideration this is the coupling of configurational displacements of atoms at the defect sites to the elastic strain induced by the propagating acoustic wave. Energetically, the two configurations corresponding to the two wells in the vibronic potential energy are somewhat asymmetric. With the acoustic wave frequency low relative to the frequency of thermal phonons, the wave does not interact with the phonons directly but rather modulates the well asymmetry. This modulation disturbs the thermal equilibrium of the wells and the phonon ensemble, which is re-established by configurational flux from one well to the other until new thermal occupations settle down. This enhances the entropy of the phonon ensemble, leading to the loss of energy of the acoustic wave. In a sense the wave serves as a feedback to the relaxation process and, when in phase or out of phase with it, leads to dispersion of velocity or to absorption of energy respectively. Correspondingly, the energy losses depend on the relaxation time τ according to [10]

$$Q^{-1}=\frac{n\beta^2}{4\rho v^2 k_b T}\,\frac{\omega\tau}{1+\omega^2\tau^2} \tag{1}$$

where ω is the acoustic wave circular frequency, β is the deformation potential introduced by $E'=E+\beta\eta$, which shows how an external elastic strain η alters the energy inequivalence between the two wells, ρ is the mass density of quartz, v is the acoustic wave velocity and n is the concentration of defect centres.

The relaxation time τ is assumed to depend Arrhenius-wise on the temperature: $\tau=\tau_0\exp(E_b/k_bT)$, where E_b is the activation energy of the defect. In the present case E_b is the barrier height between the two wells (in electronvolts), while τ_0 is an effective "attempt frequency"; τ is the sum only of the relaxation times for sub- and over-barrier transitions, because the time for quantum mechanical tunnelling is negligibly small.

Four relaxation times (in seconds) are included corresponding to the E'_1–E'_1 interconversions back and forth as follows [6, 8]:

$$\tau_{(E'1-E'1)\mathrm{ex}}=2.34\times10^{-14}\exp\left(\frac{0.66}{k_bT}\right)$$

$$\tau_{(E'1-E'1)\mathrm{en}}=2.34\times10^{-14}\exp\left(\frac{0.73}{k_bT}\right)$$

$$\tau_{(E'4-E'2)}=7.34\times10^{-14}\exp\left(\frac{0.56}{k_bT}\right)$$

$$\tau_{(E'2-E'4)}=7.34\times10^{-14}\exp\left(\frac{0.64}{k_bT}\right)$$

The relaxation time (in seconds) for the H^- ion only in one direction is taken into account:

$$\tau_{H^-}=9.95\times10^{-14}\exp\left(\frac{0.062}{k_bT}\right)$$

The relaxation time for the reverse transition is a constant equal to 9.95×10^{-14} s within the temperature range [7], which is why this relaxation time is neglected in the calculations.

For calculating Q^{-1}, we chose an AT-cut quartz resonator with shear waves in thickness along the X axis and $v=3300$ m s^{-1} at 5 MHz. A value for β of 1 eV for SiO_2 is taken from ref. 11. The defect concentrations of all the relaxation components (with the exception of the H^{-1} ion) are assumed to be the same and set equal to 4×10^{23} m^{-3}, at which value the resulting total loss matched the experimental measurement at 480 K as shown in Fig. 2 [2]. The concentration of H^{-1} ions is chosen to be 2.5×10^{22} m^{-3} in accordance with ref. 12.

With the above-mentioned values of the various quantities we computed the temperature dependence

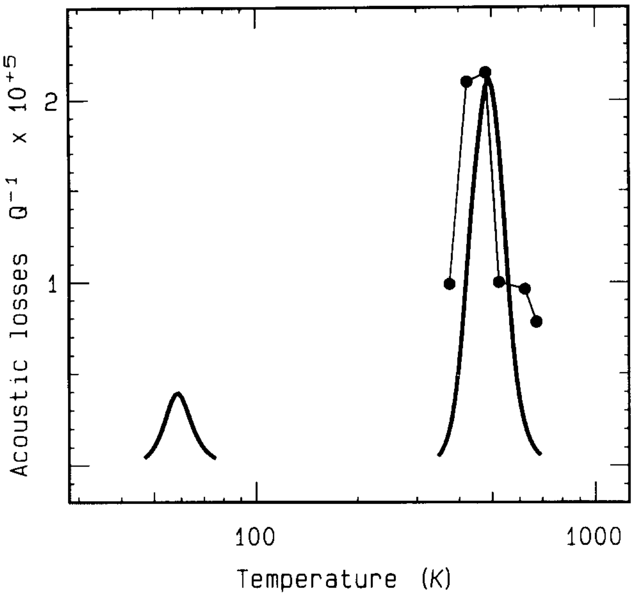

Fig. 2. Calculated temperature dependence of acoustic losses Q^{-1} of an AT-cut quartz resonator due to E′ series defect centres and the H^- ion at the E'_4 defect centre. The curve with circles shows experimental losses of an AT-cut resonator measured at 5 MHz following irradiation with 1.2×10^{18} neutrons cm^{-2} [2].

of Q^{-1} presented in Fig. 2. In these calculations the contributions of each relaxation time component were computed using eqn. (1) and then summed to give the total loss at each particular temperature.

4. Comments

The temperature dependence $Q^{-1}(T)$ at 5 MHz displays two peaks. One of them is at 501 K and corresponds to E'_1, E'_2 and E'_4 defect centre switch-over transitions. The second peak at 56 K is related to the relaxation of the H^{-1} ion at the E'_4 defect centre. Both peaks show a form in agreement with the relaxation theory. The value of Q^{-1} is proportional to the defect concentration and amounts to about 2.1×10^{-5} at $n=4\times10^{23}$ m^{-3} at 501 K and 3.5×10^{-6} at $n=2.5\times10^{22}$ m^{-3} at 56 K. For comparison, an experimental Q^{-1} (T) dependence for a synthetic quartz crystal measured at 5 MHz following neutron irradiation is shown as the curve with circles. The agreement may be considered to be satisfactory in view of the possible contribution of defects other than the E′ species to the experimental loss curve.

The calculated acoustic losses due to the relaxation of the H^{-1} ion are evidence of a typical single-relaxation process at low temperature, connected with the small value of its activation energy. The calculated value for Q^{-1} in the temperature-independent transition is 10^4 times lower. This fact explains the reason why the above-mentioned process is not taken into account in the calculations. The strong difference between the two peaks shows that the relaxation of the H^{-1} ion accompanying the relaxation of the E'_4 defect centre is very small and has little influence on the E'_4 defect centre relaxation behaviour.

5. Conclusions

We have calculated the acoustic losses (ultrasonic attenuation) in an AT-cut quartz resonator as a function of the temperature by taking into account the relaxation processes due to E′ series defect centres in α-quartz. The relaxation processes involve E'_1–E'_1 and E'_2–E'_4 interconversions and the relaxation of the H^- ion at the E'_4 defect centre. The relaxation times used in the calculations are those computed earlier based on the pseudo-Jahn–Teller defect and the reaction rate method. The obtained loss curves follow the general trends predicted by the relaxation theory and agree fairly with experimental loss data from the literature. These agreements show the feasibility of our calculations, which may be expected to improve further as information on the underlying oxygen vacancy centres becomes available. The present calculations may be useful in forecasting the response of quartz resonators to irradiation with high energy particles.

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