NMR Investigation of the Quadrupolar Glass $Na(CN)_xCl_{1-x}$

Static and Dynamic Behaviour of the CN Molecules in the Quadrupolar Glass $Na(CN)_xCl_{1-x}$ Studied by ^{23}Na and ^{35}Cl NMR *

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The freezing process of the CN dumbbells in the orientational glass $Na(CN)_xCl_{1-x}$ was studied by ^{23}Na and ^{35}Cl NMR for several concentrations x. The systems with $x \gtrsim 0.7$ undergo structural phase transitions, whereas systems with $x \lesssim 0.7$ stay cubic on the average down to lowest temperatures. For concentrations $x \approx 0.65$, the temperature dependences of the NMR line widths give evidence that the transition into the glass state essentially consists in a deformation of the local potential leading to a formation of preferential directions for the orientations of the CN ions. The temperature dependence of the spin lattice relaxation time T_1 shows that the motion of the CN ions in their deformed potentials remain fast. With decreasing concentration x, the influence of the collective interactions between the CN ions become less pronounced and a gradual transition to systems with decoupled CN ions can be observed.

Introduction

Orientational glasses have recently attracted a considerable amount of interest. Among these systems, the quadrupolar glass $K(CN)_xBr_{1-x}$ is one of the examples most studied. In this system, the CN ions form elastic quadrupoles whose interactions are assumed to determine the anomalous static and dynamic properties. In the present work, we deal with the analogous system $Na(CN)_xCl_{1-x}$ containing the nuclei ^{23}Na and ^{35}Cl, which are very suitable for investigating the local static and dynamic properties by quadrupolar perturbed NMR. By that method, essentially the static and fluctuating parts of the electric field gradient tensor (EFG) at the site of the nucleus are employed in order to obtain information on the freezing process of the CN molecules. In this system structural phase transitions occur for $x \gtrsim 0.7$, whereas below that limit no phase transition can be detected and the crystal stays cubic on the average down to lowest temperatures. Moreover, the collective behaviour of the CN dumbbells presumably is diminishing with decreasing CN concentration. Therefore, in crystals with concentrations $x \approx 0.65$, the collective transition to a glass-like low temperature state is proposed to be most pronounced. Some of our results will be published elsewhere [1] and we may refer to this work for some more particulars.

Static Electric Field Gradients

Although systems which do not undergo a phase transition ($x \lesssim 0.7$) stay cubic on the average down to lowest temperatures, the local environments of the ^{23}Na nuclei generally deviate from the cubic symmetry and, thus, a static EFG occurs. The shapes observed for the ^{23}Na ($I = 3/2$) central line and satellite lines in these systems could be explained by assuming that the principal axes of the EFG at the Na site are oriented along the axes of the average cubic structure and that the principal components of the EFG are distributed according to a Gaussian law. The first result is related to the fact that the CN molecules freeze in with their axes parallel to one of the axes of the cubic structure. The local potentials in which the CN dumbbells are moving are correspondingly deformed. Moreover, the width b of the Gaussian distribution is a measure for the mean local deviation from the cubic structure. Figure 1 demonstrates that, on

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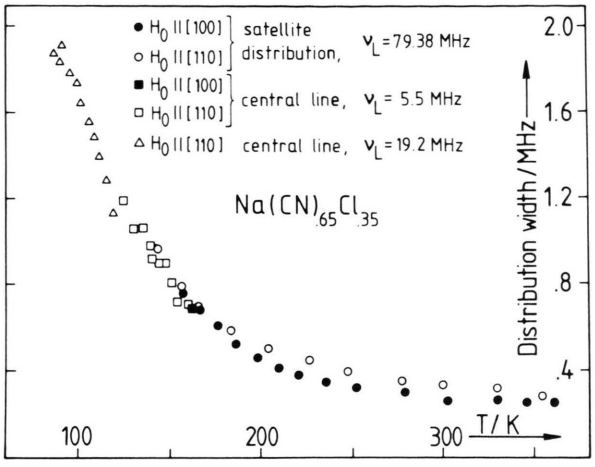

Fig. 1. Temperature dependence of the width of the EFG distribution at the Na site as determined from the distributions of the ^{23}Na central line and satellite lines.

passing from about 200 to 100 K, this quantity increases continuously by about one order of magnitude. This effect is a consequence of the freezing-in of the CN ions. We stress that in systems, which do not undergo a phase transition, a continuous behaviour of b is observed, whereas b behaves discontinuously in case that a phase transition occurs [1, 2]. The temperature dependence of b presented in Fig. 1 should be related to the temperature dependence of the local order parameter which has been measured quite recently by X-ray diffraction methods for the system under consideration [3]. According to these experiments, the saturation of the order parameter should become noticeable below about 100 K. Unfortunately, in that temperature region, the transition from the fast motion to the slow motion case takes place in the ^{23}Na experiments and, therefore, we would not determine the distribution width b below 100 K.

The deformations of the local potentials of the CN ions which occur at decreasing temperature lead to a readjustment of the equilibrium positions of the neighbouring Na atoms, too. As a consequence, the cubic symmetry at the sites of the Cl nuclei is disturbed and one should observe also in this case a distribution of electric field gradients. For the ^{35}Cl ($I = 3/2$) and the ^{37}Cl ($I = 3/2$) nuclei, this should lead to an inhomogeneous braodening of the central line and to a wide spread of satellite frequencies. Because of the relatively small NMR sensitivity of the Cl nuclei, we could not detect the satellite distribution and we, therefore, focussed our attention on the temperature dependence of the ^{35}Cl central line. The full width at half-height, which is related to the EFG distribution width, was measured at $\nu_L = 29.40$ MHz for samples with different concentrations x none of them undergoing a phase transition. In all cases, the line width decreases with increasing temperature. The high temperature value, which is reached in an asymptotic way, essentially does not depend on the concentration. In Table 1, the line widths measured at 300 K are listed and are compared to the line widths calculated by the well-known Van Vleck formalism, including the ten nearest neighbours. Obviously, the line widths measured cannot be explained by taking into account only the dipolar magnetic interactions. Nevertheless, the strong orientational dependence can be understood on the basis of Van Vlecks formula. Presumably, also at high temperatures, there remains a residual contribution of quadrupolar interactions because even in the case of fast reorienting CN dumbbells, the cubic symmetry at the Cl sites is not strictly maintained in the mixed systems. The temperature dependence of the line width was measured with $H_0 \parallel [110]$ since the dipolar broadening has a minimum in this orientation. With decreasing temperature, the interactions between the CN ions become important. Also in this case, the gradual occurrence of the preferential directions results in a perturbation of the cubic symmetry at the Cl sites and, thus, in an increase of the EFG distribution width at that site. According to Fig. 2, continuous transtions into the glass state take place for all concentrations x in the same temperature range between 200 K and 100 K. In particular, for the concentrations $x = 0.65$ and $x = 0.50$, the line width is saturated below 100 K. (In

Table 1. ^{35}Cl NMR line width in $Na(CN)_xCl_{1-x}$ (in kHz) as measured at 300 K and calculated by the Van Vleck formula.

x	Measured		Calculated	
	$H_0 \parallel [100]$	$H_0 \parallel [110]$	$H_0 \parallel [100]$	$H_0 \parallel [110]$
0.65	2.38	1.26	0.928	0.504
0.50	2.33	1.34	0.929	0.508
0.40	2.40	1.45	0.930	0.510
0.20	2.05	0.95	0.931	0.514

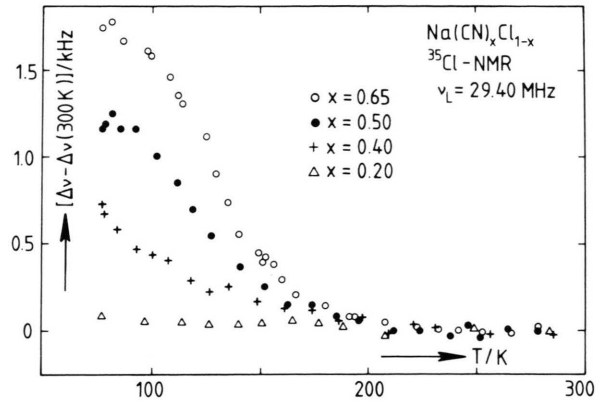

Fig. 2. Difference between the widths of the ^{35}Cl central line at the temperature T and at 300 K as a function of T for samples with different concentrations x. H_0 was parallel to [110].

case of the ^{35}Cl resonance, the problems mentioned above for the ^{23}Na resonance do not occur.) The step of the line width becomes less pronounced with decreasing concentration x, giving evidence to the fact that the interactions between the CN ions become less effective and, thus, the deformations of the local potentials are less pronounced. For the sample with $x = 0.20$ no increase of the line width can be observed at all and, thus, the CN ions essentially are decoupled. A similar feature of the dependence of the freezing process on the concentration x is observed by X-ray experiments on $K(CN)_xBr_{1-x}$ [4]. Also, in this system the freezing takes place in the same temperature range for all x and the step of the line width decreases with decreasing x. Since the X-ray and the NMR line widths both measure the deviations from the cubic symmetry [3], both results are consistent.

Dynamical Behaviour

It is well-known that the spin lattice relaxation time T_1 of a nuclear species is related to dynamical processes in the system. In pure NaCN above the phase transition at 288 K, a thermally activated process is observed for the ^{23}Na-T_1 (Fig. 3), which can be attributed to the fast reorientational motions of the CN dumbbells in their local potentials showing cubic symmetry. Below T_c, the ^{23}Na-T_1 can well be described by a BPP-type behaviour related to the 180° flip motions of the CN dumbbells. The characteristic minimum occurs at a temperature for which $2\omega_L \tau_c \approx 1$, where τ_c is the correlation time of the flip motions of the CN molecules, which was shown to follow the temperature dependence $\tau_c = \tau_\infty \exp(U/kT)$. Also in the diluted systems the relaxational behaviour of the ^{23}Na nuclei is governed by the motions of the CN dumbbells. The system with $x = 0.9$ still performs a phase transition of the first order at 245 K. At that temperature, a discontinuity of T_1 and of the activation energy are observed. For samples with $x = 0.7$ (Fig. 3) and $x = 0.65$, a phase transition could be observed neither in T_1 nor in the line shape. Rather near 200 K there is a continuous increase of the apparent activation energy with decreasing temperature. Similar to the change of the activation energy observed at T_c in systems which udergo a phase transition, this effect is related to the collective interactions between the CN dumbbells. In these cases, a broad BPP-type minimum with different slopes on both sides is observed indicating a distribution of local potentials and, thus, of activation energies. For even smaller x, the broadened minima are shifted to lower temperatures (Figure 3). For the system with $x = 0.4$, the minimum is reached, whereas the crystal with

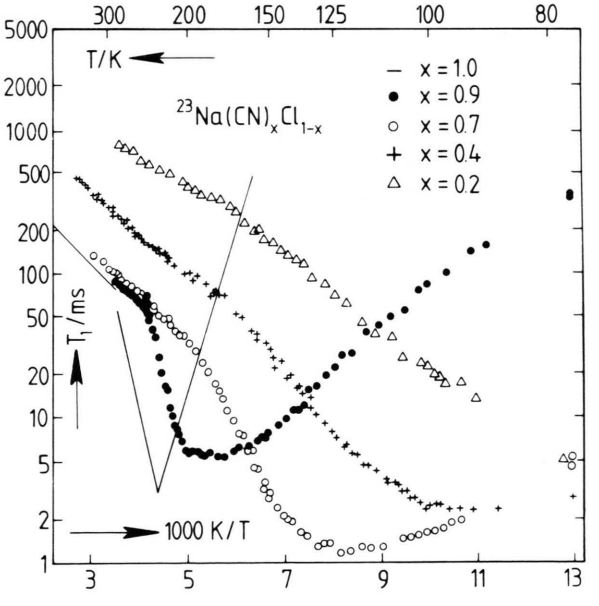

Fig. 3. Arrhenius plot of the temperature dependence of the ^{23}Na spin lattice relaxation time T_1 of the central line for samples with different concentrations x obtained at $\nu_L = 79.38$ MHz.

$x = 0.2$ remains in the fast motion regime down to LN temperature. Since the change in activation energy observed at about 200 K for $x \approx 0.7$ is related to the interaction between the CN dumbbells, it becomes less and less pronounced on lowering x. In all cases, at high temperatures the same activation energy is observed indicating that the motions of the CN dumbbells in their local potentials are fast. The same type of motion occurs in the high temperature phase of pure NaCN.

For the extremely diluted system NaCl:CN, i.e. for small x, the CN molecules in the NaCl matrix are decoupled. One therefore expects a pure BPP-type behaviour of the ^{23}Na-T_1 in the entire temperature range, provided that the relaxation mechanism is still governed by the motions of the CN molecules. Assuming that the prefactor τ_∞ and the activation energy U are the same as in the high temperature phase of pure NaCN, the BPP minimum is expected to occur near 65 K. We measured the ^{23}Na-T_1 for a sample with $x = 0.03$ (Figure 4). Below 125 K, it is clearly smaller than the background value of about 5 s and reaches a value of $T_1 = 250$ ms at LN. The values measured between 280 K and 140 K in pure NaCl (Fig. 4), are consistent with those obtained previously [5] at $\nu_L = 12$ MHz. Extrapolating these results to LN, yields a difference of more than three orders of magnitude between the ^{23}Na-T_1 values of pure NaCl and $NaCl_{.97}(CN)_{.03}$. This drastic effect can be attributed only to the motions of the CN ions. As expected, the temperature dependence of T_1 indicates that the dynamics of the diluted dumbbells are in the fast motion regime ($\omega_L \tau_c \ll 1$) down to LN. With increasing temperature, the relaxation mechanism, due to the motions of the CN ions, becomes less and less effective and above 125 K another process (probably paramagnetic impurities) constitutes the dominant relaxation mechanism. We separated the contribution of the CN dynamics (circles) by subtracting the background relaxation rate (dashed line) from the measured data (points). We could then determine the activation energy $U = 0.058$ eV, a value close to that of pure NaCN above T_c. It again describes the fast reorientations of the CN dumbbells in the cubic potential, regardless whether nearest neighbours are spherical Cl ions or other fast reorienting CN ions. Since the BPP minimum is not reached down to LN, it is only possible to give an upper limit for the prefactor, $\tau_\infty (x = 0.03)$

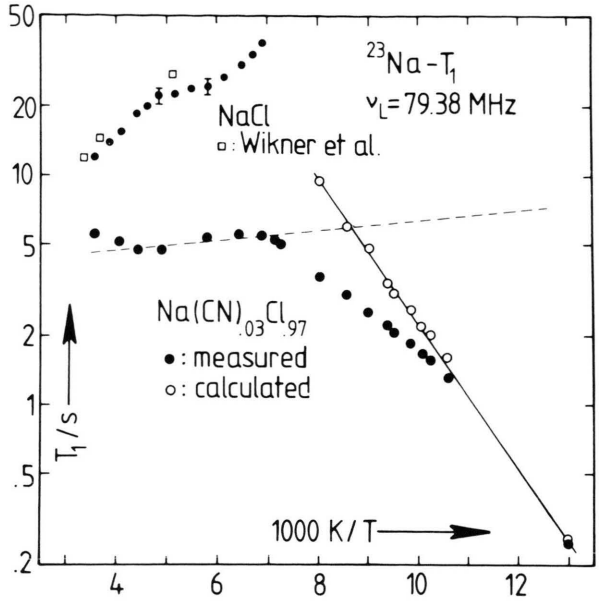

Fig. 4. Arrhenius plot of the temperature dependence of the ^{23}Na-T_1 in the very diluted system ($x = 0.03$) and in pure NaCl. For the pure NaCl, besides our data also the results of a previous work [5] are given.

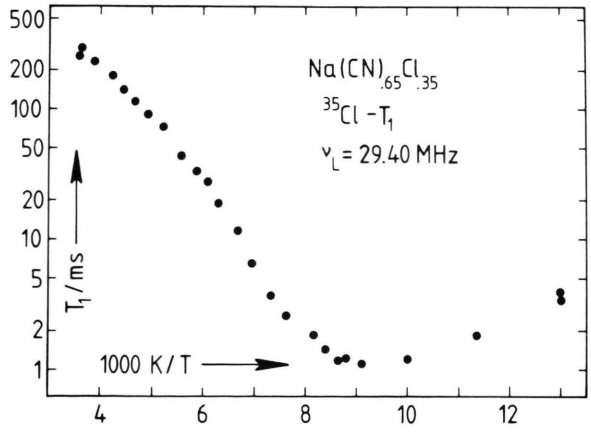

Fig. 5. Arrhenius plot of the temperature dependence of the ^{35}Cl-T_1 for one concentration $x = 0.65$.

$< 1.3 \cdot 10^{-13}$ s. This contrasts with the large value ($\tau_\infty = 1.2 \cdot 10^{-9}$ s) obtained for $K(CN)_{.04}Br_{.96}$ from the dielectric behaviour [6].

The spin lattice relaxation time of the ^{35}Cl nucleus in $Na(CN)_{.65}Cl_{.35}$ shows the same temperature dependence as the ^{23}Na-T_1 (Figure 5). This is expected since in both cases the motions of the CN dumbbells constitute, via quadrupolar interactions,

the main relaxation mechanism. Comparing the T_1 values of ^{35}Cl and ^{37}Cl at ambient temperature, 460 ms and 300 ms respectively, indeed shows that the relaxation is of purely quadrupolar type. The ratio of 1.53 fits within the experimental errors to the value 1.60 expected for the pure quadrupolar case taking into account the values of the nuclear quadrupole moments. At high temperatures, the ^{35}Cl-T_1 data can be described by an Arrhenius law with an activation energy of $U = 0.06$ eV. As in the case of the ^{23}Na-T_1, it can be ascribed to the fast reorientational motions in the cubic potential. At low temperature, one observes a broadened BPP-type minimum indicating a distribution of relaxation times. Near 180 K, there is a smooth change in the activation energy corresponding to a similar behaviour of the ^{23}Na-T_1. It reflects, too, the deformation of the local potentials. In the same temperature range, the width of the central line begins to increase (Figure 2). This effect is also related to the occurrence of preferential directions. Compared to the ^{23}Na-T_1, the position of the minimum should be slightly shifted to lower temperatures because of the smaller Larmor frequency. This can indeed be observed, although the effect is not very drastic. A quantitative comparison is difficult because the position of the minima depends on the irradiation conditions which might be slightly different in both cases.

Acknowledgements

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