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Short-time-scale specific heat experiments on smoky quartz

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Résumé. — Des mesures de chaleur spécifique en temps courts ont été effectuées sur des échantillons de quartz naturel irradiés par rayonnement gamma. Elles ont été réalisées avec des temps de l'ordre de la milliseconde aux températures de l'hélium liquide. Une réduction de la chaleur spécifique a été mise en évidence dans cet intervalle de temps entre 1,4 K et 4,2 K.

Abstract. — Short-time-scale specific heat measurements have been performed on gamma irradiated natural quartz crystals in the millisecond time-scale at liquid helium temperatures. Evidence for a reduction of the specific heat has been observed in this time-scale between 1.4 K and 4.2 K.

1. Introduction. — It is well known that in γ -irradiated natural quartz a hole (electron defect) is trapped at an oxygen site near a substitutional aluminium impurity [1]. Experimental data support the idea that at low temperatures the hole moves in a double well potential in which the particle may tunnel through the potential barrier between two inequivalent minima associated with the two oxygen ions nearest to an aluminium impurity [2, 3], generating a two level system (TLS). Random electric fields due to ionized defects and local strains result in a broad distribution $N(E)$ of the energy splittings, confirmed by the large linearly temperature-dependent contribution to the specific heat [4, 5], and by the dielectric results [2, 5]. A localization temperature T_L proportional to the width of the distribution is estimated to vary between 2 and 9 K [2, 5]. T_L characterizes the degree of imperfection of the crystal. The long dielectric relaxation time ($T_1 \approx 10^{-3}$ s at 4 K) suggests that the electronic defects are weakly coupled to the lattice phonons. Moreover, the thermal conductivity is unchanged in comparison with non-irradiated quartz below 1 K [5, 7], and no resonant absorption is detected in high frequency ultrasonic attenuation experiments [6].

A consequence of the tunneling model is that the specific heat should depend on the time-scale of measurement t because the defects with relaxation time T_1 longer than t will not influence the measurements, leading to a reduction in the apparent specific heat.

We report results obtained with a heat pulse techni-

que performed on a sample of natural quartz irradiated with gamma rays at a dose of 10^7 rad. A transient behaviour of the temperature is observed in the millisecond time-scale. Such an effect is not observed with the same sample submitted to a thermal bleaching for two hours at 400 °C. The experimental results are compared with the dielectric and long-time specific heat results obtained with the same sample [5].

2. Experimental set-up. — The sample is a disk (15 mm in diameter, 1 mm in thickness) cut from a natural quartz sample furnished by the Valpey Fisher Corporation. It was irradiated at room temperature with gamma rays at a dose of 10^7 rad. The same sample (sample 1 in Ref. [5]) was used previously in long-time specific heat and dielectric measurements [4, 5]; the impurity content is mainly aluminium at a concentration of 37 ppm. The heater and thermometer are thin films made by spraying a colloidal suspension of graphite across evaporated electrical contacts. The internal time constants are short, about 100 μ s [9]. The electrical resistance of each is about 500 Ω at liquid helium temperatures. The time constant of the electronic measurement system is less than 100 μ s. The sample is mechanically pressed against the cold source in an evacuated chamber of a ^4He cryostat [8]. The external thermal time constant is about 0.2 s. An electrical pulse of about 2 V height and 20 μ s width is applied to the heater. The resistance of the detector is measured by having a constant 10 μ A bias current and monitoring the voltage [9]. The

change of voltage due to the heat pulse is viewed on a storage oscilloscope at a repetition rate of about 1 Hz. The temperature of the cold source is measured with a carbon resistor. The temperature rise of the sample is about 10 % with a heat pulse energy of about 1 erg.

Temperature rises observed on the storage oscilloscope at different temperatures of the cold source are shown in figure 1. Our experimental time scale is 1

Fig. 1. — The temperature rises recorded after a heat pulse was applied at the initial time $t = 0$ are given in figure 1 with arbitrary units (a.u.) at different temperatures.

to 3 orders of magnitude slower than in recent published experiments [10, 11]. No sophisticated treatment of the signal has been performed, and the parameters have been deduced directly from the experimental curves displayed on the storage screen. It has been checked many times that the amplitude of the transient $\Delta T_M - \Delta T_E$ decreases when the mean temperature of the sample increases above 1.3 K, with all other experimental conditions maintained constant. It has also been checked experimentally that this transient is not observed on the same sample after it has been submitted to a thermal annealing for 2 hours at 400 °C. The thermal phonons are in thermal equilibrium in the millisecond time-scale t ; t is four orders of magnitude larger than the phonon relaxation time for boundary scattering.

3. Experimental results. — Experimental temperature rises ΔT due to short heat pulses applied at initial time $t = 0$ are shown in figure 1 for the irradiated sample. Each curve corresponds to a constant temperature of the cold source. At the lowest temperatures

a short-time transient contribution to ΔT is observed in the millisecond time range. The slow time variation of ΔT is the thermal relaxation between the sample and the cold source with a thermal time constant of about 0.2 s. The amplitude of the short-time contribution decreases continuously when the mean temperature of the sample increases, and vanishes completely around 4 K.

The parameters ΔT_M and ΔT_E are defined in figure 1. ΔT_M is the temperature rise about 100 μ s after the end of a heat pulse, and ΔT_E is the value extrapolated to the initial time $t \approx 0$ from the slow variation of ΔT . The values of $\Delta T_M/\Delta T_E$ obtained at different temperatures are given in table I. The values of C_{ir}/C_{ph} deduc-

Table I. — ΔT_M is the value of the temperature rise at the initial time $t = 0$ in figure 1.

— ΔT_E is the value of the slow variation extrapolated to the initial time $t = 0$ in figure 1.

— C_{ir} is the specific heat measured in the same irradiated sample (sample 1 of Ref. [5]) in the long-time experiment given in references [4, 5]. C_{ir} is the sum of the TLS and lattice contributions, $C_{ir} = C_{ph} + C_T$. The lattice contribution C_{ph} have been measured in the non-irradiated crystal Refs. [4, 5].

$T(K)$	$\frac{\Delta T_M}{\Delta T_E}$	$\frac{C_{ir}}{C_{ph}}$
—	—	—
1.4	1.7	2
1.5	1.4	1.6
2	1.3	1.3
2.3	1.2	1.28
4.2	1	1

ed from the long-time specific heat results are reported in the same table I. C_{ph} is the lattice contribution obtained without irradiation, and C_{ir} is the long-time specific heat measured with the same irradiated sample (sample 1 in Ref. [5]). The values in columns 2 and 3 of table I agree to within the experimental accuracy of 20 %; both decrease progressively to 1 when the temperature increases up to 4.2 K.

The short-time transient contribution to ΔT in the millisecond time range is deduced by subtracting the extrapolated slow-time contribution. It can be fitted within experimental accuracy with a single exponential function with a time constant τ_{th} of about 2×10^{-3} s.

We define the time constant τ by :

$$\tau = \tau_{th} \cdot \frac{\Delta T_M}{\Delta T_E}. \quad (1)$$

τ , deduced from the values of τ_{th} and $\Delta T_M/\Delta T_E$, is shown in figure 2 for different temperatures. The experimental values of τ are inversely proportional to the temperature, and in agreement with the values of the relaxation time obtained in dielectric measurements (Fig. 4 of Ref. [5]).

Fig. 2. — The time constants obtained by the relation (1) defined in the text, (■) together with dielectric time constants (○) (fig. 4 of Ref. [5]) at different temperatures.

4. Discussion. — The results obtained in the long-time specific heat measurements with the same sample permit an analysis of the time variation of the temperature rise ΔT .

The specific heat C_{ir} of the irradiated sample is the sum of the tunneling level contribution C_T and the phonon contribution C_{ph} , $C_{ir} = C_T + C_{ph}$. C_T increases linearly with temperature below 1 K and shows a broad bump around 2 K [4, 5]. The values of C_{ir}/C_{ph} at the temperatures of interest are given in table I.

The thermal conductivity K shows a nearly T^3 dependence below 3 K due to scattering of phonons by the sample boundaries [5, 6]. The thermal diffusivity of the sample is characterized by a time $t_R \approx D^{-1} L^2$, where the length of the sample, L , is 1 mm. The diffusivity D obtained from K gives $t_R \sim 10^{-7}$ s around 1 K. Consequently the temperature becomes uniform through the sample if the time-scale t is larger than this value. This condition is obviously satisfied in the millisecond range. Any further time dependence in the millisecond time range of the temperature rise ΔT due to heat pulses must be attributed to an increase of the specific heat resulting from tunneling levels with long-time constants coming into thermal equilibrium with the lattice.

The temperature rises ΔT_M and ΔT_E are directly connected to the lattice (C_{ph}) and defect (C_T) contributions. In the long-time limit, $t \gg T_1$, all the defects are in thermal equilibrium with the lattice. The temperature rise produced by a heat pulse of energy q is $q/(C_{ph} + C_T)$, equal to ΔT_E . In the short-time limit, 10^{-7} s $\ll t \ll T_1$, the lattice absorbs all the energy q and its temperature rise is q/C_{ph} equal to ΔT_M measured at ≈ 100 μ s (Fig. 1).

The ratio of the temperature rises in the two limits is therefore :

$$\frac{\Delta T_M}{\Delta T_E} = \frac{C_{ph} + C_T}{C_{ph}}. \quad (2)$$

The relation (2) is well satisfied by the experimental results, as shown in table I.

The time dependence of the temperature rise ΔT observed within the sample (Fig. 1) is analysed with the tunneling model [12, 13]. Defects characterized by a time constant T_1 come into thermal equilibrium for experimental times t comparable to T_1 ; in that time range ΔT must change with t . The thermal equations have been analysed in detail [12, 13]. Here we need the case where the temperature is homogeneous through the sample. The dynamic specific heat of defects with a density of states $N(E)$ and a relaxation rate T_1^{-1} is given at frequency S and temperature T by

$$C_T(S) = \int_0^\infty k \left(\frac{E}{2kT} \right)^2 \frac{1}{\text{Ch}^2(E/2kT)} \frac{N(E) \cdot dE}{(1 + ST_1)}. \quad (3)$$

The relaxation time T_1 at temperature T (larger than E/k) varies linearly with T^{-1}

$$T_1 \approx \frac{\pi \hbar^4 \bar{\rho} \bar{c}^5}{\bar{B}^2 \Gamma^2 k} \cdot \frac{1}{T} \quad (4)$$

where $\bar{B}$ is the mean coupling between defects and phonon, Γ is the tunnel splitting of defects, $\bar{c}$ is the mean sound velocity and ρ is the quartz density. The other parameters have their usual meaning. The coefficient relating the dielectric relaxation time to T^{-1} is 5.56×10^{-3} sK (Fig. 2). The dielectric relaxation time is not distributed in the temperature range 1 K-4 K, the width of the dielectric curve is comparable with that of a Debye curve [2, 5].

The time dependence of ΔT is deduced from the Laplace transform equation :

$$S \tilde{\Delta T} = \frac{\delta \tilde{q}}{\delta t} [C_{ph} + C_T(S)]^{-1} \quad (5)$$

where $\tilde{\Delta T}$ is the Laplace transform of ΔT . Numerical calculations were performed using the gaussian distribution $N(E) = N(0) \exp - (E/kT_L)^2$ with

$$N(0) = 1.6 \times 10^{46} \text{ MKS}$$

and $T_L = 6$ K. Both numbers are deduced from the long-time specific heat measurements [4, 5]. The most important contribution to $C_T(S)$ is due to the defects which have a relaxation time T_1 given by relation (4), so that all defects can be considered to have the same time constant T_1 at a given temperature T . ΔT deduced from (5) gives an exponential variation :

$$\Delta T(t) = \frac{q}{C_{ph}} \left[\frac{C_{ph}}{C_{ph} + C_T} + \frac{C_T}{C_{ph} + C_T} e^{-t/\tau_{th}} \right] \quad (6)$$

with
$$\tau_{th} = \frac{C_{ph}}{C_{ph} + C_T} \cdot T_1.$$

Expression (6) is in agreement with the exponential time variation ΔT observed in the millisecond time range and also with the experimental values obtained in the short- and long-time limits (table I).

In conclusion, there is evidence that the time dependence of the temperature rise ΔT observed in the millisecond time range results from the time dependence of the specific heat of tunneling defects. The tunneling model described in reference [2] explained

both specific heat and dielectric properties which are caused by the same kind of electronic defects trapped at aluminium impurities [2, 4, 5]. The relatively long relaxation time T_1 of the known defects means that the time dependence of the specific heat predicted by the tunneling model is detectable without too much difficulty, as opposed to the case of complex amorphous systems [10, 11].

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References

- [1] For an extensive bibliographical review, see WEIL, J. A., *Radiat. Eff.* **26** (1975) 261.
- [2] DE VOS, W. J. and VOLGER, J., *J. Physica* **47** (1970) 13.
- [3] SCHNADT, R. and SCHNEIDER, J., *Phys. Kondens. Mater.* **11** (1970) 19.
- [4] SAINT-PAUL, M., PICOT, B. and NAVA, R., *Phys. Lett.* **66A** (1978) 389.
- [5] CHAUSSY, J., GILCHRIST, J. le G., LASJAUNIAS, J. C., SAINT-PAUL, M. and NAVA, R., *J. Phys. Chem. Solids* **40** (1979) 1073.
- [6] SAINT-PAUL, M. and NAVA, R., *J. Physique* **39** (1978) 786.
- [7] WASIM, S. and NAVA, R., *Phys. Status Solidi (a)* **51** (1979) 359.
- [8] CHAUSSY, J., to be published.
- [9] CANNON, W. C. and CHESTER, M., *Rev. Sci. Instrum.* **38** (1967) 318.
- [10] KORCYNKYJ, Y., SHERLOCK, R. A., WYATT, A. F. G., *Proceedings of LT 14* (1975).
- [11] GOUBEAU, W. M. and TAIT, R. A., *Phys. Rev. Lett.* **34** (1975) 1220.
- [12] KUMMER, R. B., DYNES, R. C. and NARAYAMURTI, V., *Phys. Rev. Lett.* **40** (1978) 1187.
- [13] BLACK, J. L., *Phys. Rev.* **B17** (1978) 2740.
- [14] RAMMAL, R., Thèse Université Grenoble (1977) (unpublished).