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Acoustic phonon absorption and dispersion in hydroxyl-doped KCl crystals at low temperatures

J. F. Berret, J. Pelous and R. Vacher

Laboratoire de Spectrométrie Rayleigh-Brillouin (*), Université des Sciences et Techniques du Languedoc, Place E. Bataillon, 34060 Montpellier Cedex, France

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Résumé. — Nous avons mesuré par diffusion Brillouin entre 1 et 50 K les propriétés acoustiques de cristaux de KCl dopés par KOH. Pour les échantillons contenant plus de 200 ppm de OH^- , on observe un pic d'atténuation vers 20 K et une augmentation importante de l'absorption lorsque la température décroît, au-dessous de 5 K. Ces résultats présentent quelques similarités avec ceux que l'on observe dans les verres. Nous les avons décrits en supposant l'existence de processus relaxationnels et résonnants pour l'absorption des phonons.

Abstract. — The acoustic properties of hydroxyl-doped KCl crystals have been measured by Brillouin scattering in the temperature range 1 to 50 K. For samples with OH^- content higher than 200 ppm, two features dominate the temperature dependence of the attenuation, namely an absorption peak around 20 K and a strong increase of the damping with decreasing temperature below 5 K. The results bear some similarities to the behaviour observed in glasses and have been accounted for by assuming relaxational and resonant phonon absorption processes.

1. Introduction.

Several independent studies of OH^- doped KCl crystals [1-3] have given evidence of an excess specific heat at low temperatures in these materials. For concentrations lower than 100 ppm, a Schottky anomaly was found, which was assigned to tunnelling states of the hydroxyl impurity. At higher concentrations, approaching the solubility limit, the excess specific heat increases monotonically with temperature up to 1 K. The measurements in reference [3] show a broad maximum of the excess specific heat centred at about 1.5 K. These results show the existence of a broad and flat density of states, which bears some similarities with that observed in glasses [4]. This « glass-like » behaviour has already been emphasized by several authors [5, 6], who interpreted dielectric absorption and dispersion experiments on the basis of the two-level system [TLS] model used for the phenomenological description of similar experiments in glasses [7].

The tunnelling states of impurities in crystals are known to couple strongly with phonons, giving rise to a phonon scattering which has been observed in thermal conductivity measure-

(*) Equipe de recherche associée au C.N.R.S. N° 460.

ments [8]. More information on this coupling can be obtained by measuring the acoustic wave velocity and absorption in ultrasonic or Brillouin scattering experiments. Up to now, there has been, to our knowledge, only one ultrasonic experiment performed on KCl crystals whose OH^- concentration was imperfectly known [9]. Our motivations for performing a Brillouin scattering study of KCl : OH were twofold : i) it was interesting to measure the acoustic properties of the same high concentration samples already used for the specific heat experiments in reference [3] (one of our samples was also of the same origin as that used in the dielectric experiments of ref. 6) and ii) the energy of the phonons probed in Brillouin experiments is of about 1.5 K : A coupling with the tunnelling levels responsible for the maximum in the excess specific heat can therefore be expected. We present here measurements of the velocity and attenuation of 30 GHz longitudinal phonons in the temperature range 1-50 K and interpret our results on the basis of a coupling of phonons with low-energy excitations related to hydroxyl impurities. Part of these measurements was published previously [10].

2. Experimental method and samples.

The Brillouin scattering experiments were performed on a high resolution spectrometer whose performances were especially adapted for the study of light scattering by thermal acoustic phonons at low temperatures [11]. With this instrument, we were able to measure the frequency shift and linewidth of Brillouin lines down to 1 K in KCl : OH crystals. It must be noted, however, that the accuracy of the low-temperature measurements is limited here by the very large width of the lines at these temperatures. We estimate the accuracy to be not better than 10 MHz (200 cm^{-1}) on the linewidth (attenuation) below 3 K. The relative uncertainty of the frequency (velocity) measurement is of about 5×10^{-4} .

The KCl : OH samples, kindly loaned to us by Dr J. C. Lasjaunias, originate from the Laboratory of Atomic and Solid State Physics at Cornell University. We used five samples having various OH^- concentrations [12], given in table I.

Samples 4 and 5 are those used for the specific heat measurements in reference [3], which have nominal concentration of 0.5 and 1 %, respectively.

The samples were cut of parallelepipeds by cleavage and polished to get good optical transparency. We studied longitudinal phonons propagating along the (1, 0, 0) direction, for which a maximum coupling with OH^- elastic dipoles can be expected.

3. Results.

The measurements of the attenuation for the five samples are given in figure 1. Velocity measurements are plotted in figure 2 for samples 1, 4, 5 only for clarity.

In samples 1 and 2, corresponding to OH^- contents lower than $8 \times 10^{17} \text{ cm}^{-3}$ the attenuation, due to anharmonic three-phonon interactions, becomes smaller than the experimental uncertainty below 30 K. Correspondingly, the velocity tends to be constant with decreasing temperature. In contrast, the attenuation curves for samples 3, 4, 5, having a hydroxyl content higher than $3.2 \times 10^{18} \text{ cm}^{-3}$, show a sharp maximum near 20 K. This absorption peak, which is a common feature for disordered solids in ultrasonic experiments [13, 14], is original at hypersonic frequencies : To our knowledge, such a well-defined attenuation maximum has never been observed for frequencies higher than 10 GHz in solids. At almost the same temperature, a plateau is observed in the velocity curves for these samples.

The amplitude of the absorption peak seems to be proportional to the OH^- concentration in samples 3 and 4 ; the non-observation of this peak in samples 1 and 2 having small hydroxyl contents is consistent with this proportionality. On the contrary, no sizeable variation of the amplitude is observed between samples 4 and 5 while the OH^- content is twice in the second. This departure from proportionality seems difficult to explain. Uncertainties in concentration determinations can be at the origin of this observation.

Table I. — *Numerical data for KCl : OH samples.*

Sample number	1	2	3	4	5
OH ⁻ concentration (cm ⁻³)	≈ 0	< 8 × 10 ¹⁷	3.2 × 10 ¹⁸	1.6 × 10 ¹⁹	3.2 × 10 ¹⁹
τ ₀ (s)	—	—	—	0.5 × 10 ⁻¹²	1 × 10 ⁻¹²
E _a (K)	—	—	—	56	52
Phonon frequency at 5 K (MHz) ^(a)	30 210	30 080	30 300	28 680	28 680
Density of states at the phonon frequency (erg ⁻¹ cm ⁻³) ^(b)	—	—	1.6 × 10 ³⁴	5.9 × 10 ³⁴	7.3 × 10 ³⁴
$N = \int n(E) dE$ (cm ⁻³)	—	—	1.2 × 10 ¹⁹	3.4 × 10 ¹⁹	4.3 × 10 ¹⁹
M (eV)	—	—	0.22	0.14	0.14

^(a) The variations in the phonon frequency are due mainly to changes of the scattering angle and incident laser frequency prescribed for experimental reasons.

^(b) From specific heat measurements [3].

The second interesting feature on these curves is the strong increase of the attenuation with decreasing temperature. It should be noted that, below 5 K, the attenuation does not vary appreciably with hydroxyl content for samples 3, 4 and 5. In the same temperature range, the velocity shows no noticeable variation within the accuracy of the experiments.

4. Discussion.

4.1. TEMPERATURE RANGE BETWEEN 10 AND 50 K. — The absorption peak can be described phenomenologically on the basis of a thermally-activated relaxational process with a single relaxation time following an Arrhenius law : $\tau = \tau_0 \exp(E_a/kT)$. The values corresponding to the best fit for samples 4 and 5 are given in table I, and the corresponding curve drawn in figure 3 for sample 4. The activation energy for the two samples is close to 50 K. With the same set of parameters, the temperature dependence of the velocity has been calculated for the two samples (see dashed line in Fig. 4 for sample 4). It can be seen in figure 4 that the addition of the relaxational process and anharmonic phonon-phonon interactions accounts well for the observed temperature dependence of the velocity. The values of the parameters would also predict a peak at a temperature of about 5 K for 60 MHz ultrasonic waves, in reasonable agreement with the measurements of Brugger and coworkers [9].

It is tempting to make a connection between this value of the activation energy and the 32 cm⁻¹ (46 K) level which is observed in infrared absorption and Raman scattering measurements [15, 16]. This level has been assigned to librational motions of the centre of mass of the hydroxyl molecule. The cusp observed around 14 K in the thermal conductivity of KCl : OH has been explained

Fig. 1. — Temperature dependence of attenuation in KCl : OH crystals. ○ : sample 1 (« pure » KCl); ◆ : sample 2 ($< 8 \times 10^{17} \text{ cm}^{-3}$); ▲ : sample 3 ($3.2 \times 10^{18} \text{ cm}^{-3}$); ● : sample 4 ($1.6 \times 10^{19} \text{ cm}^{-3}$); ■ : sample 5 ($3.2 \times 10^{19} \text{ cm}^{-3}$). Solid lines are guides for eye only.

through a strong mechanism of phonon scattering related to this level [8]. We therefore suggest that the above mechanism is also at the origin of the relaxational process observed here.

4.2. LOW-TEMPERATURE RANGE. — Our attenuation measurements below 5 K give evidence of a very large hypersonic damping at low temperatures in samples 3, 4 and 5. The inverse mean free path of 30 GHz phonons measured at 1 K in sample 4 is about 3000 cm^{-1} , almost one order of magnitude higher than the attenuation observed in fully disordered solids (glasses [11] and amorphous polymers [17]) at the same frequency. Either relaxational or resonant effects can be at the origin of such a strong phonon scattering mechanism.

The microscopic process involved in low-temperature relaxation mechanism of hydroxyl-doped KCl crystals is the reorientational motion of OH^- molecules [18]. The relaxation time determined for this motion is of about 10^{-8} s at 1.3 K [19]. This time is very long, as compared to the period of the hypersonic phonons probed in our experiments ($\approx 0.3 \times 10^{-10} \text{ s}$). It seems therefore very unlikely that these processes could be responsible for the strong acoustic absorption observed. Thermally activated mechanisms have proven inadequate to describe a number of previous studies of the OH^- relaxation in alkali halides as, for instance, the electric field dependence of the relaxation time in electro-optical measurements and its variations with stress in dielectric loss experiments [18]. Furthermore, neither thermally activated nor phonon-assisted tunnelling relaxations would lead to the observed temperature dependence of absorption, namely an increase of the attenuation with decreasing temperature [20]. A similar effect has been observed by Brugger *et al.* [9] at ultrasonic frequencies. In order to explain the $1/T$ dependence of the

Fig. 2. — Temperature dependence of velocity change in KCl : OH crystals. ○ : sample 1 (« pure » KCl); ● : sample 4 ($1.6 \times 10^{19} \text{ cm}^{-3}$); ■ : sample 5 ($3.2 \times 10^{19} \text{ cm}^{-3}$). Solid lines are guides for eye only. The curves have been translated arbitrarily for clarity.

damping, these authors proposed a model in which relaxation is allowed between the two levels of a stepwise potential. The model leads to a constant relaxation time, equal to $0.4 \times 10^{-8} \text{ s}$ for KCl : OH. Straightforward numerical calculations show that such a process gives a negligible contribution at hypersonic frequencies.

Evidence of resonant processes in OH^- doped alkali halides has already been given by Hess and DeConde [5] who demonstrated the existence of a saturation of dielectric absorption at very low temperature in RbCl : OH. It seems therefore that resonant absorption of phonons by tunnelling systems is the best candidate to explain our results. The actual microscopic description of isolated OH^- impurities in KCl lattice involves three fundamental energy levels A_{1g} , T_{1u} and E_g with splittings $\Delta_0/k_B \approx 0.72 \text{ K}$ and 0.36 K , respectively [21]. In highly doped samples, the temperature dependence of the specific heat [1-3] indicates a broadening of the distribution of the energy splitting of tunnelling systems, which most likely occurs from elastic and electric interactions [22].

If we assume the low-energy excitations to be two-level systems according to the picture widely used in glasses, we can deduce the TLS density of states from the excess specific heat. Figure 5 shows the density of states $n(E)$ calculated for samples having the same OH^- concentrations as our samples 3, 4 and 5. As expected, a flat density of states extending up to 6 K is observed in the two samples with highest hydroxyl content, while a peak with a maximum around 400 mK and a width of about 1 K accounts for $n(E)$ in sample 3 (OH^- content : $3.2 \times 10^{18} \text{ cm}^{-3}$). On

Fig. 3. — Comparison of experimental values and calculations for the attenuation in sample 4 (1 000 ppm). Dashed-dotted line : contribution of anharmonic phonon-phonon interactions taken from pure KCl; dashed line : thermally activated relaxation process; dotted line : resonant absorption by tunnelling systems.

the other hand, the total number of two-level systems $N = \int n(E) dE$ compares well with the impurity concentration. A definitive comparison between both quantities must be based on the actual three-level system model. In the following, the absolute value of $n(E)$ will be considered as indicative only.

The longitudinal thermal acoustic waves of frequency $\omega/2\pi$ probed in Brillouin experiments carry a very low acoustic power, and the resonant absorption is therefore non-saturated. Then, the resonant attenuation calculated from the TLS model is given by [20]

$$\alpha_{\text{res}} = \frac{\pi n M^2 \omega}{\rho v^3} \tanh \frac{\hbar \omega}{2 k T}, \quad (1)$$

where n is the density of states with an energy splitting equal to $\hbar \omega$, ρ is the mass density, v is the velocity of acoustic phonons and M is the deformation potential for the longitudinal phonons. The deformation potential has been calculated from the values of the frequency and attenuation measured in our experiments for samples 3, 4 and 5, and the values of n deduced from specific heat measurements. The values, given in table I, show little variations around 0.2 eV, that we consider as non-significant in view of the large uncertainties involved in this determination. It seems nevertheless that there is no clear influence of the interaction between dipoles on the deformation potential, even at the highest hydroxyl content.

Fig. 4. — Comparison of experimental values and calculation for the velocity change in sample 4 (1 000 ppm). Dashed-dotted line : contribution of anharmonic phonon-phonon interactions taken from pure KCl; dashed line : thermally activated relaxation process; solid line : sum of both contributions.

Equation (1) predicts an ω^2 variation of α_{res} , while a comparison of our results to the ultrasonic measurements of reference [9] rather indicates an ω dependence. Even if uncertainties in the concentration determination cannot be ruled out it should also be noted that ultrasonic waves at 60 MHz couple resonantly with tunnelling systems having splitting of 3 mK. The specific heat has only been measured down to 35 mK and the density of states at very low energies is thus unknown. Therefore the set of constants used to describe our experiments is probably not adapted to the analysis of the coupling of phonons having energies smaller by three orders of magnitude.

A further test which is needed to confirm the adequacy of the model is the simultaneous fit of the acoustic velocity measurements. Our results do not show any clear variation of the velocity below 8 K, within the accuracy of the experiments. The temperature dependence of the velocity due to resonant absorption of phonons by TLS can be expressed as [23]

$$\frac{\delta v(T, \omega) - \delta v(T_0, \omega)}{v} = \frac{\Delta v}{v} = \frac{M^2}{\rho v^2} \int_0^{E_{\text{max}}} \frac{E(E^2 - \hbar^2 \omega^2 + \hbar^2/T_2^2) (\tanh(E/2 kT_0) - \tanh(E/2 kT))}{(E^2 - \hbar^2 \omega^2 + \hbar^2/T_2^2)^2 + 4 \hbar^4 \omega^2/T_2^2} n(E) dE, \quad (2)$$

T_2 is the homogeneous transverse relaxation time of TLS.

Fig. 5. — Density of states of TLS deduced from specific heat measurements in ref. 3. Solid line : sample 3; dashed line : sample 4; dashed-dotted line : sample 5.

In the case of insulating glasses where T_2 is very long as compared to the period of the acoustic wave, and under the further assumptions that $\hbar\omega \ll kT$ and $n(E)$ is independent of energy, an explicit expression can be obtained for this integral. The temperature dependence of the velocity can then be calculated without need of any new parameter. None of the above assumptions are fully verified here. A numerical calculation of equation (2) on the basis of the known parameters is necessary. Our measurements indicate a velocity change smaller than 1×10^{-3} which can be accounted for by assuming T_2 smaller than 1×10^{-11} s at 1 K. This value, which is shorter by three orders of magnitude than that determined in insulating inorganic glasses, must be compared to the previous determinations in hydroxyl doped alkali halides. Dipolar echo measurements performed on highly doped KCl : OH samples of the same origin than ours indicate T_2 values about 50 times smaller than in vitreous silica around 20 mK [24]. However, the extrapolation at 1 K of these measurements is not achievable, as the temperature dependence of T_2 is incompletely known. Dielectric absorption measurements in RbCl : OH, which have been performed up to 0.5 K [5], also indicates very small values of the transverse relaxation time : their extrapolation gives $T_2 \simeq 10^{-10}$ s at 1 K for a sample containing 1.5×10^{18} at.cm⁻³ OH⁻. The same experiments show that T_2 decreases by more than two orders of magnitude when increasing the concentration by a factor of ten. We therefore conclude that a T_2 -value smaller than 10^{-11} s is reasonable in highly doped KCl : OH samples.

5. Conclusion.

The above measurements give evidence of a strong scattering of 30 GHz thermal phonons in KCl : OH at low temperature. Our analysis shows all together differences and similarities with the behaviour of glasses. The results above 10 K are well described through a thermally activated process. In contrast to structurally disordered materials, the relaxation time appears to be single

valued. The related mechanism can be related to the 32 cm^{-1} librational level of the OH^- molecule. Below 5 K, the increase of the damping with decreasing temperature can be accounted for by assuming a resonant absorption of phonons by tunnelling systems, which has been described here in the framework of the TLS model. A more complete description of these results on the basis of the known microscopic model of OH^- impurities in alkali halide lattices is now in progress.

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