Dielectric Behaviour of the Ferroelectric $AgNa(NO_2)_2$ and Spin Lattice Relaxation of ^{23}Na

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The characteristic ferroelectric dispersion of the dielectric constant of $AgNa(NO_2)_2$ 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 T_1 of ^{23}Na in $AgNa(NO_2)_2$ is measured by $90°-t-90°$ pulse sequences. In the entire temperature range the temperature dependence of T_1 is governed by a thermally activated process which is ascribed to a diffusional motion. There is only a small influence of the dielectric instability on T_1.

I. Introduction

Recently it has been shown by Gesi [1, 2] that $AgNa(NO_2)_2$ is a ferroelectric crystal which undergoes a phase transition of the first order at about 38 °C. In analogy to the similar ferroelectric $NaNO_2$ the transition is assumed to be of the order-disorder type with the NO_2^--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 10^7 to 10^{11} 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 $AgNa(NO_2)_2$ appears in the kHz regime. Thus in this substance the motions of the electrical dipoles are comparatively slow.

In two recent works [3, 4] the behaviour of the spin lattice relaxation time T_1 of ^{23}Na in $NaNO_2$ was related to the critical dielectric behaviour by assuming that the strong increase of T_1^{-1} 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 f_L is small if compared with the characteristic dielectric relaxation frequency f_ε. This is true for $NaNO_2$ but it is not true for $AgNa(NO_2)_2$. Thus one would expect that T_1 of ^{23}Na will be not or only little affected by the dielectric instability of the latter substance. We therefore measured T_1 of ^{23}Na in $AgNa(NO_2)_2$ 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 Gesi [5].

II. Sample Preparation and Experimental Details

Employing well known methods [5, 6] at constant temperature (about 25 °C) single crystals of $AgNa(NO_2)_2$, approximately $4 \times 4 \times 12$ mm³ in size, were grown from aqueous solution containing 9.8 wt% $AgNO_2$ and 37.2 wt% $NaNO_2$ 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 $AgNa(NO_2)_2$ 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 $\pm 0.05\,^{\circ}C$ 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°-t-90° 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 50 °C by a Cole-Cole formula, i. e.

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\,\omega\,\tau_\varepsilon)^{1-h}} = \varepsilon_s \frac{1 + (i\,\omega\,\tau_\beta)^{1-h}}{1 + (i\,\omega\,\tau_\varepsilon)^{1-h}}$$
$$= \left\{\beta_\infty - \frac{\beta_\infty - \beta_s}{1 + (i\,\omega\,\tau_\beta)^{1-h}}\right\}^{-1} = \{\beta(\omega)\}^{-1}. \qquad (1)$$

By ε and β we denote the complex dielectric constant and its reciprocal, the dielectric modulus, which both depend on the frequency ω and the temperature T. The index s refers to the static and the index ∞ to the high frequency value of the material quantities. The quantities τ_ε and τ_β 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 temperatur dependence of the static dielectric constant ε_s and of the relaxation time τ_ε (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 ε_s but it is not valid exactly for τ_ε. We found $C = 3.44 \cdot 10^3$ K and $C' = 520$ K for the Curie Weiß constants of the paraelectric and ferroelectric phase, respectively.

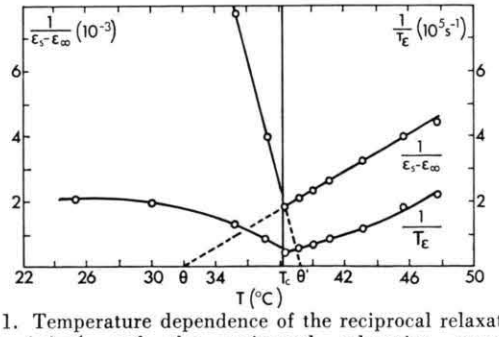

Fig. 1. Temperature dependence of the reciprocal relaxation time $(\tau_\varepsilon)^{-1}$ and the reciprocal relaxation strength $(\varepsilon_s - \varepsilon_\infty)^{-1}$ of the dielectric constant of $AgNa(NO_2)_2$ in the b-direction, near T_c

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 Θ and Θ'. 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 β_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 τ_β and h are the same for both the total sample and the bulk. But, of course, β_s and τ_ε 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 β_s^m and the relaxation time τ_ε^m measured at the total sample

$$\beta_s^m \beta_s^{-1} = (\tau_\varepsilon^m)^{-1} \tau_\varepsilon = 1 + d_1 \beta_1 / d\beta_s. \qquad (2)$$

Thus the quantities β_s and τ_ε^{-1} 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 β_s^m and $(\tau_\varepsilon^m)^{-1}$ are related to those of the bulk by a translation (note that $(\tau_\varepsilon)^{-1}\beta_s$ is nearly temperature independent). Thus, this model exactly describes the discrepancies between our results and those of Gesi [5]. If one assumes β_1 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 [7, 8]. Assuming this model we may consider the relaxation time $\tau = \tau_0 C/T$ of the non-interacting dipole system, where the relaxation time τ_0 is given by [7]

$$\tau_0 = \tau_\varepsilon / (\varepsilon_s - \varepsilon_\infty) \ . \tag{3}$$

Then one obtains

$$\tau_0 = \Gamma^{-1} e^{U/kT} \tag{4}$$

where Γ 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 [9]. According to Fig. 2 both works, discussed here, yield the same values for τ_0. This result should be expected from the above surface layer model because for the bulk according to (1) and (3) $\tau_\beta = \tau_\varepsilon \varepsilon_\infty / \varepsilon_s \approx \tau_0 \varepsilon_\infty$ holds and for $h \ll 1$ and $\varepsilon_\infty \ll \varepsilon_s$ according to (2) for the data obtained from the total sample $\varepsilon_\infty{}^m = \tau_\beta (\beta_s{}^m \tau_\varepsilon{}^m)^{-1} = \tau_\beta (\beta_s \tau_\varepsilon)^{-1} = \varepsilon_\infty$ holds. Thus $\tau_0 \approx \tau_\beta / \varepsilon_\infty$ 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 Γ 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 kT_c and Γ in the order of $10^{12}\ s^{-1}$ (see Reference [9]). For $NaNO_2$ one obtains $U = 0.28$ eV [10].

Our values of U and Γ also differ from those reported by Gesi [5] although according to Fig. 2 the τ_0 values are nearly equal in both works. The reason is that this author assumes Γ 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, $\tau_\infty = h/kT$ and τ 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 Γ can be calculated from dielectric measurements. In the case of $AgNa(NO_2)_2$ one obtains

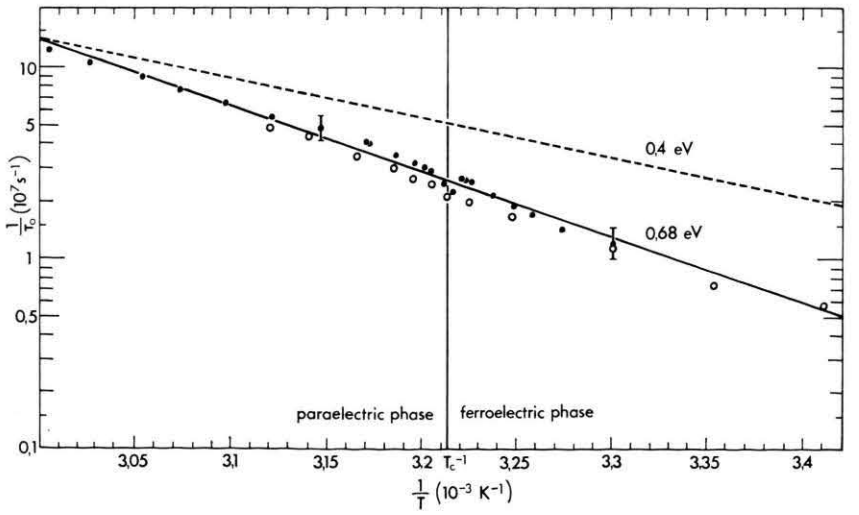

Fig. 2. Semilogarithmic plot of τ_0^{-1} versus T^{-1}. The points · were calculated from the values reported by Gesi [5], the points o were obtained from our measurements

$h\Gamma/kC$ in the order of 10^4. This yields $S \approx 8 \cdot 10^{-4}$ eV/K which is a reasonable order of magnitude [12].

Taking into account the rather high value of U we may describe the nonlinear temperature dependence of the reciprocal relaxation time τ_ε^{-1} reported in Figure 1. Since $\varepsilon_s - \varepsilon_\infty$ obeys a Curie Weiß law on both sides of T_c and since according to (4) τ_0 is a monotonically decreasing function of the temperature T τ_ε^{-1} must show a nonlinear temperature dependence. In most ferrelectrics 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 $\omega \tau_c \gg 1$ holds where ω is the Larmor frequency and τ_c denotes the characteristic relaxation time of the process we obtain

$$T_1 \propto \omega^2 \tau_c . \qquad (5)$$

For τ_c 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.

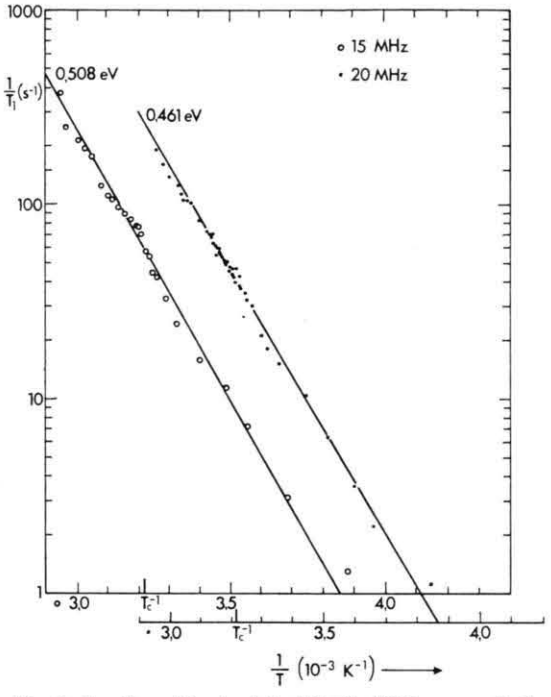

Fig. 3. Semilogarithmic plot of T_1^{-1} of ^{23}Na versus T^{-1}.

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_{1f}^{-1} may be separated from the measured values according to $T_1^{-1} = T_{1f}^{-1} + T_{1n}^{-1}$ where the normal part T_{1n}^{-1} is given by the general behaviour of T_1 in Figure 3. The behaviour of T_{1f} should be understood by applying methods outlined

in [3, 4, 15]. According to these works T_{1f} is expected to become nearly temperature independent when the characteristic dielectric frequency τ_ε^{-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. τ_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 on 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 $AgNa(NO_2)_2$ [16]. But in the case of $\omega\tau_\varepsilon \gtrsim 1$, this interaction cannot cause an increasing relaxation rate near T_c. Rather T_1 should increase, if τ_ε becomes large. Most probably, the theory [3, 4] 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 τ_ε. Thus, the theory should be replaced by a "strong collision" theory for such slow processes. $T_{1\varrho}$ measurements could elucidate this point.

Acknowledgement

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