

The possibility of  $\text{Li}^+$  off-centre ion tunnelling in  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  studied by second-harmonic generation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 7227

(<http://iopscience.iop.org/0953-8984/7/36/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:05

Please note that [terms and conditions apply](#).

# The possibility of $\text{Li}^+$ off-centre ion tunnelling in $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ studied by second-harmonic generation

V Vikhnin†, P Voigt‡ and S Kapphan‡

† A F Ioffe Physico-Technical Institute, Politeknicheskaya 26, 194021 St Petersburg, Russia

‡ University of Osnabrück, FB Physik, D-49069 Osnabrück, Germany

Received 5 December 1994, in final form 22 May 1995

**Abstract.** Time-dependent second-harmonic generation experiments in  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  crystals for the first time yield a Li concentration dependence of the activation energy of the Arrhenius-like reorientation process of the  $\text{Li}^+$  ions. The experimental data support the assumption of a  $\text{Li}^+$  off-centre ion tunnelling via excited and ground vibrational states. With increasing Li concentration, the tunnelling reorientation is suppressed in favour of a thermally activated over-barrier hopping. The suppression of the tunnelling reorientation can be explained by a model of cooperative tunnelling in a percolation dipole cluster and destruction of the tunnelling resonance condition by internal electric dipole fields.

## 1. Introduction

The incipient ferroelectric  $\text{KTaO}_3$  remains a cubic inversion-symmetric crystal down to lowest temperatures. Doping of  $\text{KTaO}_3$  with small substitutional off-centre ions like Li, Na and Nb in the per cent range is known to induce ferroelectric properties at low temperature. The impurity-induced phase transition of  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  has been intensively investigated during the last twenty years and is still under discussion as being either a ferroelectric or a dipole glasslike transition [1, 2]. The complex dynamics of the phase transition is mainly determined by the reorientation of the  $\text{Li}^+$  ions. Dielectric and nuclear resonance experiments have shown a thermally activated Li hopping via  $90^\circ$  jumps between equivalent  $\langle 100 \rangle$  off-centre positions. The activation energy  $E_A = 1000$  K of this relaxation process has been found previously to be independent of Li concentration. Therefore this process has been interpreted as the reorientation of single  $\text{Li}^+$  ions [3, 4]. However, recent second-harmonic experiments of Voigt *et al* [5, 6, 7] have shown that the Li reorientation can no longer be regarded to be Arrhenius-like over the whole investigated temperature range, and that there is evidence for two relaxation processes with different time scales. These results are supported by dielectric experiments of Wickenhöfer *et al* [8, 9]. Moreover, second-harmonic generation experiments of [6, 7] show a strong concentration dependence of the activation energy of the Li reorientation. Concentration dependent activation energies of  $E_A = 1000$  K and  $E_A = 2500$  K have been found previously by Christen *et al* [10] for Li concentrations  $x = 0.025$  and  $0.033$ . The importance of a possible  $\text{Li}^+$  ion tunnelling in order to explain this concentration dependence has been pointed out in [11]. In this paper, we propose a model to explain our recent second-harmonic experiments on the basis of tunnelling reorientation and cooperative effects of the  $\text{Li}^+$  ions. The key role in the concentration dependence of the  $\text{Li}^+$  reorientation is attributed to a cooperative interaction of dipoles.

## 2. Experimental results

The investigation of dynamic SHG intensity changes under time dependent electric fields is based on the strong field-induced SHG intensity increase up to a, concentration dependent, electric field  $E_{sat}$  [5, 6, 7, 12]. The time dependence of the SHG intensity of our  $K_{1-x}Li_xTaO_3$  samples ( $0.008 \leq x \leq 0.063$ ) has been investigated at various constant temperatures in the phase transition region after a fast switch on ( $0 \rightarrow E$ ) and subsequent switch off ( $E \rightarrow 0$ ) of an electric field  $E \geq E_{sat}$ . Details of this experimental procedure including the determination of the concentration dependent phase transition temperature have been reported earlier [7, 13]. The time dependence of the SHG signal after switching the DC electric field on or off is followed for each concentration at several constant temperatures indicated in the experimental data plotted in [7]. Therefore the  $T_c(x)$  relation is measured and mentioned explicitly in [13, 7]. Since we are interested in the temperature dependence of the relaxation behaviour for various concentrations, we measure and consider all the data explicitly and therefore a treatment with a reduced temperature  $T/T_c$  does not seem to shed any new light on the discussion. The crystal growth and the determination of the Li concentration of the investigated samples is described in [7, 13]. The time dependent SHG data can be analysed with respect to three concentration ranges [7]. The data of the low concentration range ( $x \leq 0.016$ ) can be fitted using a superposition of two exponential time dependences describing two different relaxation processes (figure 1(a)). The fast process,  $\tau_1$ , with amplitude  $A$  cannot be resolved experimentally in its temporal dependence, because the pulse repetition rate of the Nd:YAG laser (1 kHz) limits the fastest detectable time constants to  $\approx 0.1$  s [7]. However, the amplitude,  $A$ , of this process can be obtained. This fast process may contain both the response of the soft paraelectric  $KTaO_3$  matrix itself as well as the reorientation of single non-interacting defects. The contribution in terms of the SHG amplitude of the pure lattice is generally very small [14] and is determined experimentally [7] to constitute only a small part of amplitude  $A$ . The amplitude  $A$  of this fast process decreases with decreasing temperature and nearly vanishes at the phase transition [7].

The relaxation time,  $\tau_2$ , of the slow process can be measured in detail; its temperature dependence is displayed in figure 2. In the intermediate concentration range ( $0.022 \leq x \leq 0.036$ ) the time dependence of the SHG data can be fitted using only one exponential function with time constant  $\tau_2$  (see figure 1B and [7]), the temperature dependence of which is also displayed in figure 2. For the high concentration range ( $x \geq 0.043$ ) the field-induced change of the SHG intensity is very small ( $x = 0.043$ ) or completely vanishes ( $x = 0.063$ ). Therefore no temporal intensity change of the SHG intensity could be measured.

The analysis of our SHG data yields an Arrhenius-like temperature dependence (figure 2) for the time constant  $\tau_2$  of the slow process

$$\tau_2(T) = \tau_0 \exp\left(\frac{E_A}{kT}\right) \quad (1)$$

with the activation energy  $E_A$  strongly increasing with Li concentration from 170 K (for  $x = 0.008$ ) to 810 K (for  $x = 0.016$ ) and to 1000 K (for  $x \geq 0.022$ ). This concentration dependence directly reflects the cooperative effects of the  $Li^+$  reorientation.

From the strong dispersion of the SHG data (figure 1) we conclude that cooperative effects between the Li dipoles must be accounted for. Generally, dipole-dipole interaction leads to a distribution of dipole relaxation rates. Additionally an inhomogeneous distribution of dipoles can result in an essential changing of the distribution of internal dipole fields, which leads to a broadening of the distribution function of the relaxation rate. This effect

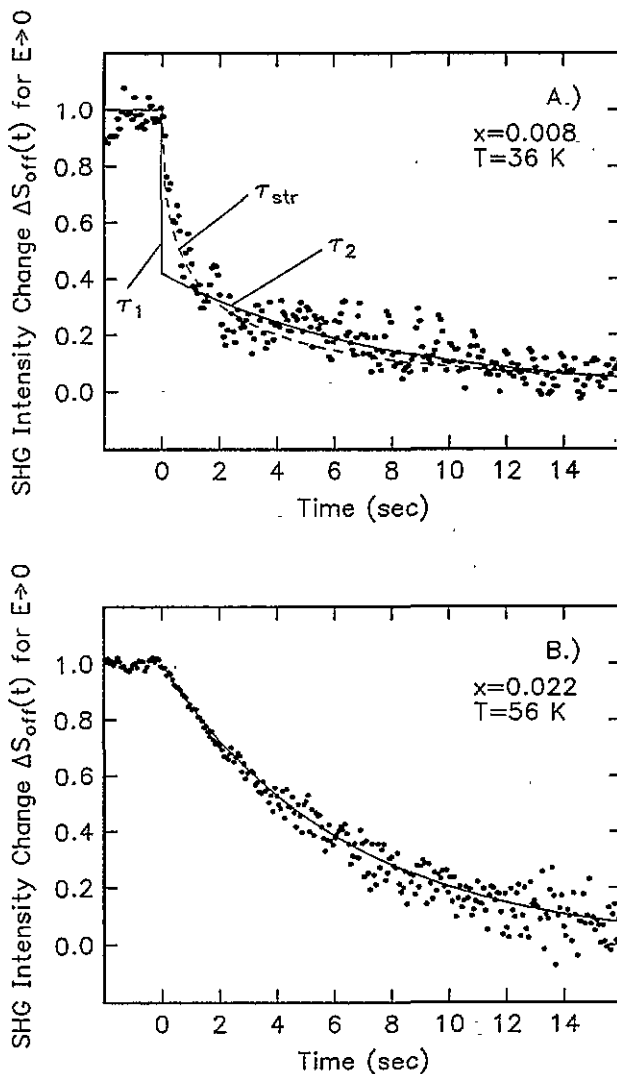


Figure 1. ((a)) Time dependence of the integral SHG intensity change  $\Delta S_{off}$  after a fast switching off ( $E \rightarrow 0$ ) of an electric field  $E = 200 \text{ kV m}^{-1} > E_{sat}$  at  $T = 36 \text{ K}$  for  $x = 0.008$ . The dashed line corresponds to a least-squares fit using a stretched exponential time dependence according to equation (3) with  $\tau_{str} = 1.4 \text{ s}$  and  $\beta = 0.45$ . The solid line represents a fit using a superposition of two exponential functions with time constants  $\tau_1 < 0.1 \text{ s}$ ,  $\tau_2 = 7.5 \text{ s}$  and  $A = 0.58$  according to equation (15) of [7]. ((b)) Time dependence of the integral SHG intensity change  $\Delta S_{off}$  after a fast switching off ( $E \rightarrow 0$ ) of an electric field  $E = 200 \text{ kV m}^{-1} > E_{sat}$  at  $T = 56 \text{ K}$  for  $x = 0.022$ . The solid line corresponds to a single exponential function according to equation (15) of [7] with time constant  $\tau_2 = 6.3 \text{ s}$  and  $A = 0$ .

is also important for the above low Li concentrations where the mean-field description and the model of single-particle relaxation ( $\tau$ -approach) cannot be applied. In contrast to this behaviour, in the case of large Li concentrations strong dipole-dipole correlations lead to a strong internal mean field. But for low concentrations the distribution of relaxation times must be taken into account. This conclusion is confirmed by our experimental results (figure 1(a)). Therefore our data of the lowest-doped sample are additionally analysed using

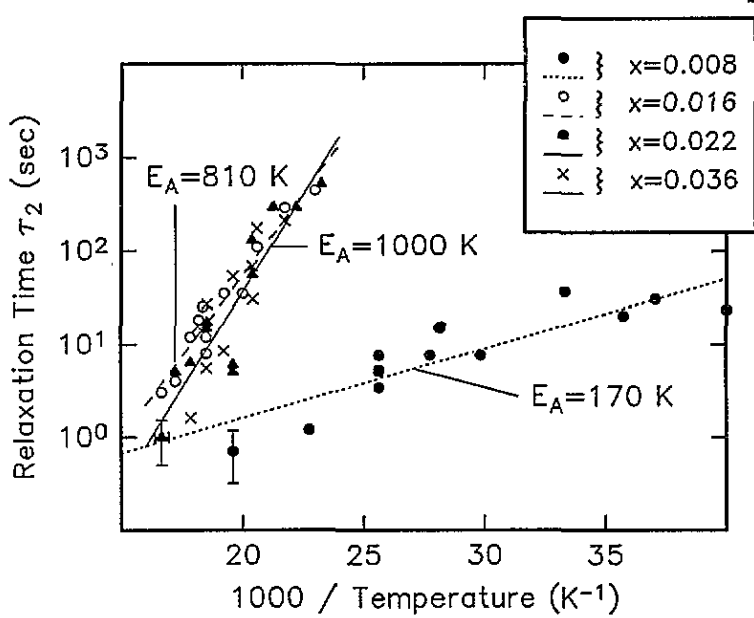


Figure 2. Temperature dependence of the relaxation time  $\tau_2$  of the slow process in  $K_{1-x}Li_xTaO_3$  for  $x = 0.008$  ( $\tau_0 = 2.5 \times 10^{-2}$  sec),  $x = 0.016$  ( $\tau_0 = 4.6 \times 10^{-6}$  s),  $x = 0.022$  ( $\tau_0 = 7.5 \times 10^{-8}$  s), and  $x = 0.036$  ( $\tau_0 = 7.5 \times 10^{-8}$  s) for an applied electric field  $E = 200 \text{ kV m}^{-1} > E_{sat}$ . The time dependence of the integral SHG intensity changes  $\Delta S_{on}$  and  $\Delta S_{off}$  for switching on and off of an external applied electric field have been fitted using a superposition of two usual exponential functions [6, 7].

the empirical stretched exponential time dependence [15, 10]

$$\Delta S_{on} \propto 1 - \exp\left(-\frac{t}{\tau_{str}}\right)^\beta \quad (2)$$

$$\Delta S_{off} \propto \exp\left(-\frac{t}{\tau_{str}}\right)^\beta \quad (3)$$

with  $\Delta S_{on}$  and  $\Delta S_{off}$  being the SHG intensity changes for switching an externally applied electric field  $E$  on and off, respectively. The stretched exponential fit allows a direct comparison with the work of Kleemann *et al* [15] and of Christen *et al* [10]. The latter work gives some meaningful microscopic interpretation to stretched exponential fits for specific models (hierarchically constrained dynamics). One example of this fitting procedure according to equation (3) is shown in figure 1A for the  $x = 0.008$  sample at  $T = 36$  K. The corresponding temperature dependence of  $\tau_{str}$  and  $\beta$  can be seen in figure 3 with the temperature dependence of  $\tau_{str}$  being used to determine the activation energy  $E'_A = 190$  K (figure 3(a)). This value is nearly the same as the corresponding value using the superposition of two usual exponential functions [7]. For this sample the exponent  $\beta$  strongly decreases with decreasing temperatures (figure 3(b)) indicating increasing cooperative effects and a broadening of the distribution of relaxation times with decreasing temperature. This behaviour of  $\beta$  agrees with the observations of Christen *et al* [10] and of Kleemann *et al* [15]. Since the stretched exponential time dependence automatically takes into account a distribution of relaxation times, it reflects the coexistence of different reorientation processes. Consequently we have been able to excellently fit the

SHG data over the whole time interval of each experimental run without assuming the previously discussed two relaxation processes  $\tau_1$  and  $\tau_2$  (see figure 1(a)).

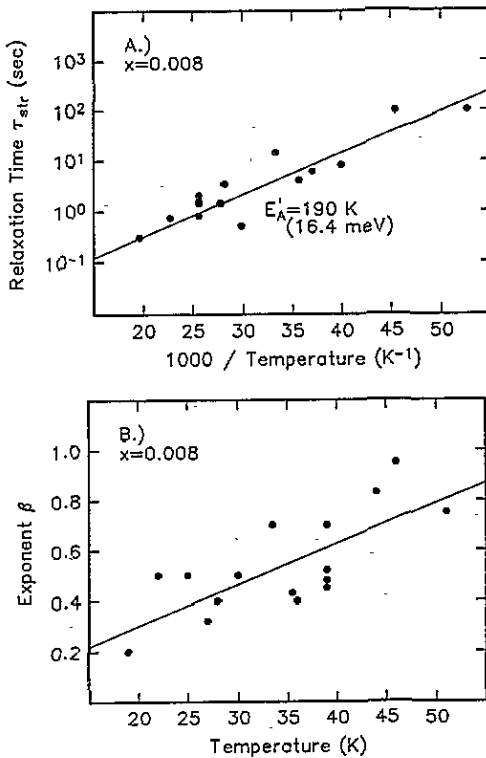


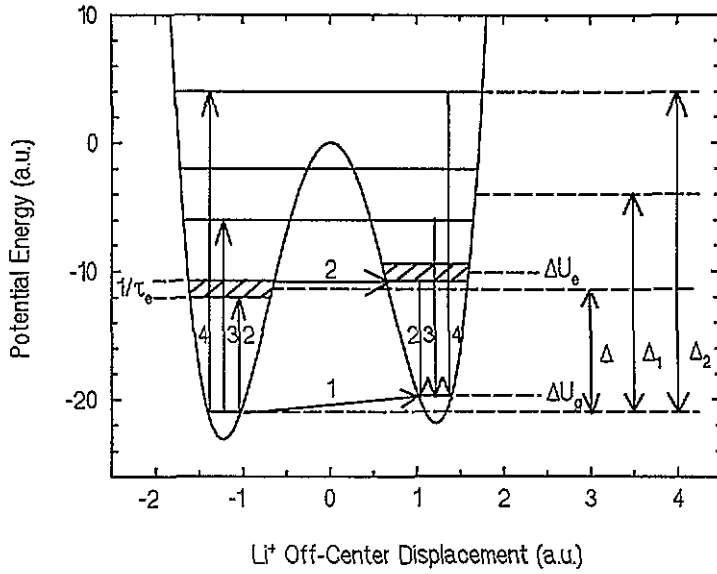
Figure 3. Temperature dependence in  $K_{1-x}Li_xTaO_3$  with  $x = 0.008$  of ((a)) the relaxation time  $\tau_{stir}$  and of ((b)) the exponent  $\beta$  according to equations (2) and (3). Note the strong deviations of  $\beta$  from unity at low temperatures and the value of the activation energy  $E'_A = 190 \text{ K}$ , which is very close to the value of  $E_A$  in figure 2.

For higher concentrations ( $x \geq 0.022$ ) it turns out that  $\beta = 1$ , and the fit for  $\tau_2$  and the stretched exponential coincide. Therefore both fit procedures yield essentially the same activation energies.

Both empirical fitting functions—superposition of two usual exponential functions [7] or the stretched exponential function—yield similar activation energies ( $E_A = 170 \text{ K}$  or  $E'_A = 190 \text{ K}$ , respectively) for  $x = 0.008$ . These values are practically identical within experimental error. Therefore we conclude that there should be an energy level of the size  $E_A = 170\text{--}190 \text{ K}$  in the  $x = 0.008$  sample which is related to a definite energy level in the individual  $Li^+$  ion system.

### 3. Model and discussion

In the following we consider resonance tunnelling via ground and excited states as the main mechanisms of the  $Li^+$  dipole reorientation in  $K_{1-x}Li_xTaO_3$ . The rates of resonance tunnelling via ground and excited vibrational states are denoted as  $1/\tau_{gr}$  and  $1/\tau_{ex}$ , respectively. In an earlier publication [16] these rates of reorienting off-centre ions have



**Figure 4.** Schematic representation of the mechanisms of  $\text{Li}^+$  reorientation in a single particle multi-well potential of  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ .  $1/\tau_g$  and  $1/\tau_e$  are the natural widths of the single well vibrational states and  $\Delta U_g$  and  $\Delta U_e$  are the relative energy shifts of the vibrational states where the indices  $g$  and  $e$  denote the corresponding variables of ground and excited state, respectively. Process 1 represents the usual phonon assisted tunnelling between the narrow ground states of different wells in the internal field. Process 2 describes resonance tunnelling via localized excited vibrational states with energy level  $\Delta = E_A = 170\text{--}190$  K (see equation (5)). Process 3 shows thermally activated tunnelling via a coherent higher vibrational under-barrier state with  $\Delta_1 = E_A = 810$  K and process 4 is thermally activated over-barrier hopping with  $\Delta_2 = E_A = 1000$  K.

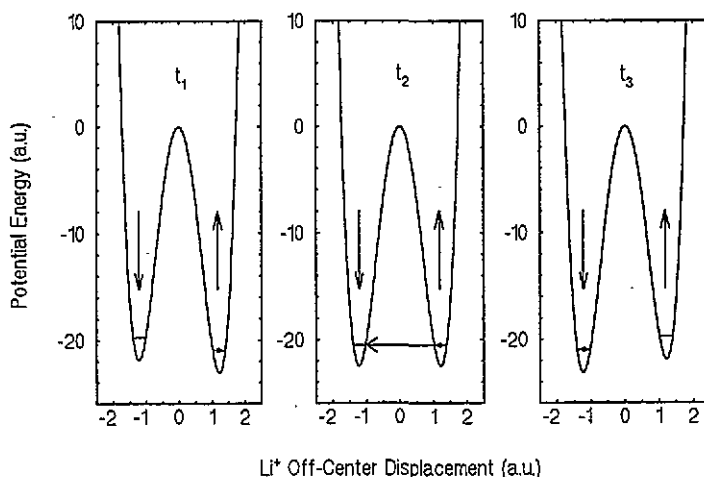
been shown to have the following form

$$\frac{1}{\tau_{gr}} = \frac{(2\Gamma_g)^2}{\frac{1}{\tau_g} + (\Delta U_g)^2 \tau_g} \quad (4)$$

$$\frac{1}{\tau_{ex}} = \frac{(2\Gamma_e)^2}{\frac{1}{\tau_e} + (\Delta U_e)^2 \tau_e} \exp\left(-\frac{\Delta}{T}\right) \quad (5)$$

where  $\Gamma_g$  and  $\Gamma_e$  are the tunnelling matrix elements,  $1/\tau_g$  and  $1/\tau_e$  are the natural widths and  $\Delta U_g$  and  $\Delta U_e$  are the relative energy shifts of the single-well vibrational states. The indices  $g$  and  $e$  denote the corresponding variables of the ground and excited state, respectively, and  $\Delta$  is the energy of the excited vibrational state which is involved in the reorientation process. The expressions (4) and (5) are valid only if the conditions  $1/\tau_g > \Gamma_g$  and  $1/\tau_e > \Gamma_e$  are fulfilled, respectively, which means the absence of coherent tunnelling states [16].

A direct support of a tunnelling reorientation of the  $\text{Li}^+$  via excited vibrational states is the very low pre-exponential factor ( $\tau_0^{-1} \approx 40 \text{ s}^{-1}$  for  $x = 0.008$  [7]) according to equation (1) and the low activation energy ( $E_A = 170\text{--}190$  K for  $x = 0.008$ ). The value  $\tau_0^{-1}$  is proportional to the square of the tunnelling matrix element  $\Gamma_e^2$  which is consequently very small. The size of  $E_A$  represents an adequate value of the quasilocal vibrational frequency in a single well of a multi-well potential.



**Figure 5.** Temporal development of vibrational ground state energy levels of the Li<sup>+</sup> single particle multi-well potential in K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub>. Resonance tunnelling via ground vibrational states in K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub> due to a compensation of the internal defect field and the time dependent external applied electric field. The resonance condition is fulfilled for different Li<sup>+</sup> centres at different times  $t_2$  with  $t_3 \geq t_2 \geq t_1$ . The fast process  $\tau_1$  which has been observed in SHG experiments (see section 2 and [7]) can be interpreted by this kind of tunnelling reorientation.

The experimentally observed concentration dependence of the Li<sup>+</sup> reorientation (see section 2) strongly supports the idea of a resonance tunnelling of the Li<sup>+</sup> reorientation. The tunnelling matrix element and the tunnelling conditions reveal a very sharp dependence from the characteristics of the orientational many-dipole state. Thus resonance tunnelling strongly depends on the nature of the orientational many-dipole states involved.

We therefore conclude that there is a resonance tunnelling process via excited vibrational states for K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub> at small concentrations.

The condition

$$((\Delta U_g)^2)^{\frac{1}{2}} \gg \frac{1}{\tau_g} \quad (6)$$

is usually fulfilled in real crystals with the second moment  $((\Delta U_g)^2)$  being related to random static internal defect fields. Therefore resonance tunnelling via ground states is usually suppressed. But external applied electric fields  $\Delta U_g^{ext}$  or stress fields may compensate the  $\Delta U_g$  value for a definite part of centres resulting in the condition

$$(\Delta U_g + \Delta U_g^{ext}) \leq \frac{1}{\tau_g}. \quad (7)$$

Due to a distribution of defect fields, only for a definite fraction of centres is condition (7) valid, which describes an external field-induced resonance tunnelling via ground states. This effect was discovered for the first time in [17]. The same situation may be present for Li<sup>+</sup> in KTaO<sub>3</sub> as observed by our SHG experiments.



The situation for resonance tunnelling via excited vibrational states is essentially different. Here, the conditions

$$\langle (\Delta U_e)^2 \rangle^{\frac{1}{2}} \ll \frac{1}{\tau_e} \quad (8)$$

$$\Gamma_e \gg \Gamma_g \quad (9)$$

are usually fulfilled, which means that resonance tunnelling via excited vibrational states is usually possible even without the presence of a compensating external applied electric field. Such tunnelling reorientation has been discovered for many model systems with off-centre impurities [18]. In the following we describe two mechanisms for the suppressing of this tunnelling process with increasing defect concentration, which are both connected with the influence of percolating dipole clusters. The percolation phenomenon in Li doped  $\text{KTaO}_3$  is determined by indirect dipole-dipole interaction via a soft TO mode. This dipole-dipole interaction has been shown to strongly increase in a highly polarizable matrix such as  $\text{KTaO}_3$  with soft-mode behaviour and to be controlled by the correlation radius  $r_c$  [19, 20].

We have to consider that the energy of the percolation cluster state changes if a single dipole changes its orientation in such a cluster. Therefore in principle all dipoles in such a percolation cluster take part in the resulting tunnel transition and consequently in the corresponding overlap integrals of the wavefunctions in different potential wells. Here we can use the sum of single-particle Hamiltonians as the total Hamiltonian of the tunnel problem. That means we neglect the dipole-dipole interaction effect as it is a small effect relative to the single-particle Hamiltonian which forms the tunnel matrix element. However, the total wavefunction is a product of non-independent single-dipole wavefunctions. In these wavefunctions we must take into account the dipole-dipole interaction effect, which involves the directions of interacting dipoles. The latter connects with non-interacting dipole orientational degeneracy which is lifted by dipole-dipole interaction. The resulting tunnel matrix element  $\Gamma_e$  can be written as

$$\Gamma_e = \Gamma_e^{(0)} \prod_i Y_i^{(0)} \quad (10)$$

where  $i$  denotes the dipoles in the percolating cluster which change their orientation together with a given dipole under conservation of the resonance condition according to equation (8) in the case of simultaneous presence of static defect and dipole fields. Here,  $Y_i^{(0)}$  is the single-particle overlap integral (with  $Y_i^{(0)} \ll 1$ ) and  $\Gamma_e^{(0)}$  is the single-particle tunnel matrix element of the excited vibrational states. The last expression can be rewritten in the following form (with  $Y_i^{(0)} = Y_j^{(0)}$ )

$$\Gamma_e = \Gamma_e^{(0)} \left( Y_i^{(0)} \right)^\alpha \quad (11)$$

where  $\alpha$  is the effective number of strongly coupled dipoles in the percolating cluster which take part in resonance tunnelling with

$$\alpha = V N_{res}. \quad (12)$$

Here,  $V$  is the dimensionless mean cluster size (number of dipoles in the percolation cluster) [21] and  $N_{res}$  is the relative number of dipoles in the cluster whose correlated reorientation does not change the resonance conditions for tunnelling. In the percolation model [21]

$$V \propto |x - x_c|^{-\gamma}. \quad (13)$$

In equation (13)  $x_c$  is the threshold concentration of the percolation and  $\gamma$  is the corresponding critical index ( $\gamma = 1.69$ – $1.80$  for the 3D case [21]). From the experimental

data [7] the value of  $x_c$  can be estimated as  $0.022 \leq x_c \leq 0.036$ . This estimation is based on the bell-like concentration dependence [7] of the maximum value of the integral SHG intensity  $S_{zzz}^{max}(E \geq E_{sat})$  at  $T = 20$  K, which can be interpreted as the concentration dependence of the mean radius of the dipolar percolation cluster.

For analysing the concentration dependence of the rate of tunnel reorientations we have to discuss the fulfilling of the resonance condition of tunnelling via excited vibrational states

$$\Delta U'_e \leq \frac{1}{\tau_e} \quad (14)$$

where  $\Delta U'_e = \Delta U_e + \Delta U_d$ . Here,  $U_d$  is induced by reorienting dipole fields, whereas  $U_e$  is induced by random static internal defect fields. Here,  $\Delta U_e$  and  $\Delta U_d$  satisfy the corresponding distribution functions. Namely, according to the central limiting theorem for concentrations  $x$  near the critical concentration  $x_c$ , the symmetrical part of the distribution function of this internal cluster field is nearly Gaussian-like. In the case of possible ferroelectric ordering in the percolation cluster we must take into account a shift of the centre of the distribution function (first moment or mean field  $M_1$ ). This Gaussian-like dipole field distribution must be described by both the first moment  $M_1 = \langle \Delta U_d \rangle$  and the second moment  $M_2 = \langle (\Delta U_d)^2 \rangle$ . If the random static internal defect field is also Gaussian-like, we can replace the last expression for  $M_2$  by the following expression

$$M_2 = \langle (\Delta U_e)^2 \rangle + \langle (\Delta U_d)^2 \rangle. \quad (15)$$

The role of higher moments for concentrations  $x$  in the vicinity of  $x_c$  ( $V \gg 1$ ) is negligible. Critical increasing of  $\langle (\Delta U_d)^2 \rangle$  in the region under consideration allows us to neglect the first term in equation (15). That is why we can replace the resonance condition of tunnelling (equation (14)) by a simpler expression

$$\langle (\Delta U_d)^2 \rangle^{\frac{1}{2}} \leq \frac{1}{\tau_e}. \quad (16)$$

Taking into account the important role of the mean field  $M_1$  in dipole percolation clusters we can add to equation (16) the second resonance condition of tunnelling

$$M_1 = \langle \Delta U_d \rangle \leq \frac{1}{\tau_e}. \quad (17)$$

On the basis of these arguments it can be easily seen that resonance tunnelling via excited vibrational states is suppressed by internal percolation cluster fields, which are connected with dipole-dipole interaction.

Indeed, a percolation dipole cluster is characterized by the following property. Namely, the reorientation of a single dipole which is under the action of non-zero internal dipole field in the percolation cluster immediately leads to reorientations of all such dipoles in that cluster. The energy difference between final and initial dipole states in these conditions is of the order of  $(2 \langle \Delta U_d \rangle)^{1/2}$ . In addition, the mean-field value  $\langle U_d \rangle$  is not changed under the action of this collective reorientation of dipoles due to isotropic behaviour of  $\langle U_d \rangle$  in K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub>. As a result, the collective reorientation of dipoles under consideration does not change the resonance condition of tunnelling as seen from equation (16) and (17). That is why we can use equation (11) for the tunnel matrix element with  $V \approx \alpha$  (that is  $N_{res} \approx 1$ ), and can substitute this expression in equation (5). Consequently we have to deal with the fast decreasing of  $\Gamma_e$  in equation (11) and  $\tau_{ex}^{-1}$  in equation (5) with  $x$  increasing and approaching  $x_c$ . Such behaviour takes place due to critical increasing of  $M_1$  and  $M_2$  for concentrations close to  $x_c$  (but with fulfilling of equations (16) and (17)). The latter circumstance is not valid very close to the percolation threshold or for not so

small concentrations  $x$ . Indeed for the first ( $M_1$ ) and second ( $M_2$ ) moments we have in the percolation model

$$M_1 \propto V \propto |x - x_c|^{-\gamma} \quad (18)$$

$$\langle (\Delta U_d)^2 \rangle \propto V \propto |x - x_c|^{-\gamma}. \quad (19)$$

For concentrations close to  $x_c$  (or for large concentrations) we have the conditions

$$M_1 \gg \frac{1}{\tau_e} \quad \text{and} \quad \sqrt{2M_2} \gg \frac{1}{\tau_e}. \quad (20)$$

Here we have an additional concentration dependent mechanism for the suppression of tunnelling, which is connected with the breakdown of the resonance condition equations (16) and (17). As a result the resonance tunnelling condition in the case  $x \rightarrow x_c$  disappears for the majority of the dipoles. For the majority of the dipoles the inequality  $(M_1 - \Delta U_d) \leq \sqrt{2M_2}$  is fulfilled and the corresponding dipoles belong to the bell-like part of the distribution function (without its wings).

However, resonance tunnelling is still possible in the case under consideration (the critical case where  $x \rightarrow x_c$  and equation (20) is valid) for a small number of special-type dipoles. Their tunnel matrix element is a usual single-particle tunnel matrix element without any cooperative suppression effect. The number of special-type dipoles is suppressed with increasing concentration  $x \rightarrow x_c$ . The relative number  $N_{res}$  of these dipoles ( $N_{res} \ll 1$ ) obeys the following equation for the actual Gaussian-like distribution of internal dipole field

$$N_{res} = \frac{1}{2} \operatorname{erf} \left( \frac{M_1 + \frac{1}{2\tau_e}}{\sqrt{2M_2}} \right) - \frac{1}{2} \operatorname{erf} \left( \frac{M_1 - \frac{1}{2\tau_e}}{\sqrt{2M_2}} \right) \quad (21)$$

where  $\operatorname{erf}(x)$  is the error integral [22] with

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt. \quad (22)$$

The inequalities (20) lead to the following expression for  $N_{res}$  on the basis of equation (21)

$$N_{res} \approx \left[ \frac{d \operatorname{erf}(x)}{dx} \right] \Big|_{\frac{M_1}{\sqrt{2M_2}}} \left( \frac{1}{\frac{2\tau_e}{\sqrt{\pi M_2}}} \right). \quad (23)$$

On the basis of equations (15), (18) and (19) and for concentrations  $x$  near  $x_c$  (or for large concentrations) the factor  $M_1/\sqrt{2M_2}$  strongly increases with  $M_1/\sqrt{2M_2} \gg 1$ . In this case we obtain from equation (23)

$$N_{res} \approx \exp \left( -\frac{M_1^2}{2M_2} \right) \left( \frac{1}{\frac{2\tau_e}{\sqrt{\pi M_2}}} \right). \quad (24)$$

Equation (24) reflects with respect to equations (18) and (19) the fast decreasing of  $N_{res}$  for these special-type zero-field dipoles in the vicinity of the percolation threshold and for large  $x$ . The critical decreasing of  $N_{res}$  near the percolation threshold is caused by internal dipole fields which make a resonance situation for single dipoles rarer for  $x \rightarrow x_c$ . In this limiting case only a very small number of 'zero-field' dipoles take part in resonance

tunnelling via excited vibrational states but with a relatively high corresponding tunnelling rate ( $\Gamma_e \approx \Gamma_e^{(0)}$ ). The same situation exists for large concentrations  $x$ .

The results of the preceding model discussion explain the 'switching off' of resonance tunnelling via an excited vibrational state with increasing concentration. The resonance tunnelling is reduced via both the interaction terms in the wavefunctions reducing the overlap integrals and due to the mean field influence on the energy levels in regions of correlated dipoles. In the following we explain in the framework of the above model the concentration dependence of the activation energy of the SHG data due to the Li relaxation in K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub> (see figure 4). The relaxation process of the  $x = 0.008$  sample with the activation energy  $E_A = 170\text{--}190$  K can be interpreted as a resonance tunnelling via localized excited vibrational state (see process 2 in figure 4) with energy  $\Delta$ . This tunnelling process is suppressed with increasing Li concentration in favour of a thermally activated tunnelling via the high excited under-barrier coherent tunnelling state with energy  $\Delta_1 = E_A = 810$  K for the  $x = 0.016$  sample (see process 3 in figure 4). This type of tunnelling process is dominant for  $\Gamma_e \geq M_1$  and  $\Gamma_e \geq \sqrt{M_2}$ . Due to the highest corresponding single-particle tunnelling matrix element,  $\Gamma_e^{(0)}$  this process is suppressed for higher Li concentrations.

With further increasing Li concentration ( $x \geq 0.022$ ) only hopping of the Li<sup>+</sup> ions over barriers with the activation energy  $\Delta_2 = E_A = 1000$  K is realized (see process 4 in figure 4). Resonance tunnelling is strongly suppressed in this concentration range due to the increase in the internal percolation cluster field (see equations (24) and (23)) in spite of the relatively large tunnelling splitting of the higher excited under-barrier states with energy  $\Delta_1$ .

For high concentrations ( $x > 0.022$ ) the ferroelectric ordering dominates ( $M_1 \gg \sqrt{M_2}$ ). Therefore the mean-field effect in ferroelectric microdomains leads to 'switching off' of resonance tunnelling according to equation (24).

For small Li concentrations ( $x \leq 0.016$ ) an additional fast relaxation process (with relaxation time  $\tau_1$  and amplitude  $A$ ) has been observed in the SHG experiments under time dependent external applied electric fields. This process can be interpreted as resonance tunnelling of the Li<sup>+</sup> ions via vibrational ground states (figure 5). The resonance condition for this kind of tunnelling process is a compensation (at different time for different centres) of external applied electric field and internal electric and elastic fields according to equation (7). Such resonance tunnelling induced by an external alternating electric field in random internal fields has been observed earlier (e.g. off-centre Co<sup>2+</sup> in SrO [17]). The difference compared to the situation of K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub> is the large width of distribution of internal defect fields due to the soft matrix of the KTaO<sub>3</sub> host.

In summary, we conclude that in K<sub>1-x</sub>Li<sub>x</sub>TaO<sub>3</sub> ( $x \leq 0.036$ ) resonance tunnelling via both ground and excited states takes place, which is strongly influenced by internal dipole field effects. Such a kind of tunnelling reorientation is also expected for Ca<sup>2+</sup> off-centre ions in incipient ferroelectric SrTiO<sub>3</sub> [23].

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Postdoktorandenprogramm and German–Russian project 436 RUS 113/39 OS 1994), the International Science Foundation (SOROS Fund), and the Russian Fund of Fundamental Investigations (project 94-02-06292-a).

## References

- [1] Höchli U T, Knorr K and Loidl A 1990 *Adv. Phys.* **39** 405
- [2] Vugmeister B E and Glinchuk M D 1990 *Rev. Mod. Phys.* **62** 993
- [3] van der Klank J J, Rytz D, Borsa F and Höchli U T 1983 *Phys. Rev. B* **27** 89
- [4] Höchli U T and Maglione M 1989 *J. Phys.: Condens. Matter* **1** 2241
- [5] Voigt P and Kapphan S 1991 *Ferroelectrics* **124** 243
- [6] Voigt P and Kapphan S 1994 *Ferroelectrics* **157** 239
- [7] Voigt P and Kapphan S 1994 *J. Phys. Chem. Solids* **55** 853
- [8] Wickenhöfer F, Kleemann W and Rytz D 1991 *Ferroelectrics* **124** 237
- [9] Wickenhöfer F, Kleemann W and Rytz D 1992 *Ferroelectrics* **135** 333
- [10] Christen H M, Höchli U T, Châtefain A and Ziolkiewicz S 1991 *J. Phys.: Condens. Matter* **3** 8387
- [11] Vikhnin V, Voigt P and Kapphan S 1993 *Proc. 8th Int. Meeting Ferroelectricity (IMFE) (MD, 1993)* P1:200. p 119
- [12] Voigt P, Betzler K, Schmidt N and Kapphan S *Ferroelectrics* **106** 149
- [13] Voigt P, Hesse H and Kapphan S 1992 *Proc. 20th Spring Conf. on Ferroelectricity (Güntersberge, 1992)* University of Halle-Wittenberg, Germany: FB Physik p 24
- [14] Fujii Y and Sakudo T 1976 *Phys. Rev. B* **13** 1161
- [15] Kleemann W, Kütz S, Schäfer F J and Rytz D 1991 *Phys. Rev. Lett.* **66** 762
- [16] Vikhnin V S 1978 *Fiz. Tverd. Tela* **20** 1340 (in Russian); 1978 *Sov. Phys.-Solid State* **20** 771
- [17] Vikhnin V S, Sochava L S, Krylov V A and Tolparov Y N 1984 *Zh. Eksp. Teor. Fiz. Pis'ma* **40** 426 (in Russian); 1984 *JETP Lett.* **40** 1248
- [18] Vikhnin V S and Sochava L S 1991 *Crystals with Off-Centre Ions as a Model Object in Solid State Physics preprints* 1539 A F Ioffe Physico-Technical Institute, St Petersburg
- [19] Vikhnin V S and Borkovskaja Y B 1978 *Fiz Tverd. Tela (in Russian)*; **20** 3603; 1978 *Sov. Phys.-Solid State* **20** 2082
- [20] Vugmeister B E and Glinchuk M D 1980 *Zh. Eksp. Teor. Fiz.* **79** 947 (in Russian); 1980 *JETP* **52** 482
- [21] Shklovskii B I and Efros A L 1979 *Electronic Properties of Doped Semiconductors (Moscow: Nauka)* (in Russian); Kirkpatrick S 1976 *Phys. Rev. Lett.* **36** 69
- [22] Dwight H B 1961 *Tables of Integrals and other Mathematical Data* (New York: Macmillan)
- [23] Vikhnin V and Kleemann W 1994 private communication