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LETTER TO THE EDITOR

Strain distributions in the dipolar glass $KTaO_3$: Li

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Abstract. A single crystal of $K_{0.97}Li_{0.03}TaO_3$ has been studied by neutron diffraction. The freezing into the dipolar glass state is accompanied by a strong increase of the Bragg intensities. The Bragg intensities are analysed in terms of an extinction model. It is proposed that the partial relief of extinction at the freezing temperature is due to a fragmentation of the crystal into strained regions. The width of the strain distribution and the characteristic size of the regions are derived.

The low-temperature state of $K_{1-x}Li_xTaO_3$, $x < 0.04$, is regarded as the electric analogue of the spin-glass state of dilute magnetic systems (Maglione *et al* 1986). The electric dipole moments are formed by the displacements of the Li ions along ⟨001⟩ from their regular lattice sites. The freezing temperature of the dipoles has been determined from the cusp in the low-frequency dielectric susceptibility and the temperature dependence of the remanent electric polarisation after field cooling. Concomitant anomalies in the elastic constants and in NMR experiments have led to the conclusion that the freezing process involves not only the electric dipoles but also quadrupolar degrees of freedom (van der Klink *et al* 1983). This view has been further supported by an x-ray diffraction study (Andrews 1985). X-rays are practically insensitive to the Li position, but nevertheless the experiment on a sample with $x = 0.016$ showed an increase of diffuse intensity in the glass-like state due to frozen-in inhomogeneous strain fields. This behaviour has to be compared to a sample with higher Li concentration, $x = 0.05$, which shows a splitting of the Bragg reflections due to a structural phase transition from cubic to tetragonal with a saturated (homogeneous) tetragonal strain $c/a - 1$ of the order of 0.0015. Another piece of information on the strain effects comes from a neutron diffraction experiment, $x = 0.017$, where it was shown that the intensity of the (400) Bragg peak increases sharply below the freezing temperature, presumably owing to a relief of extinction (Kamitakahara *et al* 1987).

This Letter presents neutron diffraction results on the Bragg intensities of a sample with $x = 0.03$. We shall express the interpretation of the data in terms of extinction in a quantitative form and discuss the role of the strain distributions in the glass-like state.

A $K_{0.97}Li_{0.03}TaO_3$ crystal was grown at the Ecole Polytechnique Fédéral de Lausanne using the slow-cooling method (Rytz and Scheel 1982). The isotope ^7Li was chosen in order to avoid the strong neutron absorption of ^6Li. A cube-shaped sample of size 0.5 cm^3 was cut from the boule with {100} facets. An inspection of the sample between crossed polarisers showed no macroscopic inhomogeneities.

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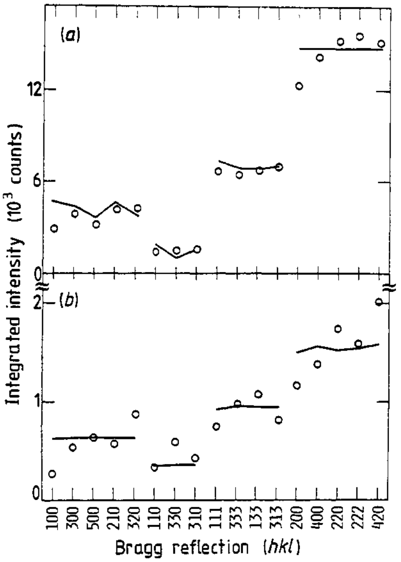

Figure 1. Integrated Bragg intensities (multiplied by $\sin 2\theta$) (*a*) at 30 K and (*b*) at 70 K. The Bragg reflections are grouped according to the scheme (ugg), (uug), (uuu), (ggg). The full curves give the intensities calculated from an extinction model.

The neutron measurements have been carried out on the 4-circle diffractometer D10 of the Institut Laue Langevin. The neutron wavelength λ was 1.04 Å. The sample has been mounted in a variable-temperature helium cryostat. The temperature stability was 0.1 K.

Seventeen Bragg reflections have been studied as a function of temperature between 70 K and 30 K. The integrated intensities of these peaks at 70 K and at 30 K as derived from ω-scans are shown in figure 1. Here we have multiplied the intensities by $\sin 2\theta$, where θ is the Bragg angle, and grouped the reflections according to the scheme (ugg), (uug), (uuu), (ggg) where u stands for an odd and g for an even Miller index. In the cubic perovskite structure the structure factors are constant within each group. The temperature dependence of the integrated intensity is shown in figure 2 for one representative of each group. The intensities are constant between 70 K and 50 K (hence we ignore Debye–Waller factors). Below 50 K all peak intensities increase. The increase, both in absolute and in relative units, is stronger for intense peaks than for weak peaks. At all temperatures the peak positions are consistent with those from a simple cubic lattice. Some selected peaks have been studied with improved instrumental resolutions by performing grid scans. The resulting intensity contours give no evidence for peak splittings or changes of the peak widths. We conclude that there is no evidence for a structural phase transition at 50 K and that the host lattice is cubic at all temperatures studied.

We have calculated the structure factor F_{hkl} of $K_{0.97}Li_{0.03}TaO_3$ in the virtual crystal approximation. It turns out that F_{hkl} is practically insensitive to a possible off-centre position of the ^7Li ion. Internal displacements of the Li ion cannot explain the strong intensity changes.

The corrected intensities strongly deviate from a proportionality to F_{hkl}^2, both above and below 50 K. Representing the four groups of reflections (ugg), (uug), (uuu), (ggg) by averaged intensities we observed at 70 K the ratios 1 : 0.7 : 1.4 : 2.5 whereas the corresponding numbers for F_{hkl}^2 are 1 : 0.28 : 2.48 : 9.66. Following the suggestion of Kamitakahara *et al* (1987) we interpret this mismatch as an extinction effect. The increase of

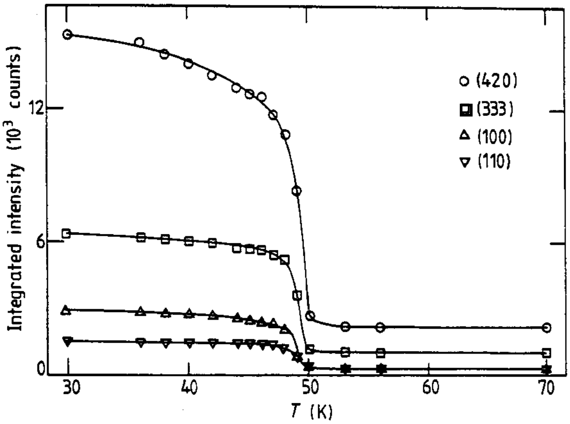

Figure 2. Temperature dependence of the intensity of four selected reflections. The curves are guides to the eye.

the peak intensities is then due to a partial relief of extinction at low temperatures.

In general, the intensity of the incident beam reaching successive net planes in a perfect crystal is attenuated by the deflection of energy into the reflected beam and by multiple reflections within the crystal. This effect, called extinction (see e.g. Azaroff 1968), leads to deviations from the proportionality of the observed Bragg intensity and F^2_{hkl}. It is assumed that a real crystal consists of small perfect blocks of linear dimension t_0. These blocks are tilted with respect to one another. The tilt angles shall be described by a Gaussian distribution with the width σ. This model—though being highly successful in explaining diffracted intensities—is considered purely artificial: the fragmentation of the crystal may not be real. Apart from the so-called primary extinction within the perfect blocks, the secondary extinction considers the fact that a block in reflecting positions casts a shadow on lower-lying blocks of identical orientation. Primary extinction increases with t_0, secondary extinction increases with σ^{-1}. The most complete treatment of extinction has been given by Becker and Coppens (1974, 1975). For the refinement of the data, however, we used the simpler expression given by Azaroff (1968) for the Laue case:

$$I_{hkl} = KQ'_{hkl}(t/\gamma)\exp(-Q'_{hkl}t/\sqrt{2\pi}\sigma\gamma)$$

$$Q'_{hkl} = Q_{hkl}\tanh A/A \qquad A = |F_{hkl}|\,\lambda t_0/V_c\gamma.$$

Here I_{hkl} is the uncorrected integrated peak intensity, K a scale parameter, γ the direction cosine between the x-ray beam and the crystal surface, V_c the cell volume, t the sample thickness, and $Q_{hkl} = \lambda^2 F^2_{hkl}/V^2_c \sin 2\theta$ the diffracting power of the crystal without extinction. We have fitted this expression to the experimental intensities by varying the free parameters K, t_0 and σ. K is assumed temperature independent whereas σ and t_0 have been optimised for each individual temperature. For 70 K and 30 K the intensities of the best fit are included in figure 2. The temperature dependencies of t_0^{-1} and σ are shown in figure 3.

Within the fragmentation model used in extinction theory the inverse size of the perfect blocks, t_0^{-1}, and the width of the distribution of tilt angles are measures of the imperfectness of a crystal. One notes from figure 3 that the degree of imperfection increases steeply below a temperature of 50 K which is just the value of the freezing temperature for $x = 0.03$ as derived from dielectric, NMR and birefringence

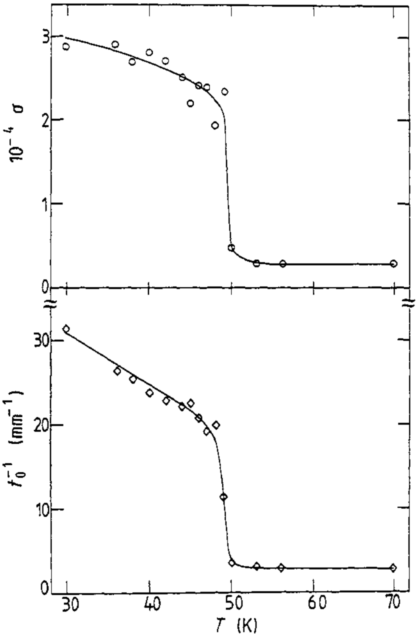

Figure 3. Temperature dependence of the inverse block size t_0^{-1} and the width σ of the distribution of tilt angles of the extinction model. The curves are guides to the eye.

measurements. Hence we suggest that the excess of the quantities σ and t_0 above their high-temperature (e.g. 70 K) values is characteristic of the disorder or—to be more specific—of the strain pattern of the glass-like state.

The width parameter σ of the extinction model in fact meets the requirement that a glass order parameter measure the width of a field distribution. Though the extinction model deals with a distribution of tilt angles, extinction is equally well relieved by a fragmentation of the crystal into blocks with slightly different lattice parameters. Guided by the observation of Andrews (1985) that a cubic-to-tetragonal transition occurs in the samples with slightly higher Li content, we mainly think of variations in $c/a - 1$. Since a local variation of $c/a - 1$ is identical with a local shear deformation we feel justified in translating the distribution of tilt angles directly into a distribution of $c/a - 1$. Accordingly, the width of the distribution of the static local tetragonal strains turns out to be of the order of 10^{-4} to 10^{-5}. Making use of the relation between strain and electric polarisation P, $c/a - 1 = gP^2$, where $g = 0.02\ \mathrm{m}^4\ \mathrm{C}^{-2}$ is the electrostrictive constant for the host lattice, we can determine that the variance of the polarisation is about 40 mC m^{-2} (from $\mathrm{var}(P) = (\mathrm{var}(c/a - 1)/g)^{1/2}$). This value is quite comparable to the experimental results on the field-cooled electric polarisation, which yields a value of 64 mC m^{-2} (van der Klink *et al* 1983): an electric field transforms the local variations of strain and polarisation into uniform strain and polarisation of comparable magnitude.

The second parameter of the extinction model gives information on the size of the blocks, which are defined as regions of constant tilt or equivalently as regions of constant local strain. The extinction model suggests block sizes of the order of 30 μm in the glass-like state, though the fit cannot discriminate in a reliable way against values that are one order of magnitude smaller. This value has to be compared with results obtained by other techniques. Andrews (1985) derives a minimum domain size of 100 to 1000 Å from the distribution of the diffuse x-ray intensity. A Raman study (Prater *et al* 1981) suggests that the characteristic length of the glass-like state when measured after cooling in zero electric field is smaller than the wavelength of light whereas it is larger than the wavelength in the field-cooled state. On the other hand birefringence patterns on the glass-like state occasionally show macroscopic regions of constant strain. We conclude that the characteristic lengths of quadrupolar coherence are distributed and that each individual method of observation detects the lengths to which it is most sensitive. It is essential to note that the mosaic units do not necessarily represent regions of homogeneous polarisation. A mosaic block can still consist of subregions of positive and negative polarisation. The correlation of polar displacements as revealed by light-mixing experiments extends in fact not beyond 100 Å in the glass-like state (Lehndorff 1986).

In summary, the present results show that extinction effects in diffraction studies are extremely susceptible to the internal strains that build up upon freezing into the glass-like state. The method can be applied to cases where the direct effect of strains on the diffraction pattern, namely the broadening of the Bragg peaks or the appearance of diffuse intensity, is beyond the detection limit. One has to keep in mind however that the extinction parameters are model dependent.

As far as the nature of the glass-like state of $KTaO_3$:Li is concerned, the present results yield the width of the strain distribution and thus clearly show that the freezing-in of the Li off-centre displacements also leads to a condensation of random strain fields. The strain pattern of the glass-like state can be regarded as a short-range version of the tetragonal low-temperature phase of the samples with slightly higher Li concentrations. This situation is analogous to the mixed alkali cyanides where the ferroelastic shear strain of the ordered phases finds its counterpart in the local shear strains of the orientational glass state (Knorr 1987) and one wonders whether the random-field model developed for the cyanides (Michel 1986) can be applied to the present system.

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