NMR study of low-energy excitations in Na β-alumina

S. G. Greenbaum, U. Strom, and M. Rubinstein
Naval Research Laboratory, Washington, D. C. 20375
(Received 10 June 1982)

^{27}Al and ^{23}Na NMR relaxation measurements are reported for Na β-alumina in the temperature range ~4–120 K. Below ~55 K, T_1 exhibits a power-law dependence on temperature similar to that observed in a wide variety of disordered solids and attributed to the presence of energetically low-lying excitations. The T_1 behavior in the temperature region ~55–120 K can be described by a thermally activated motional process with $E_A \approx 0.05$ eV. The ^{23}Na spin-spin relaxation time T_2 decreases monotonically with increasing temperature, suggesting that nuclear spin dephasing by ion diffusion in static electric-field-gradient inhomogeneities is appreciable.

INTRODUCTION

Na β-alumina has been widely studied by a variety of techniques, with special emphasis on its high-temperature ionic transport behavior. However, the low-temperature properties of Na β-alumina have recently generated considerable interest due to their similarity to those of a glass.[1–5] It is clear that both the superionic and glasslike properties of the β-aluminas derive from structural disorder in the conduction planes. The two-level system (TLS) tunneling description of anomalous low-temperature behavior in glasses has been applied successfully to heat-capacity,[3,5] low-frequency dielectric loss,[4] and microwave[1,2] measurements in Na β-alumina.

A wealth of NMR data exists for both Na and mixed alkali β-aluminas.[6–10] The mechanisms of spin-lattice relaxation in the temperature range ~100–700 K have been more or less elucidated, and the agreement between quantities such as activation energies obtained by NMR and conductivity (both dc and ac) measurements is well documented.[11] In view of the attention devoted to low-temperature properties of β-alumina, it is perhaps surprising to find a considerable scarcity of NMR data below 100 K. Bjorkstam, Villa, and Farrington[8] suggest the presence of glasslike low-lying excitations in β-alumina based on ^{23}Na NMR measurements at 10 K. We report both ^{23}Na and ^{27}Al T_1 measurements in the temperature range ~4–120 K in Na β-alumina. ^{23}Na spin-spin relaxation (T_2) data are reported and discussed as well.

EXPERIMENTAL

The sample consisted of a melt-grown single crystal with the approximate composition $1.25Na_2O \cdot 11Al_2O_3$ and was obtained from Union Carbide. The relaxation measurements were performed with a standard pulsed NMR spectrometer and He gas-flow system. The sample orientation was fixed at $\vec{c} \parallel \vec{H}_0$. T_1 was measured with a repetition-rate technique, and defined as the point where the signal amplitude is 63% of its thermal equilibrium value. Although the recovery profiles of both the ^{23}Na and ^{27}Al resonances were slightly nonexponential (more so for ^{23}Na than ^{27}Al), they were found to be independent of temperature. Hence, the above definition of T_1 provides a meaningful and consistent description of the nuclear relaxation for all temperatures considered. The ^{23}Na T_2 values were determined via the standard $90°$-τ-$180°$ pulse sequence.

The data were obtained on a sample exposed to ambient atmosphere for several months. The presence of absorbed H_2O was verified by IR absorption measurements. Annealing the sample at 350 °C in a N_2 atmosphere for several hours resulted in the complete elimination of the IR "water bands" near 3300 and 2800 cm^{-1}, but did not alter T_1 or T_2 significantly. There is some evidence that T_1 is slightly longer (typically by 20–30%) in the H_2O-free material, but all of the essential features to be discussed (such as temperature exponent and activation energy) are identical in the two samples.

RESULTS AND DISCUSSION

The T_1 dependence on temperature for ^{27}Al at 5.2 and 10.4 MHz, and for ^{23}Na at 10.4 MHz is shown in Fig. 1. Previous NMR studies[6,10] have established that the ^{27}Al spin-lattice relaxation process is driven by Na^+ motion in Na β-alumina. The parallel behaviors of the ^{23}Na and ^{27}Al T_1 values in Fig. 1 demonstrate this to be the case down to the lowest temperature investigated (4.5 K), although the nature of the Na^+ motion above and below ~55 K appears to be quite different. The ^{27}Al T_1 values exhibit little or no frequency dependence in the 4.5–50-K region. The straight line in Fig. 1 represents a least-squares fit to the 5.2- and 10.4-MHz ^{27}Al data over the same

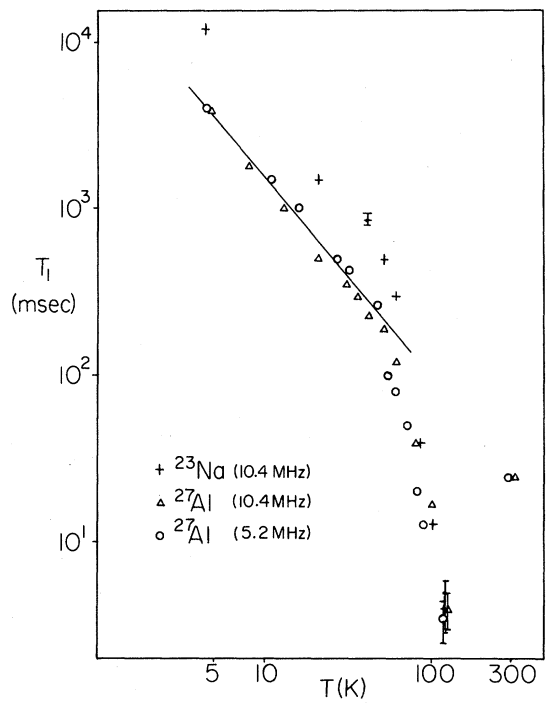

FIG. 1. Plot of T_1 vs T. The straight line represents a least-squares fit to the ^{27}Al T_1 data taken at both 5.2 and 10.4 MHz, and describes the relation $T_1 \propto T^{-\beta}$ with $\beta = 1.2$. The ^{23}Na and ^{27}Al T_1's pass through minima at 240 and 190 K, respectively.[5,6]

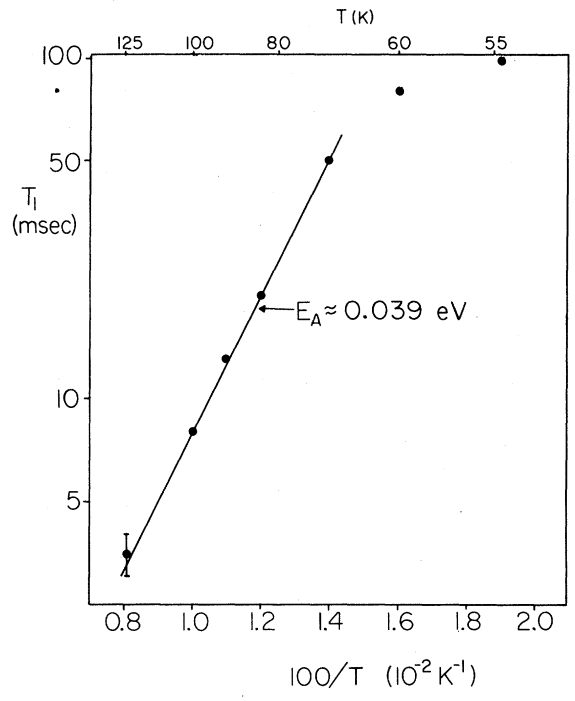

FIG. 2. ^{27}Al T_1 data at 5.2 MHz plotted against inverse temperature. The slope of the line gives the activation energy for Na^+ diffusion. A slightly higher value of E_A (0.05 eV) is obtained by subtracting the T^β relaxation rates from the experimental rates.

temperature region. The slope of the line indicates that the relaxation obeys the relation $T_1 \propto T^{-\beta}$ with $\beta = 1.2$. The power-law temperature dependence and frequency independence of the ^{27}Al spin-lattice relaxation time is strikingly similar to that observed for quadrupolar ($I > \frac{1}{2}$) nuclei in amorphous solids,[12] which is consistent with the TLS tunneling description[1,2,4] of low-temperature Na^+ motion in Na β-alumina. It is interesting to note that quadrupolar nuclei in glasses such as B_2O_3 and $Na_2B_4O_7$ also exhibit nonexponential and temperature-independent recovery profiles which, in those cases, are associated with the distribution of microscopic TLS parameters.[12]

The T_1 data in the region ~55–120 K has a roughly linear frequency dependence and exhibits exponential rather than power-law behavior. The 5.2-MHz data is plotted against inverse temperature in Fig. 2. The line drawn through the points is characteristic of a thermally activated motional process with $E_A = 0.039$ eV. Departures from the line at 61 and 54 K indicate that the relaxation rates ($1/T_1$) due to the TLS mechanism and the Arrhenius process are comparable at these temperactures. The activation energy E_A extracted from the data in Fig. 2 is within ~20% of the values reported by other investigators[6,7] in the temperature region ~120–180 K. Subtraction of the TLS relaxation rate [$(T_1)^{-1} \propto T^{1.2}$] from the experimentally determined rates in the 60–120-K region actually yields $E_A \approx 0.05$ eV, in even better agreement with the literature values above 120 K. A similar dependence of T_1 on NMR frequency above 120 K was also observed. Thus it appears that the diffusion process governing the Na^+ motion on the low-temperature side of the T_1 minimum remains dominant down to ~55 K, at which point effects due to TLS become important.

The dependence of the ^{23}Na spin-spin relaxation time T_2 on temperature is shown in Fig. 3. The monotonic decrease of T_2 with increasing T is in marked contrast to the situation described by the Bloembergen-Purcell-Pound (BPP) model[13] of nuclear-spin relaxation which predicts the onset of motional narrowing as the temperature is increased above the "rigid lattice" region, and also yields the result $T_2 \approx T_1$ on the high-temperature side of the T_1 minimum. There is no evidence of motional narrowing up to 300 K. In fact the T_1 and T_2 data over the region ~4–300 K appear to be uncorrelated. Similar anomalous behavior of T_2 has been noted in studies of V_3X superconducting compounds,[14] Li metal,[15] and niobium hydrides[16] and deuterides.[17] The T_2 anomaly in the V_3X compounds has been ascribed to the

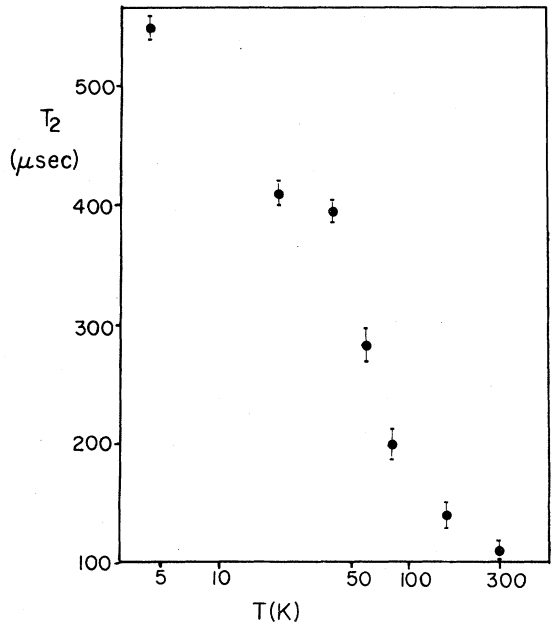

FIG. 3. Plot of ^{23}Na T_2 vs T at $\nu_0 = 10.4$ MHz.

spatial variation in magnetic field caused by a temperature-dependent fluxoid structure,[14] which is sufficient to create a difference in the magnetic field of adjacent spins on the order of 0.5 G. Such spins are no longer mutually resonant, resulting in a reduction of the effective strength of the spin-spin interaction and hence an increase in T_2 with decreasing temperature.

An alternative mechanism appears to be responsible for anomalous T_2 behavior in the cases of Li, NbH_x, and $NbDx$. For spins diffusing in a magnetic field gradient $\Delta H/l$ (l is a sample characteristic length), T_2 measured in a 90°-τ-180°-2τ-180°-2τ-180°... (Carr-Purcell) pulse sequence obeys the relation[15]

$$(T_2)^{-1}_{\text{expt}} = \left[(1/T_2) + \tfrac{1}{3}\gamma^2 \left(\frac{\Delta H}{l} \right)^2 D\tau^2 \right] , \qquad (1)$$

where γ is the nuclear gyromagnetic ratio, D is the self-diffusion coefficient, and τ is the pulse spacing. Equation (1) also predicts decreasing T_2 with increasing temperature via the dependence of D on T. Clearly, the effect of diffusion on T_2 can be minimized by utilizing closely spaced pulses as $(T_2)_{\text{expt}} \rightarrow T_2$ in the limit of small τ. One must exercise care in extracting T_2 values from 90°-τ-180° spin-echo measurements since diffusion effects can often lead to rapid decay (faster than e^{-t/T_2}) of the echo. Our measurements indicate simple exponential decay over a decade, and T_2 was determined on that basis. However, the accuracy of our measurements was insufficient to rule out the presence of a "diffusion term" in the echo-decay profile.

In the cases of Li, NbH_x, and NbD_x the magnetic field gradients exist as a consequence of the bulk susceptibility of the material. Additional broadening of the NbD_x NMR spectra has been attributed to interactions between the diffusing deuterons and quasistatic electric field gradients (EFG).[17] One might imagine the existence of an analogous situation in Na β-alumina, where the spatial magnetic field inhomogeneities are replaced by EFG inhomogeneities. The ^{23}Na quadrupole interaction and hence the NMR line shape is modulated by fluctuations in the EFG resulting from ion motion through the lattice. This process contributes to nuclear-spin dephasing in a manner similar to motion through magnetic field inhomogeneities. The term ΔH in Eq. (1) would simply become $\Delta\nu_Q$ (expressed in units of gauss), where ν_Q is the magnitude of the quadrupole splitting for a given EFG.

An important difference between the V_3X results and those of the latter three studies is that the temperature dependence of T_2 in V_3X is entirely contained in the temperature dependence of the magnetic field inhomogeneity, while T_2 is affected by actual (temperature-dependent) diffusion in quasistatic field gradients for Li, NbH_x, and NbD_x. It is therefore reasoned that the decrease of T_2 with increasing T in Na β-alumina results from ion motion in static electric field gradient inhomogeneities as in the case of NbD_x.[17] The data in Fig. 3 do in fact suggest a rather abrupt drop in T_2 in the 50–60-K region which may be associated with the onset of diffusion at ~55 K. The less rapid decrease of T_2 below 55 K reflects the tunneling (TLS) nature of the ionic motion in this temperature region. The observation of BPP-type behavior of T_1 and T_2 of protons in NH_4 β-alumina[18] lends further support to the mechanism proposed above since spin-$\frac{1}{2}$ nuclei are insensitive to EFG fluctuations and inhomogeneities.

It would be of interest to perform ^{23}Na T_2 measurements in β-alumina utilizing a multiple pulse sequence such as Carr-Purcell or Meiboom-Gill[16,19] as a conclusive test of the model proposed above, since diffusion contributions to spin dephasing would then be minimized.

CONCLUSION

Measurements of ^{23}Na and ^{27}Al T_1 values indicate that the dominant relaxation mechanism in the temperature range ~4–55 K is consistent with the TLS tunneling description of disordered solids. The Arrhenius behavior of T_1 in the temperature region ~120–180 K (Refs. 6 and 7) is preserved down to ~55 K, with roughly the same activation energy $E_A \approx 0.05$ eV. The anomalous dependence of ^{23}Na T_2 on temperature provides no evidence of motional narrowing up to 300 K, and appears to be caused by ion diffusion in EFG inhomogeneities.

ACKNOWLEDGMENTS

The authors acknowledge Dr. P. C. Taylor for many illuminating discussions. S.G.G. acknowledges support from the National Research Council.

---

[1]U. Strom, M. von Schickfus, and S. Hunklinger, Phys. Rev. B 25, 2405 (1982).
[2]S. R. Kurtz and H. J. Stapleton, Phys. Rev. Lett. 42, 1773 (1979).
[3]P. J. Anthony and A. C. Anderson, Phys. Rev. B 16, 3827 (1977).
[4]P. J. Anthony and A. C. Anderson, Phys. Rev. B 19, 5310 (1979).
[5]D. B. McWhan, C. M. Varma, F. L. S. Hsu, and J. P. Remeika, Phys. Rev. B 15, 553 (1977).
[6]R. E. Walstedt, R. Dupree, J. P. Remeika, and A. Rodriguez, Phys. Rev. B 15, 3442 (1977).
[7]M. Villa and J. L. Bjorkstam, Phys. Rev. B 22, 5033 (1980).
[8]J. L. Bjorkstam, M. Villa, and G. C. Farrington, Solid State Ionics 5, 153 (1981).
[9]R. E. Walstedt, R. S. Berg, J. P. Remeika, and R. Dupree, Solid State Commun. 37, 209 (1981).
[10]J. L. Bjorkstam, S. Manzini, and M. Villa, in *Fast Ion Transport in Solids,* edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (Elsevier North-Holland, New York, 1979).
[11]K. L. Ngai, Solid State Ionics 5, 27 (1981).
[12]J. Szeftel and H. Alloul, J. Non-Cryst. Solids 29, 253 (1978), and references therein.
[13]D. Wolf, *Spin Temperature and Nuclear Spin Relaxation in Matter: Basic Principles and Applications* (Clarendon Press, Oxford, 1979).
[14]B. G. Silbernagel, M. Weger, W. G. Clark, and J. H. Wernick, Phys. Rev. 153, 535 (1967).
[15]D. Zamir, R. C. Wayne, and R. M. Cotts, Phys. Rev. Lett. 12, 327 (1964).
[16]D. Zamir and R. M. Cotts, Phys. Rev. 134, A666 (1964).
[17]N. Salibi, D. A. Cornell, and R. E. Norberg, Bull. Am. Phys. Soc. 24, 492 (1979).
[18]R. C. T. Slade, P. F. Fridd, T. K. Halstead, and P. McGeehin, J. Solid State Chem. 32, 87 (1980).
[19]E. Fukushima and S. B. W. Roeder, *Experimental Pulse NMR* (Addison-Wesley, Reading, MA, 1981).