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Statics and Dynamics of a Glassy Crystal: a NMR- and Neutron Scattering Investigation of $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$.

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Abstract. – The statics and the dynamics of the glass transition in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ have been investigated by inelastic neutron scattering and are directly compared to NMR results. Insight into the relaxation dynamics is gained via the temperature dependence of the transverse acoustic phonon modes and via the spin relaxation time T_1 . The statics of the system is reflected by the growth of a central peak and by the distribution of electric-field gradients. Both quantities are directly related to the glass order parameter. The temperature dependence of the order parameter provides experimental evidence that in NaCl:NaCN mixed crystals the glass transition is dominated by random fields rather than by frustration effects.

The alkali cyanide-alkali halide mixed crystals $(\text{MX})_{1-x}(\text{MCN})_x$, where M is the alkali metal and X a halogen ion, are model systems for glassy crystals. Above a critical concentration x_c , these systems display ferroelastic phase transitions [1, 2]. However, below x_c the well-defined structural phase transition is replaced by a frequency-dependent glass transition [3-5]. Following a recent theoretical approach by Michel [6] the phase transition becomes suppressed through random strains created by the substitutional impurity atoms X which act as static impurity centres. The strength of the random field is determined by the volume difference of the halogen and the CN^- ions. A first experimental indication of the importance of random fields in the cyanide glasses are the very different critical concentrations for the systems investigated so far, namely $(\text{KBr})_{1-x}(\text{KCN})_x$ ($x_c = 0.6$), $(\text{KCl})_{1-x}(\text{KCN})_x$ ($x_c = 0.8$) and $(\text{NaCl})_{1-x}(\text{NaCN})_x$ ($x_c = 0.7$). Therefore, two effects can be assumed to be important at the glass transition: i) a collective freezing driven by CN^- - CN^- interactions which are mediated by lattice strains. Below a critical concentration the long-range orientational order is suppressed through frustration effects due to the dilution of the CN^- molecules and the anisotropic quadrupolar-quadrupolar interactions and ii) a single-ion freezing where the random field determines the alignment of the orientational degrees of freedom. Experimentally, the importance of these two effects can be proved by measuring

the temperature dependence of the order parameter. In a pure random strain system the order parameter exhibits a smooth temperature dependence with no anomaly at a characteristic temperature. In a frustrated system a nonzero-order parameter only exists below the glass transition temperature.

While an enormous amount of experimental data exists for $(\text{KBr})_{1-x}(\text{KCN})_x$, much less is known for $(\text{NaCl})_{1-x}(\text{NaCN})_x$ [7]. However, detailed NMR experiments have been performed in the latter system [8]. The aim of the present work was to study the statics and the dynamics of the glass transition in $(\text{NaCl})_{1-x}(\text{NaCN})_x$ via inelastic neutron scattering (INS) and to make a direct comparison with analogous results as obtained from NMR techniques. At low temperatures the dynamic structure factor of glassy crystals as measured in INS experiments exhibits two phonon side bands in addition to a sharp resolution-limited central peak [3]. The temperature dependence of the transverse-acoustic-phonon side bands shows a rounded minimum and gives direct insight into the dynamic quadrupolar susceptibility as measured at THz frequencies. The integrated intensity of the central peak is directly related to the order parameter of the glass state [4, 6]. Using NMR techniques the temperature dependence of the spin relaxation time T_1 is determined by the local dynamics of the reorienting CN^- ions. The measuring frequencies now range in the MHz regime. The electric-field gradient (EFG) defines the local statics of the system [6].

For this investigation we choose $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ which is just below the critical concentration $x_c \approx 0.7$ [7]. Good-quality single crystals were grown from the melt by one of the authors (JA). The INS experiments have been performed on a triple-axis spectrometer located at a cold neutron source at the Risø National Laboratory. The incoming neutron energy was held constant at 4, respectively, 5 meV. The collimations were 60' before and after the monochromator and analyser crystals.

A typical result of the temperature dependence of a transverse acoustic phonon along [011] with a sound velocity proportional to c_{44} is shown in fig. 1. At room temperature a well-defined phonon side band appears clearly separated from a peak at zero-energy transfer. At high temperatures this zero-energy response is predominantly due to incoherent elastic scattering. With decreasing temperatures the phonon side band softens, indicating a decrease of the elastic constant c_{44} and the central line starts to grow. The width of the central line is temperature independent and resolution limited at all temperatures. At $T \approx 200$ K the acoustic phonon frequency runs through a minimum, while the intensity of the central peak continuously increases further. A summary of these measurements, namely the temperature dependence of the squared phonon energies which is directly related to the T

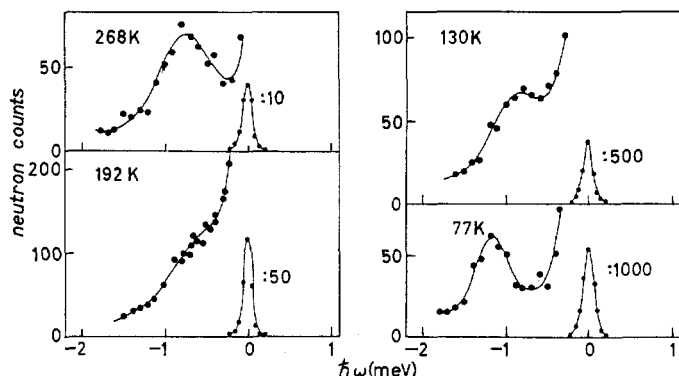


Fig. 1. - Constant Q -scans in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ at $Q = (1, 1.075, 1.075)$ at various temperatures. The lines are drawn to guide the eye. Note the drastic increase of the central line.

dependence of the elastic constant c_{44} and the intensities of the central line are shown in fig. 2. This figure summarizes the statics and the dynamics of the orientational glass NaCl:CN as probed by the THz frequencies of an INS experiment. In the time window of pico seconds the quadrupolar freezing-in of the CN^- ions appears at $T \approx 200$ K. The broad and rounded minimum in the T -dependence of the sound velocities corresponds to a cusp in the quadrupolar susceptibility and defines the freezing temperature $T_F(\omega)$. The position of this minimum depends sensitively on the frequency of the experimental method [5]. The statics of the system, namely the freezing-in of local strains and the freezing-in of orientational correlations is displayed by the integrated intensity of the central peak [4, 6].

Very analogous results can be derived using NMR techniques. They are an ideal tool to study the local statics and the local dynamics of these systems by measuring the static and the fluctuating parts of the electric-field gradient at the Na-sites: measurements of the spin relaxation time T_1 probe the relaxation kinetics of single CN^- ions, while measurements of the temperature dependence of the electric-field gradient distribution give insight into the local statics. Representative results for $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ are given in fig. 3. A detailed

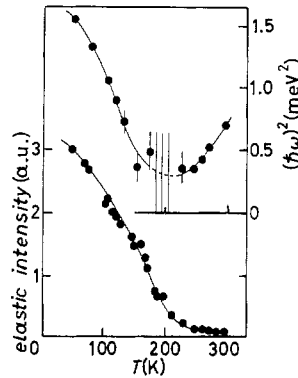


Fig. 2. - *Upper part*: squared phonon frequency in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ as measured at $Q = (1, 1.075, 1.075)$ vs. temperature. The vertical bars around $T = 200$ K indicate that due to the strong softening it was not possible to determine the phonon frequency unambiguously. The line is drawn to guide the eye. *Lower part*: intensity of the central peak vs. temperature. The line guides the eye only.

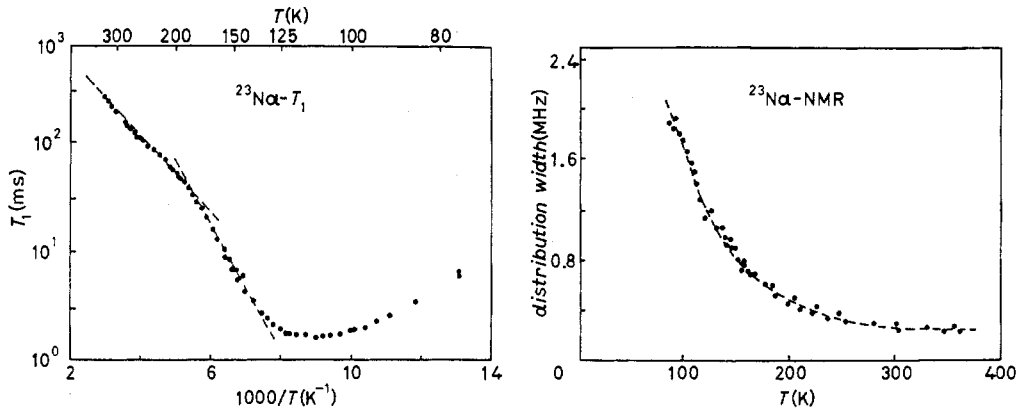


Fig. 3. - *Left*: spin relaxation time T_1 vs. $1000/T$ as measured in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ at $\nu_L = 79.38$ MHz. The broken lines are drawn to indicate the change of slope at $T \approx 190$ K. *Right*: electric-field gradient (EFG) distribution width vs. temperature as measured in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$. The data of fig. 3 have been published already in full details in ref. [7].

analysis of these results can be found in ref. [8]. The upper part of fig. 3 shows the spin relaxation time T_1 as measured at 79.4 MHz. The data are presented in an Arrhenius plot as $\log(T_1)$ vs. $1000/T$. In the high-temperature plastic phase we find an Arrhenius line with a constant slope defining the hindering barrier of the reorientational potential of the cubic phase as $E/k_B = 790$ K. At $T \approx 190$ K and in a narrow temperature range a change of slope indicates the transition into the glass state. Below, the temperature dependence of T_1 can be described by an activation energy of $E/k_B = 1300$ K. With further decreasing temperature, T_1 passes through a broad minimum where the single-particle relaxation rate equals the NMR measuring frequency. The correlation time as determined by the T_1 -minimum is a reliable value at an absolute time scale and it fits well into an extrapolated Arrhenius line as calculated from the dielectric dispersion [9]. Again we find an energy barrier of the reorientational potential $E/k_B \approx 1300$ K. These results show that within the glass phase the only relevant single-particle relaxation processes are dipolar reorientations.

Using NMR techniques, the statics of the system can be determined by measuring the T -dependence of the EFG via the inhomogeneous broadening of the central line or via the distribution of satellite frequencies. Like the central peak in the INS experiment the electric-field gradient measures the static (time independent) part of the coupled orientational-translational modes. The results of the experiments in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ are shown in the lower part of fig. 3.

These experimental observations suggest the following picture of the glass transition in $\text{NaCl}:\text{NaCN}$:

i) *Dynamics.* The glass transition in the cyanide orientational glasses is defined by the slowing-down of the CN^- reorientations coupled to local shear strains. This quadrupolar freezing is the primary relaxation. In the present experiments we proved this α -relaxation at THz frequencies via inelastic neutron scattering and at MHz frequencies via NMR experiments. In the neutron scattering experiments the minimum of the transverse sound velocity defines the cusp of the quadrupolar susceptibility and gives the temperature where the quadrupolar freezing becomes active in this frequency range. The change of slope in the T_1 vs. $1/T$ curve in the NMR experiments gives the temperature where the local molecular relaxations experience distinct changes in the reorientational potential through the freezing-in of lattice strains. Both anomalies appear roughly at the same temperature (T_F (10^{12} Hz) ≈ 200 K); T_F (10^8 Hz) ≈ 190 K a fact, that demonstrates how fast the primary relaxation slows down. 180° flips within the locally distorted lattice are still possible. This secondary relaxation is proved by the T_1 experiments at temperatures $T < 190$ K. The hindering barriers as determined from the NMR measurements agree with the results from dielectric experiments showing that the only relevant relaxation processes are dipolar reorientations. This interpretation is consistent with recent results in $(\text{KBr})_{1-x}(\text{KCN})_x$, where it has been demonstrated experimentally that in the glass state dipolar and quadrupolar relaxations are fully decoupled [10, 11].

ii) *Statics.* The statics of the system is reflected by the temperature dependence of the central line in the inelastic neutron scattering experiment and by the T -dependence of the distribution of electric-field gradients. Both quantities indicate the breakdown of cubic symmetry on a local scale and are a measure of the order parameter of the glass state [6]. No significant shift in temperature is apparent although the measuring frequencies are very different. Both quantities seem to probe essentially static properties of the crystal. In the case of a spin glass analogue we would expect a nonzero-order parameter only below the glass transition temperature. Within the framework of Michels theory $\Psi \propto y/T^2$, where y is only weakly temperature dependent. In this case of a random field problem we find an order parameter which is finite at all temperatures and increases smoothly with decreasing

temperatures. To compare the theoretical predictions with our experimental results, we plotted the logarithm of the intensity of the central peak and the logarithm of the EFG distribution width *vs.* $\log T$ (fig. 4): here the elastic incoherent scattering has been

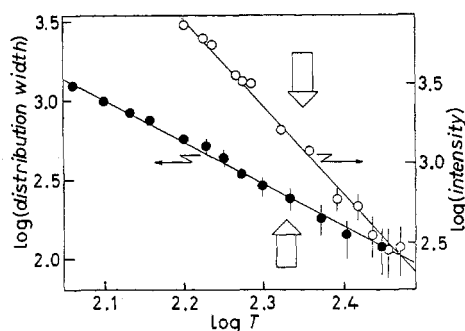


Fig. 4. – The logarithm of the integrated intensity of the central peak ($\log(\text{intensity})$: empty symbols) and the logarithm of the EFG distribution width ($\log(\text{distribution width})$: full symbols) *vs.* the logarithm of temperature ($\log(T)$) in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$. The arrows mark the temperature where in $(\text{NaCl})_{0.35}(\text{NaCN})_{0.65}$ the dynamic freezing-in appears in the neutron scattering experiment (upper arrow) and in the NMR experiment (lower arrow).

subtracted from the observed central-peak intensity and the NMR data have been corrected for the disturbance of the crystal field due to the pure chemical disorder. Using this representation, both quantities are described fairly well by straight lines. No anomalies appear over a wide temperature range ($120 \text{ K} \leq T \leq 300 \text{ K}$). Of course, at low temperatures both quantities saturate. The arrows in fig. 4 indicate the temperatures where the dynamic freezing-in occurs in the two experiments. Within the experimental uncertainties the order parameters appear smooth at these temperatures. The slope of the $\log(\text{intensity})$ curve is approximately 4, while the slope of the $\log(\text{width})$ curve is approximately 2. Note that the order parameter ψ is proportional to the square of the thermal average of the orientational distribution of the CN^- molecules [4]. Thus the central peak intensity gives directly the order parameter ψ [4], while the EFG distribution width, which depends linearly on the orientational variable [12], is proportional to $\sqrt{\psi}$ [12]. We think that fig. 4 gives strong evidence that the freezing-in in $\text{NaCl}:\text{NaCN}$ is dominated by random fields rather than by frustration effects. However, the observed T -dependence of the order parameter is much stronger than theoretically predicted. It seems that random fields are a common feature of dipolar and quadrupolar glasses ⁽¹⁾ and we propose that similar studies should be performed in a series of orientational glasses with a different strength of random fields.

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⁽¹⁾ In a recent work on the dipolar glass RADP Courtens *et al.* [13] reported a nonzero-order parameter above T_G . It may be that in these glasses random fields play an important role, too.

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