Dielectric Behaviour of the Ferroelectric AgNa(NO₂)₂
and Spin Lattice Relaxation of ²³Na

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The characteristic ferroelectric dispersion of the dielectric constant of AgNa(NO₂)₂ is measured near the ferroelectric phase transition. In accordance with other works an extremely slow relaxation is observed which can be related to a thermally activated motion of the electrical dipoles. The nuclear spin lattice relaxation time T₁ of ²³Na in AgNa(NO₂)₂ is measured by ⁹⁰–→⁹⁰° pulse sequences. In the entire temperature range the temperature dependence of T₁ is governed by a thermally activated process which is ascribed to a diffusion motion. There is only a small influence of the dielectric instability on T₁.

I. Introduction

Recently it has been shown by Gesi¹,² that AgNa(NO₂)₂ is a ferroelectric crystal which undergoes a phase transition of the first order at about 38 °C. In analogy to the similar ferroelectric NaN₂ the transition is assumed to be of the order-disorder type with the NO₂⁻-groups forming the permanent electrical dipoles. In most of the order-disorder ferroelectrics a characteristic ferroelectric relaxation of the dielectric constant can be observed with the characteristic frequency in the order of 10⁷ to 10¹¹ Hz even in the close vicinity of the transition temperature T_c. On the other hand, the characteristic relaxation frequency of the dielectric constant of AgNa(NO₂)₂ appears in the kHz regime. Thus in this substance the motions of the electrical dipoles are comparatively slow.

In two recent works³,⁴ the behaviour of the spin lattice relaxation time T₁ of ²³Na in NaN₂ was related to the critical dielectric behaviour by assuming that the strong increase of T₁ near T_c is related to a corresponding increase of the polarization fluctuations. It is important to note that this argument only holds if the Larmor frequency j_L is small if compared with the characteristic dielectric relaxation frequency j. This is true for NaN₂ but it is not true for AgNa(NO₂)₂. Thus one would expect that T₁ of ²³Na will be not or only little affected by the dielectric instability of the latter substance. We therefore measured T₁ of ²³Na in AgNa(NO₂)₂ single crystals. In order to compare our NMR-data with the dielectric behaviour we also measured the temperature and frequency dependence of the complex dielectric constant. It is the purpose of the present paper to report and to interpret the results of these measurements. The results of our dielectric measurements will be compared with those of a study which recently has been published by Gesi⁵.

II. Sample Preparation and Experimental Details

Employing well known methods⁵,⁶ at constant temperature (about 25 °C) single crystals of AgNa(NO₂)₂, approximately 4×4×12 mm³ in size, were grown from aqueous solution containing 9.8 wt % AgNO₃ and 37.2 wt % NaN₂ by an evaporation technique. No macroscopic defects could be observed at our transparent and yellow crystals. When the crystals were stored in air of normal humidity during 10 days a black layer on the surface of the crystals was formed containing free and neutral silver atoms. This effect could not be observed when the crystals were stored in air of extremely reduced humidity. Performing a chemical analysis of this phenomenon we found that the nitrite ions of the surface are transformed by the water molecules of the air to nitrate ions and, correspondingly, the Ag⁺-ions are reduced to neutral silver atoms.

The samples needed for the dielectric measurements were prepared from the single crystals with a wet thread saw using a nearly saturated aqueous solution of AgNa(NO₂)₂ as solvent. We obtained plates with a thickness of 1 mm (ferroelectric axis) and an area of 3×3 mm². The electrodes were prepared by a silver paste. The frequency and temperature dependent capacity of the plate was measured between 150 Hz and 10 MHz with Wayne-Kerr Bridges B224 and B201. In the dielectric measure-
ments the temperature stability was better than ±0.05 °C over the measuring time and no temperature gradient could be detected over the probe volume.

In the $T_1$ measurements a single crystal was oriented in that way that the ferroelectric $b$-axis was perpendicular to the static magnetic field $H_0$ and parallel to the rf-field $H_1$. $T_1$ was measured by $90^\circ$-t-$90^\circ$ pulse sequences. For more particulars concerning our NMR equipment and the temperature stability in these measurements we refer to 4.

III. Experimental Results and Discussion

A) Dielectric Data

The results of the dielectric measurements may be summarized by the statement that the dielectric constant in the ferroelectric $b$-direction can be represented in the entire temperature range between 20 and 30 °C by a Cole-Cole formula, i.e.

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i \omega \tau_\beta)^{-1}} = \varepsilon_s + (i \omega \tau_\beta)^{-1}$$

$$= \left[\frac{\beta_\infty - \beta_s}{1 + (i \omega \tau_\beta)^{-1}}\right]^{-1} = \left[\beta(\omega)\right]^{-1}. \quad (1)$$

By $\varepsilon$ and $\beta$ we denote the complex dielectric constant and its reciprocal, the dielectric modulus, which both depend on the frequency $\omega$ and the temperature $T$. The index $s$ refers to the static and the index $\infty$ to the high frequency value of the material quantities. The quantities $\tau_\beta$ and $\tau_s$ are the relaxation times of the dielectric constant and the dielectric modulus, respectively. In our experiments $h \ll 1$ holds i.e. in good approximation the ferroelectric dispersion can be represented by a single Debye relaxation. The critical dielectric behaviour manifests itself in a strong temperature dependence of the static dielectric constant $\varepsilon_s$ and of the relaxation time $\tau_\beta$ (Fig. 1), whereas all other material quantities are nearly constant. These results should be expected from phenomenological theories 7. We observed a phase transition of the first order which is close to a second order one. A Curie Weiß law holds for $\varepsilon_s$ but it is not valid exactly for $\tau_\beta$. We found $C = 3.44 \times 10^8$ K and $C' = 520$ K for the Curie Weiß constants of the paraelectric and ferroelectric phase, respectively.

Our maximum value of the dielectric constant is about 550 whereas Gesi 5 finds 5000. Correspondingly we observed much larger differences between $T_c$ and the Curie temperatures $\Theta$ and $\Theta'$. This difference may be accounted for if it is assumed that the crystals used in our experiments have a non ferroelectric surface layer. This is a reasonable assumption since the surface of AgNa(NO$_2$)$_2$ is very sensitive to external manipulations. If one assumes that a sample of the total thickness $d$ is build up by the bulk material, the dielectric constant of which is given by (1), and by two surface layers of total thickness $d_1$ with temperature and frequency independent dielectric modulus $\beta_1$, then the measured dielectric modulus $\beta^m(\omega)$ which refers to the total sample can be easily calculated. The result is a relation of the form of (1) where $\tau_\beta$ and $h$ are the same for both the total sample and the bulk. But, of course, $\beta_s$ and $\tau_s$ will generally be different for the bulk and for the total sample. We do not need to take into account this most general case. We consider the special case $h \ll 1$ and $d_1 \ll d$ which certainly holds for our measurements. Then one obtains the following relation for the static dielectric modulus $\beta^m_s$ and the relaxation time $\tau^m_\beta$ measured at the total sample

$$\beta^m_s \beta_s^{-1} = (\tau^m_\beta)^{-1} \tau_\beta = 1 + d_1 \beta_1/d \beta_s. \quad (2)$$

Thus the quantities $\beta_s$ and $\tau_s$ measured at a real sample are influenced in the same way by the surface layer. If one plots the temperature dependence of these quantities (see Fig. 1) the measured quantities $\beta^m_s$ and $(\tau^m_\beta)^{-1}$ are related to those of the bulk by a translation (note that $(\tau_\beta)^{-1} \beta_s$ is nearly temperature independent). Thus, this model exactly describes the discrepancies between our results and those of Gesi 5. If one assumes $\beta_s$ to be in the order of $10^{-1}$ the thickness of the surface layer is approximately 20 μm.
We are now interested in a molecular interpretation of these experimental results. A model which is most frequently used is the Mason model. Assuming this model we may consider the relaxation time \( T = T_0 C/T \) of the non-interacting dipole system, where the relaxation time \( T_0 \) is given by

\[
T_0 = T_0/(\epsilon_s - \epsilon_\infty) .
\] (3)

Then one obtains

\[
T_0 = \Gamma^{-1} e^{U/kT}
\] (4)

where \( \Gamma \) denotes a constant or only little temperature dependent characteristic frequency and \( U \) the internal activation energy per dipole. Below \( T_c \) (3) is subject to some corrections which were studied extensively in. According to Fig. 2 both works, discussed here, yield the same values for \( T_0 \). This result should be expected from the above surface layer model because for the bulk according to (1) and (3) \( T_0 = T_0 \epsilon_s/\epsilon_\infty \approx T_0 \epsilon_\infty \) holds and for \( h \ll 1 \) and \( \epsilon_\infty \ll \epsilon_s \) according to (2) for the data obtained from the total sample \( \epsilon_\infty m = \epsilon_\infty \beta_s m \epsilon_\infty -1 = \epsilon_\infty \beta_s \epsilon_s \epsilon_\infty -1 = \epsilon_\infty \) holds. Thus \( T_0 \approx T_0 \epsilon_\infty \) may be determined with good approximation from values obtained from a sample with surface layers. The line in Fig. 2 corresponds to an activation energy \( U = 0.68 \pm 0.05 \) eV for the flip motion of the electrical dipoles. From this value a characteristic frequency \( \Gamma \) in the order of \( 10^{18} \) s\(^{-1}\) can be estimated. Both values differ in order of magnitude from those known from other order-disorder type ferroelectrics where one usually finds \( U \) in the order of \( k T_s \) and \( \Gamma \) in the order of \( 10^{12} \) s\(^{-1}\) (see Reference 9). For NaNO\(_2\) one obtains \( U = 0.28 \) eV\(^{19}\).

Our values of \( U \) and \( \Gamma \) also differ from those reported by Gesi\(^5\) although according to Fig. 2 the \( T_0 \) values are nearly equal in both works. The reason is that this author assumes \( \Gamma \) to be equal to a characteristic IR frequency \( kC/h \). Then for every temperature from (3) and (4) an activation energy which is in the order of 0.4 eV can be estimated. But according to Fig. 2 a plot with 0.4 eV cannot fit the experimental points. The basic argument for an interpretation of the results on this line is the assumption that Eyring's reaction rate theory\(^{11}\) can be applied to the processes in question. With respect to this point, however, the following objections may arise. An activated state (complex) which is in thermal equilibrium with one of the reaction partners is assumed to exist. Furthermore a slow oscillating motion of this activated state is assumed. Obviously in Mason's model there exists no state of the electrical dipoles which corresponds to this activated state. Nevertheless we may apply Eyring's theory to the present problem from a formal point of view. A main result of the theory is a relation of the type \( \tau = \tau_\infty \exp(F/kT) \) where \( F = U - TS \) is the free activation energy per dipole, \( S \) denotes the activation entropy per dipole, \( \tau_\infty = h/\epsilon_\infty \) and \( \tau \) is the relaxation time of the non-interacting dipole system, i.e. \( \tau = \tau_0 C/T \). But in our measurements in the kHz regime the crystal is adiabatically isolated and consequently one must consider (4) where \( \Gamma = kC h^{-1} \exp(S/k) \). Thus the activation entropy may be derived from the relation \( \exp(S/k) = h \Gamma/kC \) where \( \Gamma \) can be calculated from dielectric measurements. In the case of AgNa(NO\(_2\))\(_2\) one obtains

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**Fig. 2.** Semilogarithmic plot of \( \tau_0^{-1} \) versus \( T^{-1} \). The points • were calculated from the values reported by Gesi\(^5\); the points o were obtained from our measurements.
Taking into account the rather high value of $U$ we may describe the nonlinear temperature dependence of the reciprocal relaxation time $\tau_0^{-1}$ reported in Figure 1. Since $\varepsilon_0 - \varepsilon_\infty$ obeys a Curie Weiss law on both sides of $T_c$ and since according to (4) $\tau_0$ is a monotonically decreasing function of the temperature $T$ $\tau_0^{-1}$ must show a nonlinear temperature dependence. In most ferroelectrics this effect is not observed because usually the activation energy $U$ is only in the order of $kT_c$.

Finally the following remark should be made with respect to Figure 2. In a recent work it was shown $^9$ that for an electrostrictive crystal different slopes of the line in Fig. 2 in the paraelectric and ferroelectric phase should be observed when the crystal is mechanically clamped and nearly equal slopes should be observed when the crystal is mechanically free. Since AgNa(NO$_2$)$_2$ is not piezoelectric in the paraelectric phase $^{13}$ for a free crystal one would expect to observe a behaviour according to Figure 2. In fact we could not find any piezoelectric resonance in the ferroelectric phase below our highest measuring frequency.

B) $T_1$ Measurements

In Fig. 3 the temperature dependence of $T_1^{-1}$ is presented in a semilogarithmic plot. $T_1^{-1}$ depends strongly on the temperature over a fairly large range according to a thermally activated process with an activation energy of about 0.48 eV. Beyond experimental errors this value differs considerably from the activation energy of 0.68 eV reported above for the dielectric process. This result clearly indicates that besides the dielectric flip motion a further thermally activated process is going on in the crystal. For a description of the behaviour of $T_1$ we may use well known methods $^{14}$. Assuming a slow motion for which $\omega \tau_0 \gg 1$ holds where $\omega$ is the Larmor frequency and $\tau_0$ denotes the characteristic relaxation time of the process we obtain

$$T_1 \propto \omega^2 \tau_0 .$$

For $\tau_0$ a relation of the type of (4) is assumed to be valid. Thus, $T_1$ should depend quadratically on the frequency and exponentially on the temperature. Both predictions are fulfilled by our measured $T_1$ values. Below 290 K there are deviations from the quadratic frequency dependence of $T_1$ which possibly may be ascribed to a further process whose influence on $T_1$ becomes dominant at lower temperatures. Because of the observed order of magnitude of the activation energy the process which causes the temperature dependence of $T_1$ in Fig. 3 is most likely a diffusional motion. Taking the size of the ions in this material into consideration one would suppose a diffusion of Na$^+$-ions.

As was expected from the outset there is only a small influence of the dielectric instability on $T_1$. The relaxation rate $T_1^{-1}$ slightly increases near $T_c$ for both measuring frequencies. This effect cannot be resolved in Fig. 3 because of the logarithmic scale. The small peak of $T_1^{-1}$ superimposed on the general behaviour (Fig. 3) is smaller for 20 MHz than for 15 MHz. Because of the extremely slow dielectric relaxation this result is in accordance with a qualitative picture. In addition it confirms the assumption of two independent thermally activated processes in the material. For a quantitative interpretation a ferroelectric contribution to the relaxation rate $T_1^{-1}$ may be separated from the measured values according to $T_1^{-1} = T_{lf}^{-1} + T_{ln}^{-1}$ where the normal part $T_{ln}^{-1}$ is given by the general behaviour of $T_1$ in Figure 3. The behaviour of $T_{lf}$ should be understood by applying methods outlined.
According to these works $T_{1f}$ is expected to become nearly temperature independent when the characteristic dielectric frequency $\tau_e^{-1}$ is smaller than or in the order of magnitude of the Larmor frequency. For a rough estimation we use the smallest relaxation time which appears in the dielectric behaviour, i.e. $\tau_0$ for the largest temperature, and we then obtain $\omega \tau_0 \approx 1$. Since all other relaxation times are much larger this argument cannot describe quantitatively the observed behaviour of $T_{1f}^{-1}$. Thus, this question forms an open problem which possibly may be solved by taking into account other relaxation mechanisms.

So we may consider a relaxation via anisotropical chemical shift, which is known to play a role in the cw-data of AgNa(NO$_2$)$_2$\cite{16}. But in the case of $\omega \tau_e \gtrsim 1$, this interaction cannot cause an increasing relaxation rate near $T_c$. Rather $T_1$ should increase, if $\tau_e$ becomes large. Most probably, the theory used to describe the NMR relaxation breaks down, because near the ferroelectric transition of AgNa(NO$_2$)$_2$ $T_2$ is in the order of $\tau_e$. Thus, the theory should be replaced by a “strong collision” theory for such slow processes. $T_{1\nu}$ measurements could elucidate this point.

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2. K. Gesi, ibid. 28, 1365 [1970].
5. K. Gesi, Ferroelectrics 4, 245 [1972].