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## Effective Li–Li interactions in $K_{1-x}Li_xTaO_3$

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**Abstract.** The interaction energy of two Li impurities in a  $KTaO_3$  host lattice is calculated within a non-linear polarizable shell model as a function of Li–Li distance, dipole orientation, and bond direction. Our results show a complex dependence of the interaction on these parameters, suggesting that a large amount of information is lost when representing  $K_{1-x}Li_xTaO_3$  by means of simplified spin-glass-like models. At low impurity concentrations, where two-body interactions are dominant, it is observed that the tendency towards ferroelectric and ferroelastic ordering increases with Li concentration. However, the complexity of the interactions together with the random spatial distribution of the impurities leads to a disordered—frustrated—ground state.

### 1. Introduction

The competition between the development of long-range order and the freezing in of disorder at low temperatures has been the subject of numerous studies. Doping of the perovskite  $KTaO_3$  with a small amount of substitutional impurity yields a very suitable dipolar system for such investigations [1, 2]. Pure  $KTaO_3$  is an incipient ferroelectric, but replacing a small number of the potassium ions by lithium induces a polar state that exhibits behaviour resembling that of spin glasses or of ferroelectrics depending on the impurity concentration.

The polar character originates from the displacement—along one of the six cubic (100) directions—of the relatively small  $Li^+$  impurities which substitute the larger  $K^+$  ions on centrosymmetric sites [3]. For Li concentrations of a few per cent, the system exhibits a low-temperature disordered state, but due to fundamental experimental limits and problems of interpretation, the nature of the low-temperature phase at slightly higher concentrations is still controversial.

There has been considerable progress in the study of models for orientational glasses [4] mainly arising from the field of spin glasses [5]. Typically, these model Hamiltonians consider bilinear couplings, which are taken to be either nearest-neighbour or infinite-range interactions, and which are usually described by one or several random variables. Most recently, Vollmayr and co-workers [6] have proposed a model in which each Li is described as a six-state Potts vector, and the  $6 \times 6$  coupling matrix contains only two independent random variables distributed with Gaussian probability. The coupling thus depends on each impurity's dipole orientation, but not on the bond direction. Similarly, Doussineau *et al* [7]

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assume an Ising-like coupling and a distribution of the interaction eigenvalues according to a Wigner law, resulting in good agreement with experimental results.

Despite the success of such models, it has not yet been analysed whether this description is well suited on a microscopic scale, and in particular whether the dependence of the defect-defect interaction on bond direction and Li-Li distance can be reduced to a small number of random variables.

The impurity-impurity interaction energy in  $K_{1-x}Li_xTaO_3$  can be calculated on a microscopic basis. A non-linear shell model is available [8, 9] (described below in section 3) which yields a correct description of the lattice polarization around an Li impurity. In this article the model is applied to the study of the interaction between two impurities. A strong dependence of the two-particle interaction energies on the bond direction is found, which differs considerably from the classical dipole-dipole interaction. Important conclusions regarding the microscopic properties of the system's ground state are drawn from the analysis of the interaction energies.

## 2. Review of experimental facts

In this section we wish to summarize experimental results for  $K_{1-x}Li_xTaO_3$  samples in the concentration range of  $x \lesssim 7\%$ , in order to show that the ground state of this system cannot be attained in experiments.

The dynamics of relaxation, associated with dipole reorientations, has been studied by dielectric measurements [10, 11, 12], NMR [3, 13], ultrasound attenuation [14] and by determining of the low-frequency shear modulus [15]. The main characteristics can be summarized as follows.

The qualitative behaviour of the dynamics is essentially independent of the Li concentration  $x$  for  $x \lesssim 7\%$ . In contrast to the case of ferroelectrics, no signs of criticality either in the relaxation time or in the relaxation step are observed at any temperature. Relaxation can be by  $\pi/2$  or by  $\pi$  flips between two of the six equivalent Li positions, where the relaxation time corresponding to the latter is several orders of magnitude larger than that one corresponding to the former. However, the faster  $\pi/2$  flips are associated with an important elastic contribution and become largely inhibited below a temperature  $T_c$ , at which the  $\pi/2$  relaxation step  $\Delta\epsilon$  goes through a broad temperature maximum. Note that the term  $T_c$  is used here without implying criticality. Below  $T_c$ , motion is restricted to the much slower  $\pi$  flips, so that the dynamics seems to exhibit a jump-like slow-down at  $T_c$  [12]. At temperatures below  $T_c$ , the behaviour of the  $\pi$ -flip branch is similar to that of models involving hierarchical relaxation or collective effects [16, 17, 18], in agreement with computer simulation results on highly disordered spin-glass-like systems [19, 20].

Experiments measuring the magnitude of the electrical polarization have revealed the absence of spontaneous polarization in zero-field-cooled samples [21] and non-ergodicity [22] in much the same manner as in spin glasses [5]. Thus the terms 'polar glass' [23] and 'orientational glass' have been used to describe  $K_{1-x}Li_xTaO_3$ .

The system is described by two independent correlation functions. A dipolar correlation length  $\xi_d$  is defined as the size of the region where dipoles are parallel to one another, and a quadrupolar correlation length  $\xi_q$  is defined in a similar way but for quadrupoles, i.e. as the size of domains formed by a combination of parallel and antiparallel dipoles. These two types of domain have different spatial extents. A quadrupolar-ordered domain, which can reach macroscopic dimensions at high concentrations, consists of a number of dipolar-ordered microdomains. The size of the latter is concentration dependent (growing from 6 nm at 1.6% to 23 nm at 6% as detected by second-harmonic generation [24]), while it

remains temperature independent below  $T_c$ .

To understand the low-temperature properties, it has to be considered that samples are never in thermal equilibrium in low-temperature experiments, because reorientation of impurities below  $T_c$  is due only to the very slow  $\pi$  flips. In fact, the relevant  $\pi$ -flip relaxation time at  $T_c$  exceeds a typical experimental time scale of 1 hour, for example, for samples with a concentration of  $x \lesssim 4\%$  (1 year for  $x \simeq 3\%$ ). This means that a domain, or the polarization within a domain, will not have enough time to grow upon cooling, and therefore experiments, particularly on lower-concentration samples, are always performed in the quenched state.

In the following section, the effective Li–Li interaction energies are calculated to gain information about this experimentally inaccessible ground state.

### 3. Effective Li–Li interaction

#### 3.1. Theory and computational details

As observed experimentally [3], an off-centre Li impurity induces a polarization cloud—or ‘cluster’—around the Li, with a total dipole moment largely exceeding that produced by the bare Li displacement. Therefore, two impurities interact not only with dipolar forces but also through the indirect field of the polarized lattice. It is the purpose of this section to calculate the interaction potential between two Li impurities as a function of the Li–Li distance and bond direction as well as for different relative dipole orientations.

The model for the perfect (KTaO<sub>3</sub>) lattice was originally proposed to explain the ferroelectric behaviour in oxidic perovskites [25]. Each ion is described by a core and a polarizable shell. Both the K<sup>+</sup> and Ta<sup>5+</sup> ions are considered isotropically polarizable. However, since the oxygen polarizability strongly depends on the crystal environment, an anisotropic core–shell interaction is considered for the O<sup>2-</sup> ion. Interactions consist of long-range Coulomb terms plus short-range forces that couple the oxygen shells to the shells of the nearest K<sup>+</sup>, Ta<sup>5+</sup> and O<sup>2-</sup> ions. All interactions are treated in the harmonic approximation, except for an additional fourth-order term  $K_{OB-B}$  that couples the displacement of the oxygen cores to that of their own shells in the direction of the neighbouring Ta<sup>5+</sup> ions. The values of the model parameters were obtained in [26] from phonon-dispersion curves.

The impurities are treated by replacing the K<sup>+</sup>–O<sup>2-</sup> short-range interaction at the Li sites with an Li<sup>+</sup>–O<sup>2-</sup> potential derived from a lattice dynamics study of LiKSO<sub>4</sub> [27]. For the single-impurity problem, this approach predicts the off-centre Li displacement, the enhancement of the polar moment of the Li, and the polarization volume per impurity in very good agreement with experimental data [8, 9].

In the present article, two impurities are introduced to evaluate the Li–Li interaction modified by the polarized lattice. Both Li displacements ( $\delta_1$  and  $\delta_2$ ) and the lattice distortion are evaluated self-consistently using a Green function method extended to the non-linear polarizable model [8]. The set of displacements obtained in this way minimizes the potential energy of the system with two defects. This energy consists of the perfect lattice energy plus an effective potential ( $V_2^{\text{eff}}$ ) defined by

$$V_2^{\text{eff}} = \phi(\mathbf{u}, \mathbf{v}) + V(\mathbf{u}, \mathbf{v}). \quad (1)$$

Here  $\phi(\mathbf{u}, \mathbf{v})$  is the shell model potential for pure KTaO<sub>3</sub>, and  $V(\mathbf{u}, \mathbf{v})$  is the defect potential. The first term can be written as

$$\phi(\mathbf{u}, \mathbf{v}) = \frac{1}{2}\mathbf{u}^\dagger(S + C^{\text{zz}})\mathbf{u} + \frac{1}{2}(\mathbf{v} - \mathbf{u})^\dagger(S + \mathcal{K} + C^{\text{yy}})(\mathbf{v} - \mathbf{u})$$

$$+u^{\dagger}(S + C^{zy})(v - u) + \frac{1}{4!}K_{OB-B}\mathcal{L}(v - u)^4 \quad (2)$$

where  $u$  and  $v$  denote core and shell displacements, respectively.  $S$  is the short-range force matrix and  $C^{ij}$  represent the Coulomb force matrices between ions ( $C^{zz}$ ), between shells ( $C^{yy}$ ), and between ions and shells ( $C^{zy}$ ), where  $z$  denotes ionic charge and  $y$  shell charge.  $\mathcal{K}$  is a diagonal matrix which contains the core-shell coupling constants and the matrix  $\mathcal{L}$  selects the appropriate components for the non-linear interaction at the  $O^{2-}$  ions.

The second contribution to  $V_2^{\text{eff}}$ , i.e. the defect potential  $V(u, v)$  (where the term 'defect' stands for an  $Li^+$  ion at the off-centre position plus the  $K^+$  vacancy) can be written as the sum of a defect-lattice contribution  $V_{DL}$  plus a defect-defect interaction  $V_{DD}$ :

$$V(u, v) = V_{DL} + V_{DD} \quad (3)$$

with

$$V_{DL} = \sum_{l\kappa} \sum_{n=1}^2 V(Li_n^+, l\kappa) - V(K_n^+, l\kappa) \quad (4)$$

$$V_{DD} = V(Li_1^+, Li_2^+) - V(K_1^+, K_2^+). \quad (5)$$

$V(Li_n^+, l\kappa)$  includes short-range and Coulomb interactions between the  $Li^+$  ion at site  $n$  and a host lattice ion of type  $\kappa$  ( $\kappa = K^+, Li^+, Ta^{5+}, O^{2-}$ ) in the cell  $l$ .  $V(K_n^+, l\kappa)$  cancels the same type of interaction that would arise from the  $K^+$  ion, now replaced by the  $Li^+$ .  $V(Li_1^+, Li_2^+)$  is the Coulomb Li-Li interaction while  $V(K_1^+, K_2^+)$  cancels the missing K-K interaction.

The equilibrium condition ( $V_2^{\text{eff}} = \text{minimum}$ ) implies that

$$f_{\alpha}^c(l, \kappa) \equiv -\frac{\partial V}{\partial u_{\alpha}(l, \kappa)} = \frac{\partial \phi}{\partial u_{\alpha}(l, \kappa)} \quad (6)$$

$$f_{\alpha}^s(l, \kappa) \equiv -\frac{\partial V}{\partial v_{\alpha}(l, \kappa)} = \frac{\partial \phi}{\partial v_{\alpha}(l, \kappa)}. \quad (7)$$

For the following it is convenient to work with the relative shell-core displacements  $w = v - u$ , rather than with the absolute shell coordinates. From (6) and (7), together with (2), we obtain

$$f^t \equiv f^c + f^s = (S + C^{zz})u + (S + C^{zy})w \quad (8)$$

$$f^s = (S + C^{yz})u + (S + \mathcal{K} + C^{yy})w + \frac{1}{3!}K_{OB-B}\mathcal{L}(w)^3. \quad (9)$$

The right-hand sides of the above equations are linear in  $u$  and  $w$  except for the term arising from the non-linear interaction at the oxygen ions. Therefore, to solve the system (8) and (9), we define

$$f' \equiv f^s - \frac{1}{3!}K_{OB-B}\mathcal{L}(w)^3 \quad (10)$$

which leads to the following system of non-linear coupled equations:

$$u = Gf^t - Af' \quad (11)$$

$$w = Bf' - Cu. \quad (12)$$

The matrices  $G$ ,  $A$ ,  $B$  and  $C$  are obtained as a Fourier transformation of the following matrices in reciprocal space :

$$G = D^{-1}$$

$$A = D^{-1}(S + C^{yz})(S + \mathcal{K} + C^{yy})^{-1}$$

$$B = (S + \mathcal{K} + C^{yy})^{-1}$$

$$C = (S + \mathcal{K} + C^{yy})^{-1}(S + C^{yz})$$

where  $\mathcal{D} = (S + C^{zz}) - (S + C^{xy})(S + K + C^{yy})^{-1}(S + C^{xy})^\dagger$  is the dynamic matrix of the shell model. In the limiting case where the ions are non-polarizable, i.e.  $K \rightarrow \infty$ , the matrices  $\mathcal{A}$ ,  $\mathcal{B}$  and  $\mathcal{C}$  vanish to yield the familiar expression  $u = \mathcal{G}f^t$ . In this case,  $\mathcal{G}$  becomes the static Green function of the rigid ion model.

The forces  $f^t$  and  $f^s$  are evaluated in the distorted lattice, hence they are functions of  $u$ ,  $w$ ,  $\delta_1$  and  $\delta_2$ . Therefore, equations (11) and (12) must be solved self-consistently together with the equilibrium condition for the  $\text{Li}^+$  impurities (namely that the total force on each  $\text{Li}^+$  ion is equal to zero).

To perform the calculation, the defect-lattice Coulomb forces must be restricted to a finite region. As was shown for a single defect, there is an enhancement of the bare Li dipole moment due to the polarization of a neighbouring ellipsoidal region with a length of about five lattice constants ( $a$ ) in the polar direction [8, 9]. Hence, to avoid boundary effects, we consider a spherical lattice region large enough to include the polarized ellipsoids associated with both impurities. This sphere has a diameter of  $11.6a$  and contains 799  $\text{K}^+$  ions, 840  $\text{Ta}^{5+}$  ions and 2520  $\text{O}^{2-}$  ions. It should be noted that the only approximation imposed by a finite radius is a truncation of the defect-lattice Coulomb forces at this radius. The interactions within the host lattice, as well as the infinite lattice relaxation, are not affected by the truncation, since the Green function method ensures the inclusion of all infinite-range terms. We have verified that a further increase of the diameter of this sphere does not modify the final result.

The equilibrium solution for  $u$ ,  $w$ ,  $\delta_1$  and  $\delta_2$  is obtained iteratively by a steepest-descent procedure. The initial ionic positions are chosen to be those of the perfect lattice ( $u = w = 0$ ), except for the  $\text{Li}^+$ , which are arbitrarily displaced. Once the final configuration is obtained, the potential energy  $V_2^{\text{eff}}$  is computed according to (1), where the lattice relaxation energy  $\phi(u, v)$  is obtained from (11) and (12):

$$\phi = \frac{1}{2} f^{t\dagger} \mathcal{G} f^t + \frac{1}{2} f^{s\dagger} (\mathcal{C}\mathcal{A} + \mathcal{B}) f^s - f^{t\dagger} \mathcal{A} f^s. \quad (13)$$

Finally, the effective Li-Li interaction energy is defined as

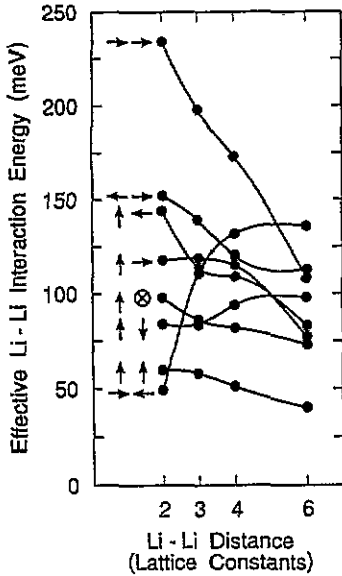
$$V_{\text{int}}^{\text{eff}} = V_2^{\text{eff}} - 2V_1^{\text{eff}} \quad (14)$$

where  $V_1^{\text{eff}}$  is the energy of an isolated defect in the infinite lattice.

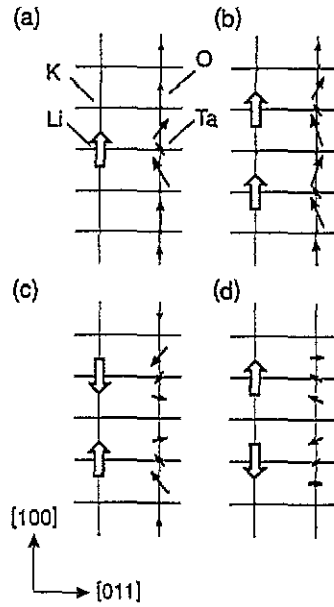
### 3.2. Results

The effective Li-Li interaction energies for two  $\text{Li}^+$  ions located at sites along the (100) cubic direction have been calculated as a function of the Li-Li distance and for all non-equivalent relative polarization directions. The result is shown in figure 1, where the orientation of the  $\text{Li}^+$  dipole moments are indicated by arrows.

In contrast to the case of classical dipoles, all interaction energies (irrespective of bond direction) are positive. In addition, the configuration  $\uparrow\uparrow$  has a lower energy than  $\uparrow\downarrow$ , again in contrast to the classical dipolar case. It is also observed that the parallel  $\uparrow\uparrow$  and antiparallel  $\uparrow\downarrow$  configurations approach each other in energy at short distances, both lying below the three perpendicular ones. On the other hand, the configuration  $\rightarrow\rightarrow$  has quite a high energy which grows rapidly with decreasing distance. The corresponding antiparallel configuration  $\rightarrow\leftarrow$  has, in contrast, an energy that decreases rapidly when the impurities approach each other. The energy of the other antiparallel configuration  $\leftarrow\rightarrow$  remains between the two previous ones. The large energy difference between these three configurations at short distances must be ascribed to the elastic interaction and higher moments of the electric charge distribution arising from the strong anisotropy of the polarized region around each



**Figure 1.** Effective Li-Li interaction energy as a function of distance for different relative displacements in the  $\langle 100 \rangle$  direction. The calculated energies are indicated by solid circles, and the orientation of the Li dipole moments is indicated by arrows to the left of each curve. Solid lines are guides to the eye.



**Figure 2.** Dipole moments resulting from core and shell displacement of the ions on a Li-K chain and its neighbouring Ta-O chain, (a) for an isolated impurity and (b), (c) and (d) for interacting configurations. The  $\text{Li}^+$  dipole moments are drawn as white arrows on a scale which is reduced by a factor of 100 with respect to one of the  $\text{K}^+$ ,  $\text{Ta}^{5+}$  and  $\text{O}^{2-}$  ions. For the latter ions, the scale has been chosen such that an arrow with the length of one lattice constant  $a$  represents a polarization of  $0.2ea$  ( $e$  = electronic charge).

Li [8]. The fact that this polarized region is smaller in the polar direction than in the opposite one accounts for the difference between the configurations  $\leftrightarrow$  and  $\rightarrow\leftarrow$ .

In figure 2 we show schematically the dipole moments of the  $\text{Li}^+$  ions, the  $\text{K}^+$  ions in the chain along the  $\text{Li}^+$  ions, and the ions in the nearest Ta-O chain. This chain of ions was shown for the case of an isolated Li to yield the most important contribution to the polarization enhancement [8]. The case of an isolated impurity (a) is compared to the pair configurations  $\rightarrow\rightarrow$  (b),  $\rightarrow\leftarrow$  (c) and  $\leftarrow\rightarrow$  (d). It is observed that in configuration (b), which has the largest potential energy, each  $\text{Ta}^{5+}$  and  $\text{O}^{2-}$  ion acquires a larger dipole moment due to the cooperative effects of the two Li impurities. It also appears that the polarized region becomes larger than in the other cases. On the other hand, competing effects between the two Li atoms are clearly observed in configurations (c) and (d) when compared to the isolated Li case (a). Turning back to figure 1, we observe that at larger Li-Li distances these configurations have similar energies, and it is to be expected that upon increasing the separation further, the energy of the  $\rightarrow\rightarrow$  configuration lies well below all others, since in that limit the impurities should behave as screened point dipoles.

The energies of the configurations  $\uparrow\uparrow$ ,  $\uparrow\downarrow$ ,  $\uparrow\leftarrow$ ,  $\uparrow\rightarrow$  and  $\uparrow\otimes$  are less affected by the Li-Li distance in comparison to the cases studied in figure 2. The reason for this is that the elastic interactions are weaker in the direction perpendicular to the dipole orientation, due to the anisotropy of the polarization cloud.

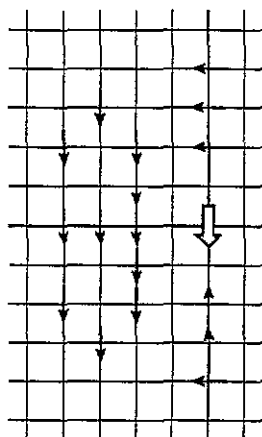


Figure 3. Schematic representation of the energetically most favourable dipole orientation of an impurity interacting only with the one at the origin (drawn as white arrow), for selected lattice sites in a  $[100]$  plane.

The dependence of the interaction energy on bond direction was studied and found to have a different behaviour from the one of classical dipoles. In figure 3, we visualize the two-particle interaction energy minima by drawing for selected sites in a  $\{100\}$  plane the direction of the most favourable orientation for an impurity that interacts only with the one at the origin. For cases where the Li–Li direction is not parallel to the polarization of the impurity at the origin, a parallel alignment is favoured. The situation changes drastically, however, if the second Li is placed on a site lying in the direction of the first impurity's polarization. In this case, the parallel configuration is the most unfavourable one, and the orientation of the lowest-energy alignment varies from perpendicular to antiparallel, according to the distance between the Li ions. In table 1 we summarize the values of the interaction energies calculated for the different relative Li–Li positions and orientations.

#### 4. Discussion and interpretation

Earlier theoretical [28] and numerical [29] studies of interacting impurities in polarizable lattices have shown strong deviations from the standard dipolar case. A mean field theory of dipoles coupled via transverse phonons, neglecting elastic interactions, has been developed by Vugmeister *et al* [2]. This model leads to interaction energies with signs depending on the relative orientation of the two dipoles. However, the behaviour of the interaction energy with distance does not depend on the orientation. This marked difference between the results of Vugmeister's theoretical study and the present calculation clearly shows the importance of elastic interactions.

The energies computed in the present article exhibit an extremely rich dependence on bond and dipole orientation, strongly suggesting frustration. Generally, frustration arises if minimization of the energy of the entire system does not dictate the orientation for each individual polar moment. The landscape of the energy function in frustrated systems exhibits, in configuration space, a large number of deep valleys (local minima) of identical or almost identical energy, separated by high barriers. The complexity of the interaction energies found in our calculations, together with the random distribution of the impurities, thus lead to further analogies with spin glasses.

Motivated by the great success of spin glass models, we shall try to describe the system with a Hamiltonian that considers only bilinear couplings (this is equivalent to postulating that two-body interactions yield a satisfactory description). Using the notation



**Table 1.** Interaction energies (in meV) for selected relative Li positions  $r_{\text{Li}-\text{Li}}$  and all non-equivalent pairs of Li orientations (the first column corresponds to the impurity at the origin). Data are grouped for  $r_{\text{Li}-\text{Li}} \parallel (100)$ ,  $r_{\text{Li}-\text{Li}} \parallel (101)$ , and for out-of-plane directions of  $r_{\text{Li}-\text{Li}}$ .

Li orientations		Effective interaction energy (meV)			
		$r_{\text{Li}-\text{Li}}$ :	(3,0,0)	(4,0,0)	(6,0,0)
+z	+z		58	51	40
+z	-z		84	94	98
+z	+x		119	115	77
+z	-x		114	109	83
+z	-y		86	82	73
+x	+x		198	173	108
+x	-x		110	132	136
-x	+x		139	117	113
		$r_{\text{Li}-\text{Li}}$ :	(2,0,2)	(3,0,3)	(4,0,4)
+z	+z		92	92	76
+z	-z		108	99	81
+z	+x		124	114	81
+z	-x		124	113	83
+z	+y		96	90	83
-z	+z		105	98	83
-z	+x		125	115	82
-z	+y		95	93	80
+y	+y		57	55	41
+y	-y		93	103	77
		$r_{\text{Li}-\text{Li}}$ :	(2,1,2)	(2,3,2)	(3,4,3)
+y	+y		107	106	95
+y	-y		125	114	91
+y	+x		128	117	93
+y	-x		127	115	89
-y	+y		125	112	94
-y	+x		130	114	93
-y	-x		128	113	88

of Vollmayr *et al* [6], this Hamiltonian reads

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} \sum_{\mu,\nu} J_{ij}^{\mu\nu} n_i^\mu n_j^\nu \quad (15)$$

where  $i$  and  $j$  represent Li sites,  $\mu$  and  $\nu$  can take six values corresponding to the possible spatial orientations of the Li off-centre displacement, and  $n_i^\mu$  is a random variable which takes the value unity if at site  $i$  there is a Li ion and it is displaced with the orientation  $\mu$ , and zero otherwise. Thus  $-J_{ij}^{\mu\nu}$  are the pair interaction energies, many of which have been calculated in this work.

Obviously, the  $6N \times 6N$  matrix  $J_{ij}^{\mu\nu}$  ( $N$  is the number of Li ions in the system) can be simplified considerably by using the symmetry of the cubic host crystal. According to our calculations, models that consider only nearest-neighbour couplings are not sufficient. In fact, if  $d_{\text{NN}}$  is the mean distance to the nearest neighbour of any impurity, then for some configurations (such as  $\rightarrow\leftarrow$  and  $\uparrow\downarrow$  of figure 1), the interaction energy still grows as a function of distance  $d$  for  $d > d_{\text{NN}}$  (for example,  $d_{\text{NN}}(1\%) = 3.0a$ ,  $d_{\text{NN}}(4\%) = 1.9a$ ).

For the purpose of a qualitative description, the complex dependence on the bond direction can be eliminated by averaging, for a given combination of dipole orientations and for a fixed Li-Li distance  $r$ , over all possible bond directions. For symmetry reasons, there

are only three independent values to be considered, namely  $J_0^{\uparrow\uparrow}(r)$  for parallel orientations,  $J_0^{\uparrow\downarrow}(r)$  for antiparallel, and  $J_0^{\perp}(r)$  for any perpendicular ones.

The averages and variances are calculated for these three quantities by considering the effective interactions between a given Li ion and a second one on a quasi-spherical shell of mean radius  $r$  (containing 26 sites).

Table 2 shows the values of these quantities obtained for three different distances. Note that the negative values of the coupling constants are given, as they correspond to the interaction energies.

**Table 2.** Mean values and variances (in meV) of parallel, antiparallel and perpendicular configurations for Li-Li distances of three, four and six lattice constants.

$r$	$-J_0^{\uparrow\uparrow}(\Delta J^{\uparrow\uparrow})$	$-J_0^{\uparrow\downarrow}(\Delta J^{\uparrow\downarrow})$	$-J_0^{\perp}(\Delta J^{\perp})$	$-(J_0^{\uparrow\uparrow} - J_0^{\uparrow\downarrow})$	$-(J_0^{\uparrow\uparrow} - J_0^{\perp})$
3	94 (35)	108 (15)	112 (15)	-14	-18
4	90 (32)	105 (9)	104 (12)	-15	-14
6	75 (25)	87 (13)	83 (6)	-12	-8

The quantities  $(J_0^{\uparrow\uparrow} - J_0^{\uparrow\downarrow})$  and  $(J_0^{\uparrow\uparrow} - J_0^{\perp})$  characterize the degree to which—on average—parallel alignment is favoured over antiparallel and perpendicular arrangements (see table 2). Both depend on distance. Considering that small interimpurity spacings are more important at higher Li concentrations, this shows that  $K_{1-x}Li_xTaO_3$  samples with a higher Li content should have a stronger tendency towards dipolar ordering than samples with a lower impurity concentration, and thus show larger dipolar- and quadrupolar-ordered microdomains, as experimentally observed. However, it has to be kept in mind that these differences are of the same order of magnitude as the variances of  $J_0^{\uparrow\uparrow}(r)$ ,  $J_0^{\uparrow\downarrow}(r)$  and  $J_0^{\perp}(r)$ , and thus that frustration remains dominant, which prevents spontaneous ordering of the system.

## 5. Conclusions

The results of the present work indicate that the interaction energies between two Li impurities in a  $KTaO_3$  host lattice show a very pronounced dependence on relative dipole orientation as well as on bond distance and direction. The description of the mixed  $K_{1-x}Li_xTaO_3$  crystal system thus goes beyond the framework of current spin glass theories. Spin glasses can typically be modelled using a Hamiltonian described by one to three random variables and a simple probability distribution. In  $K_{1-x}Li_xTaO_3$ , averaging over bond direction already results in quantities with a variance comparable to the differences between these (distance- and dipole-orientation-dependent) variables, indicating that further simplifications would result in a significant loss of information. Qualitatively, it is concluded from the spherically averaged interaction energies that  $K_{1-x}Li_xTaO_3$  has a stronger tendency towards ordering at high concentrations, corresponding to the experimentally observed larger dipolar- and quadrupolar-ordered microdomains in these samples. However, true ferroelectricity will be destroyed by the strong frustration of the interaction energies as long as two-body interactions are dominant. This indicates that at concentrations up to a few per cent, the behaviour of  $K_{1-x}Li_xTaO_3$  is described by a strongly disordered ground state.

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## References

- [1] Höchli U T, Knorr K, and Loidl A 1990 *Adv. Phys.* **39** 405 and references therein
- [2] Vugmeister B E and Glinchuck M D 1990 *Rev. Mod. Phys.* **62** 993 and references therein
- [3] van der Klink J J and Borsa F 1984 *Phys. Rev. B* **30** 52
- [4] Binder K and Reger J D 1992 *Adv. Phys.* **41** 547
- [5] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
- [6] Vollmayr H, Kree R, and Zippelius A 1991 *Phys. Rev. B* **44** 12 238
- [7] Doussineau P, Farssi Y, Frénois C, Levelut A, McEnaney K, Toulou J, and Ziolkiewicz S 1993 *Phys. Rev. Lett.* **70** 96
- [8] Stachiotti M G and Migoni R L 1991 *J. Phys.: Condens. Matter* **2** 4341
- [9] Stachiotti M G, Migoni R L, and Höchli U T 1991 *J. Phys.: Condens. Matter* **3** 3689
- [10] Höchli U T and Baeriswyl D 1984 *J. Phys. C: Solid State Phys.* **17** 311
- [11] Höchli U T and Maglione M 1989 *J. Phys.: Condens. Matter* **1** 2241
- [12] Christen H M, Höchli U T, Châtelain A, and Ziolkiewicz S 1991 *J. Phys.: Condens. Matter* **3** 8387
- [13] Rod S, Borsa F, and van der Klink J J 1988 *Phys. Rev. B* **38** 2267
- [14] Doussineau P, Frénois C, Levelut A, and Ziolkiewicz S 1991 *J. Phys.: Condens. Matter* **3** 8369
- [15] Höchli U T, Hessinger J, and Knorr K 1991 *J. Phys.: Condens. Matter* **3** 8377
- [16] Palmer R G, Stein D L, Abrahams E, and Anderson P W 1984 *Phys. Rev. Lett.* **53** 958
- [17] Dissado L A and Hill R M 1983 *Proc. R. Soc. A* **390** 131
- [18] Jonscher A K 1977 *Nature* **267** 673
- [19] Ogielski A T 1987 *Phase Transitions and Equilibrium Dynamics in Strongly Random Ising Spin Systems (Lecture Notes in Physics, 275)* (Berlin: Springer) p 190
- [20] Binder K 1990 *Ferroelectrics* **104** 3
- [21] van der Klink J J, Rytz D, Borsa F, and Höchli U T 1983 *Phys. Rev. B* **27** 89
- [22] Höchli U T, Kofel P, and Maglione M 1985 *Phys. Rev. B* **32** 4546
- [23] Höchli U T, Weibel H E, and Boatner L A 1979 *J. Phys. C: Solid State Phys.* **12** L563
- [24] Azzini G A, Banfi G P, Giulotto E, and Höchli U T 1991 *Phys. Rev. B* **43** 7473
- [25] Migoni R, Biltz H, and Bäuerle D 1976 *Phys. Rev. Lett.* **37** 1155
- [26] Perry C, Currat R, Buhay H, Migoni R, Stirling W, and Axe J 1989 *Phys. Rev. B* **39** 8666
- [27] Chaplot S and Rao K 1987 *Phys. Rev. B* **35** 9771
- [28] Vugmeister B E and Glinchuk M D 1980 *Sov. Phys.-JETP* **52** 3
- [29] Wang J 1980 *Phys. Rev. B* **22** 2725