NUCLEAR MAGNETIC RELAXATION OF $^{23}$Na IN BETA-ALUMINA ELECTROLYTES

D. JÉROMÉ

Laboratoire de Physique des Solides (*), Université de Paris-Sud, 91405 Orsay

and

J. P. BOILOT

Laboratoire de Chimie Appliquée de l’Etat Solide (*)
15, rue G. Urbain, 94400 Vitry-sur-Seine

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Résumé. — Les temps de relaxation nucléaire spin-réseau ont été mesurés dans l’alumine bêta au sodium entre 120 et 800 K. On a montré que la relaxation était due à la modulation de l’hamiltonien quadrupolaire par la diffusion des ions par translation. La RMN permet d’atteindre directement la fréquence de saut des ions. Les résultats suggèrent l’existence de 2 sortes de mouvements locaux caractérisés par les énergies d’activation 0,2 et 0,1 eV.

Abstract. — Nuclear spin-lattice relaxation times have been measured in $^{23}$Na beta-alumina between 120 and 800 K. It is shown that the relaxation is governed by the modulation of the quadrupolar hamiltonian due to translational diffusion of the ions. NMR provides a direct access to the hopping frequency of the ions. The data suggest the possible existence of two kinds of local motions characterized by the activation energies 0.2 and 0.1 eV.

Sodium beta-alumina belongs to a class of materials which is being very actively studied by different laboratories of chemistry, crystallography and physics. The interest in these materials is motivated by the extremely high mobility of the sodium ions, which makes them promising candidates as solid electrolytes in a battery device where the electrodes are liquid sodium and sulfur.

The structure of beta-alumina has been known for a long time [1, 2] and has been refined recently by Peters et al. [3]. The structure consists of spinel-like blocks composed of four layers of close-packed oxygen atoms. Three aluminum atoms are sandwiched between the oxygen layers. The spinel-like blocks are bound together by Al-O-Al bridges. The oxygen atoms lie in loosely packed planes called mirror planes in which the sodium ions are located. The alkali ions can easily migrate in the mirror planes, giving rise to two-dimensional diffusion which is responsible for the anomalously large ionic conductivity of these materials [4, 5, 6, 7, 8]. Therefore it is of great importance to investigate the diffusion properties of Na-beta alumina.

In this respect recent X-Ray diffuse scattering work performed on Ag-beta alumina by Le Cars et al. [9] (whose conclusions should be applicable to Na-beta alumina) has shown that at high temperature the cations in the mirror plane are delocalized in a two-dimensional quasi-liquid state. However, at 77 K, they tend to localize on a superstructure with a large number of vacant sites through which the diffusion can take place. There is no critical temperature above which the delocalization of the ions occurs as it does in AgI or RbAg$_4$I$_5$, but rather a continuous delocalization of the cations with temperature.

At high temperature the diffusion can be characterized by a macroscopic diffusion coefficient. This coefficient is measured by the rate of exchange of radioactive Na$^+$ between beta-alumina and a NaNO$_3$ molten salt [10]. In addition, the diffusion coefficient can be deduced from the Nernst-Einstein relation between the ionic diffusion and ionic conductivity [6, 7] while the temperature of the frequency of maximum dielectric loss factor dependence provides a measurement of the activation energy for diffusion [11].

Nuclear magnetic relaxation experiments provide very sensitive tools for studying the motion of a nuclear probe in a crystal [12]. This is the motivation...
for the NMR investigation of $^{23}$Na ($I = \frac{3}{2}$) reported in this note.

An article has been published recently [13] about the NMR line shape of $^{23}$Na in beta-alumina. The temperature variation of the width of the high or low frequency peak in the (1/2, - 1/2) transition spectrum reveals the existence of motional narrowing above 150 K. In reference [13] the width of the high (low) frequency peak was attributed tentatively to a rigid lattice dipolar width narrowed by the ionic motion.

We present measurements of spin-lattice relaxation times of $^{23}$Na between 120 K and 800 K performed with the usual pulse technique at a frequency of 21.4 MHz. We used the pulse sequence 180°-90°. The boxcar gate was opened for the free precession following the 90° pulse and the amplitude of the signal was recorded as a function of the time between the two pulses. The peak to peak amplitude of the RF field is 100 gauss, a value which is much smaller than the first order quadrupolar splitting as evaluated in [13]. Therefore, only the central transition (1/2, - 1/2) is observed in our experiment. The sample had the composition 8.5 Al$_2$O$_3$-Na$_2$O. It was fired at 400 °C for 3 days before the experiment and then put in a sealed tube.

At high temperature a perfectly exponential relaxation has been observed over two decades of the NMR signal whereas at low temperature the recovery of the magnetization after a 180° pulse was not governed by a single exponential law. It is possible to decompose the recovery into two exponential contributions characterized by the relaxation times $T_1$ and $T_1'$ (Fig. 1). The experimental data are summarized on figure 2. The ratio $T_1/T_1'$ is about 4 below 250 K and tends towards unity around 350 K. The minima in $T_1$ and $T_1'$ occur at 260 K and 300 K respectively.

![Fig. 1. — Amplitude of the NMR signal versus the time delay between the 180° and the 90° pulse, at $T = 128$ K.](image1)

![Fig. 2. — Data of $T_1$ and $T_1'$ versus the temperature. Above 400 K the relaxation is purely exponential.](image2)

The existence of a minimum in the curve $T_1$ versus the temperature gives some evidence for a motion-induced relaxation such as the nuclear relaxation due to the translational diffusion in solids [12]. The feature that two time constants govern the recovery of the magnetization after a 180° pulse led us to the conclusion that the quadrupolar interaction between the $^{23}$Na quadrupole moment and the electric field gradient provides the dominant nuclear relaxation mechanism [14-15]. A pulse experiment does not provide an accurate determination of the NMR line shape. However, very preliminary results obtained from the CW spectrum at a frequency of 40 MHz indicate the existence of a set of different sites for the Na$^+$ ions, characterized by different quadrupolar interactions. Therefore, the amplitude of the quadrupolar interaction cannot yet be determined with certainty.

An accurate determination of the relaxation times cannot be obtained without the knowledge of the translational spectrum density. For a system of spins $I = \frac{3}{2}$ the calculation of the quadrupolar relaxation of $^{23}$Na diffusing ions is identical to the result derived for the calculation of the quadrupolar relaxation of a static nucleus induced by the diffusion of charged point defects [15].

Assuming an exponential time dependence for the correlation function (i.e., $e^{-t/\tau}$) where $\tau^{-1}$ is the frequency characterizing the mean jump frequency of the diffusing ions [16], the reduced relaxation times normalized to their minimum value are given by the relations

$$\frac{T_1}{T_{1\text{min}}} = 1 + 4 \omega_n^2 \tau^2$$

(1a)

and

$$\frac{T_1'}{T_{1\text{min}}'} = 1 + \omega_n^2 \tau^2$$

(1b)

$$\tau = \frac{1}{\omega_n}$$

where $\omega_n$ is the quadrupolar coupling constant.
We notice at once from relations (1a) and (1b) that minima occur in $T_1'$ and $T_1$ for $\tau = 1/\omega_n$ and $\tau = 1/2 \omega_n$ respectively and that in the strong motional narrowing limit $\omega_n \tau \ll 1$ a unique exponential relaxation must be obtained. As a crude approximation one can assume the existence of a thermally activated hopping time $\tau$

$$\tau = \tau_0 e^{U/kT} \quad (2)$$

where $U$ is the activation energy for the translational motion of the ions.

The value of $\omega_n \tau$ can be extracted from the data of figure 2 with eq. (1a) and (1b) taking $T_1^{\text{min}} = 70 \mu s$ and $T_1^{\text{min}} = 140 \mu s$. Log $\omega_n \tau$ is plotted against the reciprocal temperature on figure 3. Instead of the unique straight line which would have been obtained on figure 3 if eq. (2) was valid we notice that two lines fit the data for the whole temperature range better. These two lines seem to indicate the existence of two activation energies of 0.1 and 0.2 eV at low and high temperature respectively. Considering the accuracy of the experimental points in figure 3 it would not be possible to fit the data with a unique value of the activation energy from 120 K to 800 K.

The corresponding sets of BPP curves (1a) and (1b) have been drawn for $U = 0.1$ eV and $U = 0.2$ eV on figure 4.

For the $U = 0.1$ eV plot the agreement between the BPP theory and the experiment is satisfying from 120 up to 400 K. The data at $T > 300$ K fit more accurately the curve obtained for $U = 0.2$ eV (the agreement of $T_1$ at 575 K with the $U = 0.1$ eV curve is probably fortuitous.) Within the frame of a BPP formulation of $T_1$ and $T_1$ these results tend to demonstrate the existence of two kinds of local motions, characterized by the activation energies 0.1 and 0.2 eV.

In the study of the CW spectrum between 173 and 520 K Kline et al. [13] have reported the existence of the activation energy 0.1 eV, in very good agreement with our measurements in the same temperature range. The existence of the second activation energy is supported by our results at high temperature, 500 K $< T < 800$ K.

The X-Ray refinement studies [3] have revealed the existence of two non-equivalent positions for the sodium ions in the mirror plane : the Beevers and Ross (BR) and mid-oxygen (mO) positions. Therefore, it is conceivable that several kinds of local motions exist on a microscopic scale, each of them being characterized by a different activation process, namely, a motion at low temperature with the activation energy 0.1 eV and another at higher temperatures characterized by an activation energy of 0.2 eV.

Other methods of measuring the ionic diffusion, such as by electrical conductivity or radioactive tracers, require a transfer of ions on a macroscopic scale and provide an activation energy of 0.164 eV [4-6-7], midway between the two extreme values found by NMR.

We must keep in mind that the BPP theory yields a good approach for the calculation of the spin-lattice relaxation time for short correlation times.
i. e. in the high temperature limit. However, when the correlation time becomes larger than the inverse Larmor frequency the spectral density function depends on the microscopic motion of the ions, and the BPP theory may not be a good enough approximation.

To check this last point a study of the relaxation at low temperature for different frequencies will be done and reported in a forthcoming extended article.

We hope we have shown that nuclear relaxation is a method particularly well suited for studying microscopic motion of the ions in beta-alumina electrolytes. This method supplements adequately X-Ray and transport properties techniques.

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References