

${}^7\text{Li}$ NMR Investigation of Li-Li Pair Ordering in the Paraelectric Phase of Weakly Substitutionally Disordered $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$

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Breaking of the average cubic symmetry in Li-doped potassium tantalate was observed with quadrupole-perturbed ${}^7\text{Li}$ NMR at temperatures (150–400 K) far above the nominal glass transition temperature (≈ 50 K for Li concentration $x = 0.03$). The observed spectrum consists of contributions from both isolated Li ions (i.e., with no nearest-neighbor Li) and from Li-Li pairs. The isolated Li ions move among six equivalent off-center sites in a potential having cubic symmetry. These have zero average electric field gradient and, hence, exhibit no quadrupole splitting. In addition, very low intensity, but well resolved, quadrupole satellites having a temperature-dependent splitting were observed. This splitting indicates that the various Li-Li pair configurations are not all equally probable. These are the first direct observations of biased Li ion ordering that persists in the paraelectric phase at temperatures high above the glass phase.

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The condensation of randomly interacting dipoles in Li-doped potassium tantalate $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ (KTL) is a textbook example of glasslike structural ordering in weakly substitutionally disordered solid solutions [1,2]. The “weak randomness” is introduced in this system by replacing a fraction of the positively charged K ions with Li ions (known as the A-site impurities). These possess a much smaller ionic radius than that of the K ions and are randomly distributed in the system. This leads to an “order-disorder” glass behavior [2]. The Li impurities act like randomly interacting electric dipoles, each with six possible instantaneous orientations pointing along the six respective $\langle 100 \rangle$ cubic axes [3]. Dielectric measurements suggest existence of a dipolar glass phase for low Li concentrations, $x \leq x_1 (\approx 0.04)$, and of a ferroelectric phase for $x > x_1$; the transition from the high temperature paraelectric phase into the glass phase takes place at the nominal temperature $T_g = 535x^{0.66}$ K (Ref. [4]), yielding, for example, $T_g \approx 66$ K for $x = 0.042$ (the highest Li concentration of the present study).

For low Li concentrations, typically $x \leq 0.1$, the statistical probability for the existence of large Li clusters is very small. In the $x \rightarrow 0$ limit, Li dipoles can be treated as independent entities. Then each of the six “eigenstates” occurs with equal probability ($w_i = w = 1/6$) in the course of time, resulting in vanishing dipolar and quadrupolar order. Such a situation has indeed been identified in weakly substitutionally disordered KTL at temperatures far above T_g . Further support was provided by ${}^7\text{Li}$ ($I = 3/2$) NMR, which detected at $T > T_g$ only a single relatively sharp resonance line, characteristic of a cubic Li environment [5]. This is somewhat surprising since, for x of the order of x_1 , the population of small Li clusters [like

Li-Li pairs, Fig. 1] populating neighboring K sites is far from being negligible. The time-averaged environment of each Li ion in such a pair is not cubic but is tetragonal.

Additional evidence about possible clustering and correlated motions of nearest-neighbor Li dipoles was earlier obtained from dielectric [6] and Li NMR relaxation time measurements [5]. Two relaxation processes were observed with activation energies of 0.215 eV and 0.086 eV, which are attributed, respectively, to 180° and 90° flips of a Li dipole. The 180° flips were assumed to arise from correlations between nearest-neighbor Li ions. This interpretation is suggested by the fact that the large activation energy was observed only in samples having greater Li concentrations ($x > 0.04$). In this prior work, no satellite lines due to broken cubic symmetry were observed in the NMR spectrum. However, density functional theory calculations also show [7] that interactions between nearest-neighbor Li ions strongly favor alignment parallel to their pair axis. The existence of a preferred configuration of a Li-Li pair thus breaks the otherwise cubic symmetry.

In this Letter we show that these Li-Li pairs indeed exist and can be detected via ${}^7\text{Li}$ NMR. Moreover, we

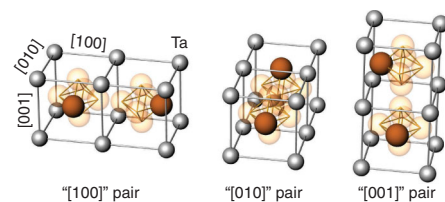


FIG. 1 (color online). Configuration of “[100],” “[010],” and “[001]” Li-Li pairs. The instantaneous Li position is shown in a solid color, whereas the other five possible states are shown in a translucent color.

demonstrate that the exchange dynamics is strongly biased for Li ions in Li-Li pair configurations in a six-well local potential, implying that some instantaneous off-center positions are more probable than the others.

NMR spectra were measured in a magnetic field $B_0 = 9.2$ T, corresponding to a Larmor frequency $\nu_L = 147.694$ MHz. A solid echo pulse sequence was used to form an echo at time τ after the second $\pi/2$ pulse. The length of each of the two pulses in the sequence was $7 \mu\text{s}$. Several single crystal KTL samples, with Li concentrations $x = 0.0035$ to $x = 0.042$ were employed in this study. KTL single crystals were grown by the spontaneous crystallization technique with Li concentrations in the melt of $x_m = 0.01, 0.02, 0.03, 0.1,$ and 0.12 , respectively. The Li concentrations inside the crystals are substantially lower than in the melt and can be estimated from $x = (0.35 \pm 0.05)x_m$ according to Ref. [8]. Depending on the Li concentration, a few hundred to a few tens of thousand scans per sample, each with a repetition time of 10 s, were typically accumulated. Temperature dependences of the spectra were measured between 130 K and 400 K. Angular dependences of the spectra were also measured at several representative temperatures by rotating the sample with respect to the magnetic field about one of the cubic axes perpendicular to \mathbf{B}_0 .

A typical ${}^7\text{Li}$ spectrum in the paraelectric phase is shown in Fig. 2(a). In addition to the dominant central line, we detected six faint but well-resolved lines that are distributed symmetrically about the central component. We believe that these lines belong to resolved ${}^7\text{Li}$ satellite transitions, signifying that some Li ions cannot be considered as isolated and are positioned at sites with noncubic symmetry. Associated with each K site are six nearest-neighbor K sites. The probability W_n for a given Li-occupied K site to be accompanied by n Li ions anywhere in the six closest K sites is given by

$$W_n = 6!x^n(1-x)^{6-n}/[n!(6-n)!]. \quad (1)$$

Specifically, $W_0 = 0.979$, $W_1 = 0.021$, and $W_2 = 0.00018$ for $x = 0.0035$, whereas $W_0 = 0.808$, $W_1 = 0.176$, and $W_2 = 0.016$ for $x = 0.035$. We note that $\sum_{n=0}^6 W_n = 1$. Thus, “isolated” Li impurities ($n = 0$) and Li-Li pairs ($n = 1$) are the prevalent configurations for low Li concentrations. By assuming that the interactions among Li dipoles are short-range, we can treat the “isolated” Li dipoles as probes of an undistorted six-well cubic potential. In contrast, the symmetry of the potential is broken for Li sites that belong to “pairs”, i.e., to $n = 1$ configurations. Those ${}^7\text{Li}$ nuclei ($\approx 18\%$ in $\text{K}_{0.965}\text{Li}_{0.035}\text{TaO}_3$, see W_n above) belonging to pairs thus experience a nonzero electric field gradient (EFG) tensor and contribute the satellites to the NMR spectrum. On the other hand, the major part, i.e., the isolated Li dipoles, gives rise solely to the central transition. This explains why we observed rather weak intensities for the satellite transitions compared to that for the

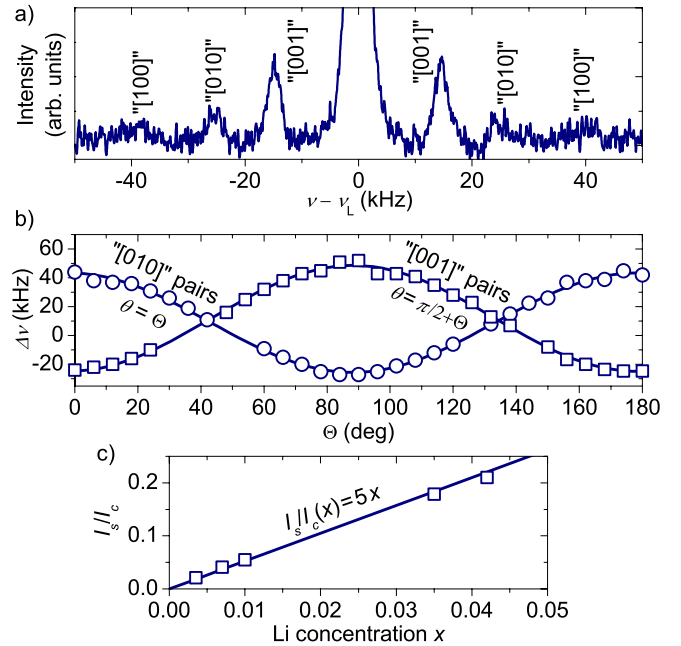


FIG. 2 (color online). (a) Room temperature ${}^7\text{Li}$ NMR spectrum in $\text{K}_{0.958}\text{Li}_{0.042}\text{TaO}_3$ at a general orientation at which three satellite doublets can be resolved, belonging to the three respective orientations of Li-Li pairs (labels above the peaks). (b) Angular dependence ($\Theta \angle [010], \mathbf{B}_0$) of the positions of the satellite transitions obtained by rotating the crystal about $[100] \perp \mathbf{B}_0$. Solid lines represent best fits to Eq. (2). (c) Concentration dependence of the relative intensity I_s/I_c of ${}^7\text{Li}$ NMR spectral components in KTL, determined from the spectra like that of Fig. 2(a).

central transition [Fig. 2(a)]. This effect was more pronounced in $\text{K}_{0.9965}\text{Li}_{0.0035}\text{TaO}_3$ than in $\text{K}_{0.958}\text{Li}_{0.042}\text{TaO}_3$ since in the former the concentration of pairs is much smaller than in the latter.

To check the above reasoning, we measured the ratio of the intensities of the satellite lines to that of the central line. In the low concentration limit, we see from Eq. (1) that $W_0 \approx 1 - 6x$ and $W_1 \approx 6x(1 - 5x)$ so that $W_1/W_0 \approx 6x$. However, the isolated Li ions experience zero EFG when averaged over all off-center sites and thus contribute only to the central line. Li-Li pairs, on the other hand, experience a nonzero average EFG and thus contribute to both the central and satellite lines. The intensity I_c of the central peak is proportional to $W_0 + 2W_1/5$ and the cumulative satellite intensity I_s is proportional to $3W_1/5$. Factors $2/5$ and $3/5$ arise from the theoretical intensity ratio $I_s/(I_c + I_s)$, which, for a nucleus of spin $3/2$, equals $3/5$. Consequently, $I_s/I_c = 3W_1/(5W_0 + 2W_1) \approx 3.6x$ in the low concentration limit. This linear dependence on x is clearly exhibited by the data of Fig. 2(c). Note that the experimental slope of 5 is somewhat higher than the theoretical slope of 3.6. However, this difference is not particularly disturbing since the values for x in our crystalline samples (on the horizontal axis) are estimates based on concentrations in the melt and are likely to be too low. The linear dependence on Li concentration shown in

Fig. 2(c) thus provides compelling evidence that the satellite lines indeed originate from Li-Li pairs and not from accidental impurities.

For a Li nucleus probing a cylindrically symmetric non-zero EFG, three resolved ${}^7\text{Li}$ NMR lines are expected. One is the first order central ($-1/2 \leftrightarrow 1/2$) transition at ν_L and the other two are the $-3/2 \leftrightarrow -1/2$ and $1/2 \leftrightarrow 3/2$ satellite transitions, which are shifted from the Larmor frequency by

$$\Delta\nu = \pm\nu_Q(3\cos^2\theta - 1)/2. \quad (2)$$

Here $\nu_Q = e^2qQ/2h$ is the quadrupole frequency, which depends on the quadrupole moment $Q({}^7\text{Li}) \approx 0.042 \times 10^{-24} \text{ cm}^2$ and on the largest eigenvalue $V_{zz} = eq$ of the EFG tensor. The angle θ denotes the tilt angle of the \mathbf{z} principal axis with respect to \mathbf{B}_0 . In the experimental spectra, three satellite pairs were observed at a general orientation of the crystal [Fig. 2(a)]. The behavior of the satellite shifts during the rotation of the crystal about the [100] cubic crystal axis, kept perpendicular to \mathbf{B}_0 , is depicted in Fig. 2(b). Note that in this case the “[100]” Li-Li pairs give rise to a doublet with a Θ -independent frequency shift $\Delta\nu \sim \pm 21 \text{ kHz}$ (not shown in the figure). Similar patterns were obtained for rotations about the [010] and [001] cubic axes. These angular dependencies are consistent with a scenario of three Li sites that are chemically equivalent (matching V_{zz}) but physically inequivalent, with the \mathbf{z} principal axes of the EFG tensor oriented along [100], [010], and [001], respectively. No EFG tensor asymmetry could be detected within the experimental precision, a fact supporting the conjecture of axial symmetry in Eq. (2).

The most interesting feature of our experimental results is the strong temperature dependence of ν_Q , shown in Fig. 3(a). Also intriguing is the lack of dependence on x of $\nu_Q(T)$. At room temperature ν_Q equals 47 kHz whereas at 150 K it reaches 80 kHz. Note that, in a previous study [5] of KTL, similar spectra with practically identical angular dependencies were observed for all investigated concentrations x at temperatures below 55 K where ${}^7\text{Li}$ ions are probed in a “rigid lattice” regime. In this regime, the exchange dynamics of isolated Li ions in the six-well potential is slow on the ${}^7\text{Li}$ NMR timescale, $\tau_{\text{NMR}} \sim \nu_{Q0}^{-1}$, and thus seemingly frozen-in, so that the six respective instantaneous off-center Li states are probed directly. It was found that under these conditions all Li sites exhibit the same behavior, and the experimentally determined $\nu_Q = \nu_{Q0} \approx 70 \text{ kHz}$, corresponding to the six instantaneous states, was independent of T . In the paraelectric state, however, Li exchange dynamics among the six sites is fast on the NMR time scale. In this “fast motion” regime, the ν_Q of Eq. (2) represents a time average $\langle \nu_Q \rangle$ over all possible configurations of an individual Li ion. Consequently, the observed temperature dependence of the average pair-state Li EFG tensor signifies that various pair configurations possess different occupation probabilities that are temperature-dependent. Such a picture is valid in

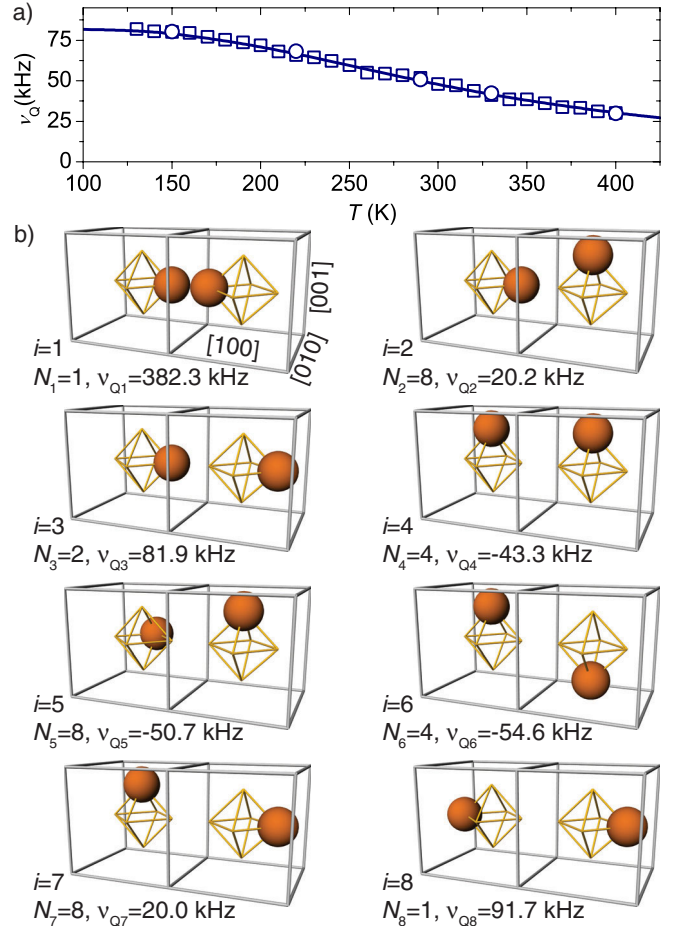


FIG. 3 (color online). (a) Temperature dependence of the ${}^7\text{Li}$ quadrupole frequency in $\text{K}_{0.9895}\text{Li}_{0.0105}\text{TaO}_3$ (circles) and $\text{K}_{0.958}\text{Li}_{0.042}\text{TaO}_3$ (squares). Solid line is a theoretical fit according to Eq. (3) with ν_{Qi} values listed in panel b. (b) Possible configurations of the two Li ions belonging to a “[100]” Li-Li pair. Only the basic configuration of each multiplet state is shown, together with the number of multiplet members (N_i) and the average multiplet quadrupole frequency ν_{Qi} .

the framework of order-disorder Li dynamics described above, given that the instantaneous Li off-center shifts are independent of T .

The temperature dependence of the average quadrupole frequency $\nu_Q(T)$ arises from differences in the Boltzmann factor characterizing the different Li-Li pair configurations. Each Li-Li pair has $6 \times 6 = 36$ possible configurations [Fig. 3(b)]. These can be regrouped by observing that there are eight physically nonequivalent configurations, denoted by $i = 1, \dots, 8$. For each i , a set of N_i configurations is obtained from the basic configuration, shown in Fig. 3(b) (cf. Fig. 6 of Ref. [7]), by either 90° rotations about the [100] axis or by mirroring in one of the cubic planes. Equivalent configurations of a given set have the same energy and are therefore equally probable. Consequently, the average EFG tensor of any set of equivalent states is cylindrically symmetric about the crystallographic axis along which the Li-Li pair is oriented. The largest effective

EFG tensor eigenaxis for any Li-Li pair thus points along one of the crystallographic axes, i.e., $\mathbf{z}_{[100]} = [100]$, $\mathbf{z}_{[010]} = [010]$, and $\mathbf{z}_{[001]} = [001]$. Note that the angular dependence of the spectra of isolated Li ions in the slow-motion regime [5] closely resembles that of the motionally averaged spectra of Li-Li pairs shown in Fig. 2(b). Specifically, the spectra of “[100],” “[010],” and “[001]” Li-Li pairs [Fig. 1] reveal exactly the same symmetry under reorientations of the crystal in the external magnetic field as the spectra of Li ions shifted along the [100], [010], and [001] cubic axes, respectively. However, in contrast to isolated Li ions at low temperatures in the slow-motion regime, the quadrupole frequency $\nu_Q(T)$ of the Li-Li pairs is strongly temperature-dependent, as evident from Fig. 3(a).

According to the model introduced above, $\nu_Q(T)$ can be calculated as

$$\nu_Q(T) = \sum_{i=1}^8 W_i(T) \nu_{Qi}, \quad (3)$$

$$W_i(T) = \frac{N_i \exp(-E_i/kT)}{\sum_{j=1}^8 N_j \exp(-E_j/kT)}, \quad (4)$$

where W_i is the probability of the i th configuration. The energies E_i of various configurations were recently calculated using a pseudopotential code within the local density approximation (LDA) (Ref. [7]). In order to also calculate the EFG tensors, we employed the all-electron full-potential local-orbital (FPLO) code (version 7.00-28) [9] with the same supercells and standard double numerical basis. The energies obtained with the two codes are very similar. Of the eight energetically inequivalent configurations shown in Fig. 3(b), the calculations show that $E_2 \approx E_4 \approx E_5$. States $i = 1, 6, 8$ have sufficiently large energies to be effectively unoccupied at temperatures below 400 K so that we set $W_1 = W_6 = W_8 = 0$. As predicted theoretically [7], the configuration $i = 3$ has the lowest energy. Accordingly we set $E_3 = 0$. Therefore, $W_i(T)$ of Eq. (4) depends essentially only on two energies, E_2 and E_7 . Values of ν_{Qi} obtained by the FPLO code (LDA model) are within 10% proportional to the values obtained with the point charge model. Using these values, the fits of Eq. (4) to the experimentally determined values of $\nu_Q(T)$ yield the solid curve of Fig. 3(a), with $E_2 = 0.082$ eV and $E_7 = 0.076$ eV.

If the exchange dynamics of the two neighboring Li ions, forming a pair-state, were completely uncorrelated (e.g., at high temperatures), all pair-state configurations would be equally probable, $W_i(T \rightarrow \infty) = N_i/36$, resulting in a temperature-independent quadrupole frequency

$\bar{\nu}_Q = \frac{1}{36} \sum_{i=1}^8 N_i \nu_{Qi} \sim 4.5$ kHz. The strong temperature dependence of $\nu_Q(T)$ shown in Fig. 3(a) provides compelling evidence that the exchange dynamics of any Li impurity belonging to Li-Li pairs is strongly biased. Our results are also in agreement with the predictions of Ref. [7] that the most favorable configuration for the Li-Li pairs corresponds to $i = 3$, (i.e., the case in which both ions exhibit off-center shifts in the same direction along a cubic axis).

Our approach would become invalid in the glass transition regime, at temperatures below 130 K, when long-range collective phenomena prevail and the satellite lines become increasingly broadened and unresolved [5].

In conclusion, in this Letter we have used quadrupole-perturbed ^7Li NMR to observe Li ordering in the paraelectric phase of Li-doped potassium tantalate. In particular we observed spectra consisting of an unshifted central line (due to isolated Li impurities) and quadrupolar satellites whose frequencies and angular and temperature dependencies confirm the existence of Li-Li pairs at off-center positions in neighboring potential wells. These are the first direct observations of such ion-pair ordering in a weakly substitutionally disordered solid at temperatures significantly above the glass transition.

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