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Low-Temperature Anomalies in the Microwave Dielectric Properties of Na β-Alumina

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(Received 24 May 1978)

At low temperatures we have observed a strong microwave absorption in Na β-alumina which increases with decreasing temperature below 4 K. At electromagnetic intensities $I \gtrsim 0.1$ mW/cm^2 saturation occurs. This absorption is ascribed to low-energy tunneling states which are associated with the Na ions.

Recently, anomalous low-temperature specific heat[1,2] and thermal conductivity[3] have been reported for β-alumina solid electrolytes, similar to those observed in glasses. These measurements indicate that a broad distribution of low-energy excitations exists. It is assumed that the disorder in the Na sublattice allows Na ions to occupy different sites and that transitions between these sites are possible even at $T = 0$ by quantum tunneling.

From specific-heat measurements the number of excitations can be deduced whereas thermal conductivity provides integral information on their dynamical behavior. Details of the dynamical aspects are obtained in acoustic and dielectric measurements. In the case of glasses, the observation of an intensity-dependent acoustic absorption ("saturation")[4] gave the first experimental evidence for the two-state nature of these low-energy excitations.[5] Recent experiments on the saturation of the microwave dielectric absorption[6] in glasses have shown that electrical coupling of these states yields information which is analogous to that deduced from acoustic experiments at low temperatures.

We report here the first observation of a saturation of the low-temperature microwave absorption in Na β-alumina. The experiments were carried out with melt-grown single crystals with the approximate composition $1.25Na_2O \cdot 11Al_2O_3$.[7] The electric field was directed along the highly conducting planes by mounting the crystal with their long axes parallel to the maximum electric field of a TM_{010}-mode cylindrical cavity. Changes in the cavity resonance frequency f and its quality factor Q were measured with an X-band frequency-stabilized microwave spectrometer. For a perturbation measurement[8] changes in f and Q^{-1} are directly related to the real and imaginary parts of the dielectric constant $\epsilon = \epsilon' + i\epsilon''$.

In Fig. 1 results are shown for ϵ'' at 11.5 GHz and temperatures between 0.4 and 60 K. Noteworthy is the increase of the absorption roughly

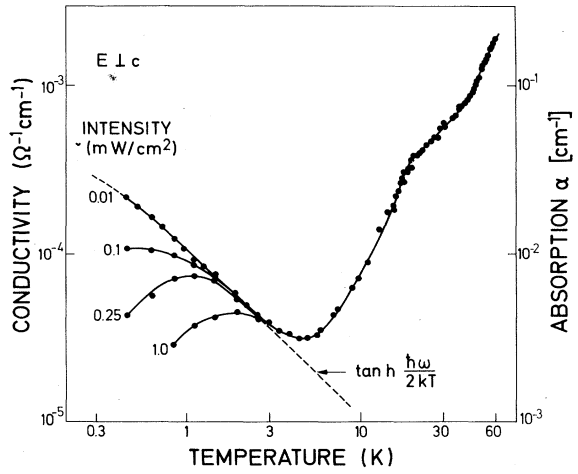

FIG. 1. Conductivity σ and absorption coefficient α vs temperature for Na β-alumina at $f = 11.5$ GHz. Here $n\alpha(\text{cm}^{-1}) = 120\pi\sigma(\Omega^{-1}\,\text{cm}^{-1})$ where $n = \sqrt{\epsilon'}$ and $\sigma(\Omega^{-1}\,\text{cm}^{-1}) = 2\pi f \epsilon_0 \epsilon''$.

proportional to T^{-1} for $T < 4$ K at low microwave power levels. Furthermore, a marked dependence of the absorption on the microwave power is observed, which is similar to what is measured in glasses.[6]

In Fig. 2 the variation $\Delta\epsilon'$ of the dielectric constant is shown, which is defined as $\Delta\epsilon'/\epsilon' \equiv [\epsilon'(T) - \epsilon'(T_0)]/\epsilon'(T_0)$, where $T_0 = 0.45$ K is our reference temperature. Similar to the absorption, a pronounced minimum is found and is again due to the opposing temperature dependence of the resonant and relaxation contributions.

Our observations can be interpreted in terms of two-level tunneling states. They have their origin in the fact that Na ions can occupy different sites of the sublattice[1] and can therefore be described as particles tunneling in double-well potentials. The energy splitting E of such a state is given by $E^2 = \Delta^2 + \Delta_0^2$ where Δ is the energy difference between the minima of the two wells and $\Delta_0 \propto e^{-\lambda}$ is the tunnel splitting due to the overlap of the wave functions. λ is the parameter which determines the tunneling probability. In the case of glasses a constant distribution of Δ and λ has to be assumed in order to describe the experimental results. For a phenomenological description it is sufficient to consider the tunneling systems simply as two-level systems (TLS) with a constant density of states $n(E) = n_0$ of their level splitting E. The microwave radiation induces resonant transitions between the two quantum states. The direct process is observed at low temperatures and small input intensities. At higher temperatures the relaxation of the TLS via this process[9] becomes dominant.

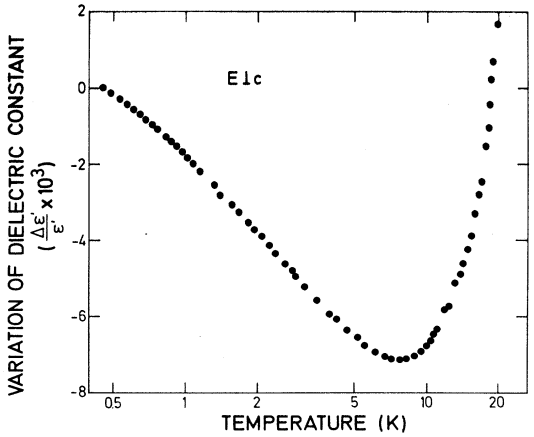

FIG. 2. Variation of dielectric constant $\Delta\epsilon'/\epsilon' \equiv [\epsilon'(T) - \epsilon'(T_0)]/\epsilon'(T_0)$ plotted as a function of T at $f = 11.5$ GHz. Here $T_0 = 0.45$ K.

The Hamiltonian of a TLS in a perturbing electric field $\vec{F}$ is given by[6]

$$H = \tfrac{1}{2}\begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix} + \tfrac{1}{2}\begin{pmatrix} \vec{\mu} & 2\vec{\mu}' \\ 2\vec{\mu}' & -\vec{\mu} \end{pmatrix} \cdot \vec{F}, \tag{1}$$

where $\vec{\mu}$ and $\vec{\mu}'$ are dipole moments associated with the motion of the Na ions. For the resonant absorption α_R of an ensemble of TLS due to the direct process one obtains[6]

$$\alpha_R = \frac{4\pi^2 \omega n_0 \mu'^2}{c\sqrt{\epsilon'}} \left(1 + \frac{I}{I_c}\right)^{-1/2} \tanh \frac{\hbar\omega}{2kT}, \tag{2}$$

where c is the speed of light in vacuum and I the microwave intensity. The quantity I_c is the critical power level at which saturation becomes significant and is defined as[6]

$$I_c = (\hbar^2 c\sqrt{\epsilon'})/8\pi\mu'^2 T_1 T_2, \tag{3}$$

where T_1 and T_2 are the relaxation times of the TLS due to their coupling to phonons and to other TLS, respectively.

Applying the Kramers-Kronig relation to Eq. (2) we expect the following contribution of the resonant absorption to the variation of ϵ'[6]:

$$\left(\frac{\Delta\epsilon'}{\epsilon'}\right)_R = -\frac{8\pi}{\epsilon'} n_0 \mu'^2 \times \left\{ \ln \frac{T}{T_0} - [g(T) - g(T_0)] \right\}, \tag{4}$$

with $\Delta\epsilon'/\epsilon' \equiv [\epsilon'(T) - \epsilon'(T_0)]/\epsilon'(T_0)$ where $T_0 = 0.45$ K is our reference temperature. $g(T)$ is significant only for $kT \lesssim \hbar\omega$ and is the real part of the digamma function $\psi(\frac{1}{2} + \hbar\omega/2\pi i k T)$. The contribution of the relaxation process to ϵ' and ϵ'' will be discussed later. In the temperature range where the direct process is dominant the predicted temperature dependence for the absorption [$\alpha_R \propto \tanh(\hbar\omega/2kT)$ for $I \ll I_c$] and for the dielectric constant ϵ' accurately fits our data. The temperature dependence of $\Delta\epsilon_R'$ reflects the energy dependence of $n_0 \mu'^2$ and is logarithmic only for $n_0 \mu'^2 = \text{const}$. In view of the tunneling model this condition can only be fulfilled if both Δ and λ exhibit a constant density of states. A broad distribution of Δ can be understood[1] in terms of variations of the local potential due to the Coulomb forces of surrounding ions which have a statistical spatial distribution. A wide variation of Δ_0 is more difficult to understand. It implies that the parameters of the double-well potential vary considerably from site to site.

From the magnitude of ϵ'' and $\Delta\epsilon'$ at temperatures below 4 K we deduce $n_0 \mu'^2 = 1.5 \times 10^{-3}$ and

1.7×10^{-3}, respectively. The agreement between the two values is remarkable and demonstrates the self-consistency of the measurements. A lower limit of the magnitude of μ' can be deduced with the aid of specific heat data.[1] From the linear term of the specific heat, a density of states of $n_0 \simeq 2\times10^{34}$ cm^{-3} erg^{-1} is obtained for the TLS (in glassy SiO_2 $n_0 \simeq 7\times10^{32}$ cm^{-3} erg^{-1}). Using this number we underestimate μ' since the quantity $n_0\mu'^2$ is a mean value into which not all TLS enter with the same weight, whereas in the specific heat measurements all systems are counted. Using our experimental value $n_0\mu'^2 = 1.6\times10^{-3}$ we obtain $\mu' \simeq 0.3$ D as a lower limit.

Knowledge of the dipole moment μ' and the critical intensity I_c allows the determination of T_1T_2 with the aid of Eq. (3). At 1 K, $J_c = 10^{-4}$ W/cm^2 and hence $T_1T_2 = 6\times10^{-11}$ sec^2. This value is several orders of magnitude larger than that measured for glasses and demonstrates the weak coupling of the ions to their environment.

In principle, T_1 can be measured by a double-pulse experiment: The delay τ_{12} between the first and the second pulse is varied. The initial pulse induces partial saturation. Any subsequent pulse induces additional saturation, i.e., a larger signal is transmitted by the cavity as a result of a lower absorption coefficient. During the time interval τ_{12} the TLS partially return to the ground state with the characteristic relaxation time T_1. The inset in Fig. 3 shows the result at a fixed temperature and varying τ_{12}. From Fig. 3 we deduce $T_1 \simeq 23$ μsec at $T = 1$ K resulting in a value of $T_2 = 2.6$ μsec if we take the value $T_1T_2 = 6\times10^{-11}$ sec^2 from the critical intensity. As was the case for T_1, the value for T_2 is much larger than that observed for glasses indicating that the coupling among the TLS is also much weaker in Na β-alumina than in typical amorphous substances.

Some caution is necessary in identifying the measured decay time of the second pulse as the true lifetime of the TLS. Firstly, the experimentally determined decay time may include the feedback effects of phonons which are generated by the recombination of the TLS and can re-excite other TLS. Thus an additional saturation is induced and hence an effectively longer "T_1" is measured. Although we believe that we observe such "phonon-bottleneck" effects at high power levels ($I > 1$ mW/cm^2), it is unlikely that such effects play a dominant role in our experiment. Secondly, we observe a temperature dependence $T_1 \propto T^{-2}$ as shown in Fig. 3 in contradiction to the expected T^{-1} dependence for the direct process.[9]

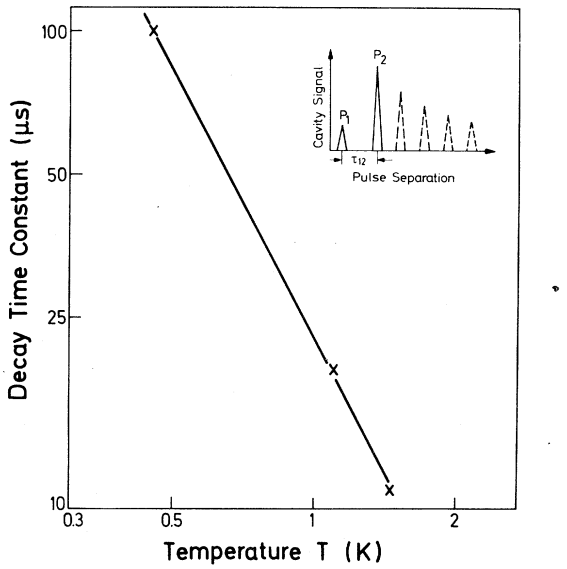

FIG. 3. Temperature dependence of the decay time of a second pulse applied after a delay τ_{12} with respect to the first pulse.

Either the excitation of the TLS is not due to this process or spectral diffusion covers the real decay.[10] In this case the value of T_1 would be even longer than the observed decay time.

The relaxation phenomena which dominate the results of Figs. 1 and 2 at temperatures $T > 5$ K will not be discussed here in detail. The predicted absorption α_{rel},[6,9] which is proportional to the diagonal dipole moment $\vec{\mu}$, is consistent with the T^3 dependence of α for $T > 5$ K up to the shoulder in the absorption near $T \simeq 20$ K. The $\alpha \propto T^2$ dependence for $T > 40$ K has been observed previously[11] and interpreted as hopping over a broad distribution of low-energy barriers. Such relaxation effects are also apparent in nuclear magnetic resonance studies.[12] The observed increase of ϵ' with temperature follows naturally from the absorption via the Kramers-Kronig relation.

In conclusion, we have observed at low temperatures a dielectric behavior of Na β-alumina which is qualitatively analogous to that of amorphous materials. The data are accurately interpreted in terms of two-level systems or tunneling states, having a constant density of states. The coupling of these states to their environment is found to be much weaker than observed in amorphous materials.

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NMR OF DILUTE o-H_2 IN SOLID p-H_2 AT TEMPERATURES BELOW 1 K. R. Schweizer, S. Washburn, and H. Meyer [Phys. Rev. Lett. 40, 1035 (1978)].

On p. 1035, second column, line 17 from the bottom, the value of the crystalline field as determined from the line width at half-maximum of C_b should be $|V_c|/k_B = 14 \pm 3$ mK instead of 25 mK. An error was made by confusing the Euler angles that describe the crystal orientation and that appear in the data analysis. Subsequent measurements on another single crystal of a different orientation have given the same value of V_c, independent of ortho concentration between 1.5% and 0.1%.

On p. 1037, first column, line 17 from the top, the correct number is $X = 0.01$.

EXAMPLE OF COLOR SCREENING. Kevin Cahill [Phys. Rev. Lett. 41, 599 (1978)].

In Eq. (10), 94 should be 93. Also the left-hand sides of Eqs. (13) and (14) should be interchanged.

THEORY OF UNIVERSAL EIGENMODES IN A SHEARED MAGNETIC FIELD. Liu Chen, P. N. Guzdar, R. B. White, P. K. Kaw, and C. Oberman [Phys. Rev. Lett. 41, 649 (1978)].

Figures 1 and 2 should be interchanged *without* interchanging the figure captions.