

Percolation with constraints in the highly polarizable oxide $\text{KTaO}_3:\text{Li}$

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Abstract. Experimental data on the temperature and electric field dependence of the Second Harmonic Generation Intensity in the solid solution $\text{KTaO}_3:\text{Li}$ is analyzed in the framework of a new percolation-type approach which considers the history of cluster formation averaged over a large number of samples. In order to take into account that two cluster dipole moments turn when joining clusters together, a constraint is imposed on the cluster growth. This constraint leads to cluster-size saturation just after the percolation threshold. Owing to this circumstance, the connected cluster coexists with free clusters in some range of the impurity concentration and temperature. There is qualitative agreement between the computational results and experiments on Second Harmonic Generation intensities. The algorithm was written in C++ which allowed realistic computations to be performed on a standard PC.

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1 Introduction

Incipient ferroelectrics, like SrTiO_3 and KTaO_3 attract much attention because they show rather interesting phenomena related to zero-point atomic quantum vibrations. Another peculiarity of these systems is that even a rather small concentration of dipole-type impurities triggers a phase transition [1,2]. Sometimes these phase transitions are thought to be of the ferroelectric-type but sometimes glass-type (random-bond or random-field) features are believed to be dominant. For example, the Li ions which are substituted for K in the soft matrix of potassium tantalate lead to the creation of off-center dipoles directed in one of 6 possible directions, owing to the rather small Li radius. On one hand these dipoles can be aligned ferroelectrically because of an ordering interaction among them but, on the other hand, random fields and bonds can lead to a glass-type behavior of this solid solution.

Much information can be obtained from experiments measuring polarization, P , and $\langle P^2 \rangle$. One such experiment is the Second Harmonic Generation (SHG) method, which measures $\langle P^2 \rangle$. The $\text{KTaO}_3:\text{Li}$ solid solution was investigated by the SHG method in [3] (see also references therein). It was shown that the SHG intensity abruptly increases in some region of temperature, which is different for different Li concentrations. The SHG intensity saturates on a further temperature decrease. The saturated

zero-field SHG intensities increase nonlinearly with concentration, x . Applying an external electric field results in a further strong increase of the SHG intensity [3]. Owing to this, there is a large difference between the zero-field and electric field saturated SHG intensities for low concentrations, while this difference disappears at larger concentrations.

The large effect observed for comparatively small Li concentrations cannot be definitely connected to the appearance of large macroscopic polarization as there is no real evidence for a ferroelectric-type phase transition, at least for concentrations less than 5–6%. Moreover, the large increase of SHG intensities in an external electric field prompts one to conclude that polarization at zero field is suppressed for some reason, although nanoscale polarized regions which can be aligned by the external electric field already exist. Such a behavior differs from the usual ferroelectric-type picture as well as from glass-type behavior. The glass-type features of this phenomenon can be connected with the random (direction and value) dipole-dipole interaction within polarized regions although inside these regions the ferroelectric-type order is already predominant. Such a picture is new and should be described theoretically.

Considering Li dipoles embedded into the soft matrix of an incipient ferroelectric, a few questions arise. The first question is: how could such a small Li concentration govern the lattice polarization? A possible answer is that it is just the softness of the host lattice of the incipient

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ferroelectric that plays the major role. Owing to the softness of the lattice, the Li ions feel each other even if separated by quite a distance. It implies that the “bonds” between Li impurities can be rather long. Because of this “bonding”, nanoscale clusters can appear at comparatively low Li concentrations. These clusters should not be confused with chemical clusters, as a random Li distribution over the sites is assumed. Nevertheless, it is precisely this randomness that plays an important role for the possible existence of percolative clusters. Indeed, owing to the random distribution, the local density of Li concentration in small volumes fluctuates strongly. This leads to local satisfaction of a condition for dipole ordering. Hence, ordered clusters can appear, owing to a large value of the correlation radius in the incipient ferroelectrics. Moreover, this radius is temperature dependent and this dependence is rather strong at low temperature. It permits the use of percolation approach with temperature dependent bond lengths.

Another question is how to prevent the cluster growth from going beyond limits. Indeed, when the percolation threshold is approached, the clusters grow rapidly and the connected cluster appears as a result. In order to make free nanoscale clusters stable with respect to a small change in the parameters (for instance, temperature or concentration) the clusters should be restricted to grow up to a definite size. Thereafter, their growth should be suppressed somehow. One of the possible ways of accomplishing this is to use constraints imposed on the cluster growth. An example of such a constraint was recently demonstrated in [4] for PMN. It was shown for their percolation approach, that for certain parameter values, the saturated value for the order parameter could be considerably lower than its maximum possible value. This suppression results partly from random fields, while some additional assumptions are taken into account. We also describe a constraint leading to the suppression of the ferroelectric phase transition in $\text{KTaO}_3\text{:Li}$ (KTL) in the framework of a simple model. This constraint allows the free clusters to coexist with the connected cluster over a wide temperature range and at small concentrations. However, the same constraint does not prevent the ferroelectric phase transition at higher concentrations.

The above mentioned experiments will be analyzed in the framework of a percolation approach. In the literature there are numerous works in the framework of the mean field approximation, and dealing with KTL using random-field approaches. The percolation approach goes beyond the mean field approximation and considers the real cluster statistics. It takes into account the random Li distribution that is rather important for small Li concentrations. This is a first attempt at performing a straight percolation computation for KTL to explain the temperature dependence of the SHG intensity.

2 Description of the model

We consider a 3D net (of minimum size $100 \times 100 \times 100$), whose sites are randomly occupied by dipole-type rigid

impurities. The first step is to create a random distribution of impurities over the sites. This is easily done with the help of a random-number generator. The second step is to establish the connected points (bonds), that is those points separated by a distance not larger than the cut-off radius. It is ineffective to solve this problem by checking the distances between all the impurities, since this would grow with the number of impurities N as N^2 . In order to avoid this difficulty we divide the sample into subcubes, or bricks.

First we find the occupation of the bricks by the impurities. Thereafter, the sites inside the bricks are again selected randomly. An impurity position now is characterized by the number of a brick and the number of a site inside the brick. It is now straight forward to find the nearest neighbors of each of the impurities as it is only necessary to search for them in the nearest bricks. Hence, the size of the bricks should be slightly larger than the largest correlation radius for the considered temperature range (we took it to be equal to $6a$, where a is the lattice constant). This procedure allows the data to be stored rather effectively; a knowledge of the number of impurities in the bricks enables arrays to be created with the appropriate length. Moreover, using dynamic memory allows the arrays to be created in the same memory location for the different samples.

What could be said about the correlation between two dipoles if the change in orientation of one of the dipoles leads to a change (of the same order) in the orientation of the other dipole? We assume that there exists a maximal distance, R , for the dipole-dipole correlation. This correlation cut-off radius can be caused by different physical mechanisms but to a good approximation it is proportional to the polarization correlation radius, r_0 . This controls the spatial decay of the electric indirect dipole-dipole interaction: $R = ar_0(T)$, where a is a parameter dependent on the mechanism of the correlation, while $r_0(T) \sim \sqrt{\varepsilon_0(T)}$, where ε_0 depends only on the soft TO-mode of the displacive type. In spite of the strong total $\varepsilon(T)$ dependence on the concentration of Li impurities, x , owing to the order-disorder effect, we neglect the x -dependence of the displacement part of the dielectric permittivity. This is an assumption mainly about the order-disorder nature of the phase transformations in KTL. This is why, in the zero approximation, we use the expression for the correlation radius corresponding to the $x = 0$ case (KTaO_3)

$$r_0 = \sqrt{\frac{A}{T_s \coth \frac{T_s}{T} - T_0}}. \quad (1)$$

Here T_s is the saturation temperature and T_0 and A are constants. These quantities are known from fitting experimental data to the dielectric susceptibility: $T_s = 27.1$ K, $T_0 = 12.9$ K, $A = (15.073a)^2$ K [5]. We assume also that the coefficient a is a weak function of x and T . Fitting the experimental data on SHG intensities [3], we find that the temperatures for large increases of the SHG intensities for different Li concentrations are semi-quantitatively

reproduced by this model at $R \approx 1.34r_0$. Hence we fix $a = 1.34$.

The cut-off radius concept implies that an impurity belongs to a cluster if its minimal distance from the cluster is less than R . We assume that all impurities inside clusters are strongly correlated and owing to this, they have the same direction of the dipole moment to zeroth approximation. We draw attention here to the fact that the ferroelectric-type electrostatic interaction among dipoles inside a cluster is not a consequence of the direct dipole-dipole interaction. Rather, an indirect interaction of dipoles through the soft mode of the host lattice is assumed [6, 7]. This interaction leads to the ferroelectric type order inside cluster, while the direction of the cluster dipole moment is random.

For a first point of view it might seem that the accuracy of the result might depend on the size of the temperature steps upon decreasing temperature. However, it turns out that only a few special temperature points are important. Indeed the cut-off radius increase can be described by a set of special values at which the cluster can accept a new impurity. This is a consequence of dealing with a network rather than a continuum. As the cut-off radius is proportional to the correlation radius and as the latter is defined by temperature (1) one deduces that there are special temperature values at which the computation should be done. The other points would not provide essential new information.

In order to study the cluster growth, we consider their set of temperatures with decreasing value. At each temperature, the clusters can accept new impurities that existed in the layer between two spheres; the sphere of the previous cut-off radius and the sphere with the new cut-off radius. After performing the study of cluster growth for a definite sample, we create another sample with a different (but random) distribution of the impurities. We repeat the study of cluster growth, up to the saturation of averages.

The cluster statistics includes the computation of the following quantities. First, one should divide the clusters into two groups: the connected clusters and the free ones. The signature for a connected cluster is: impurities in it can be met equally on both upper and lower sides of the sample (in our case it is a cube). The relative number of impurities in the connected clusters is called the order parameter

$$P_{\text{inf}} = \frac{\sum_{i \in P} s_i}{N} \quad (2)$$

where s_i is the number of impurities in the i th cluster, N is the number of impurities in the sample, and $i \in P$ implies that the cluster is connected (infinite). The order parameter is proportional to the macroscopic polarization as all dipoles inside the cluster are oriented in the same direction according to our assumption. In the infinite volume the connected cluster appears suddenly and then abruptly increases with decreasing temperature. Note that the sum over the connected clusters appears in (2) because, in principle, the number of connected clusters is not limited.

However, the connected cluster is usually alone. Nevertheless, when treating a finite sample there are very rare cases when the connected clusters are not single. Moreover, the constraint we have introduced in this work leads to an increase in the probability of the appearance of several connected clusters.

Averages that are computed besides the order parameter are:

$$\langle s \rangle = \frac{\sum_i s_i^2}{\sum_i s_i} \quad \langle s \rangle_{\text{F}} = \frac{\sum_{i \in P} s_i^2}{\sum_{i \in P} s_i} \quad (3)$$

In percolation theory the second average is named “*the average cluster size*” (see *e.g.* [8]). In fact the average geometrical cluster size, ξ , has nothing to do with $\langle s \rangle$. Nevertheless, we follow the standard definition of this term and on stating “*the cluster size*”, we imply $\langle s \rangle$ defined above. Note that in the first definition, the average includes all clusters inside the sample while in the second one, only free clusters are included.

The first average is proportional to the SHG Intensity. Indeed this intensity is proportional to the mean squared polarization, $\langle P^2 \rangle$, [5]. Note that this polarization sums all dipole moments, not only those of the free clusters. There is some uncertainty here because the connected clusters are not infinite in the computations because the cube size is finite. Hence, this scheme is rigorous only when considering the Hyper-Rayleigh scattering case [5] in the paraelectric regime. Nevertheless, the inclusion of the connected clusters gives, in principle, a possibility to consider the general case for the SHG intensities [5], but an infinite volume will be necessary in this case. In order to obtain the result for the infinite volume, it is possible to use the dependence of the result on cluster size. This dependence is usually critical and after finding the corresponding exponent one can obtain the necessary extrapolated value [8].

In the Hyper-Rayleigh scattering case, when the wavelength of the laser beam is smaller than the cluster size, one has (considering only incoherent SHG scattering in the forward direction)

$$I \sim \langle P^2 \rangle \sim \frac{\sum d_i^2}{N} = \frac{d_0^2 \sum s_i^2}{\sum s_i} = \langle s \rangle d_0^2 \quad (4)$$

Here d_0 is the dipole moment of a single Li impurity, d_i is the i th cluster dipole moment. It can be seen that the SHG intensity is proportional to the average cluster size. It should be noted that d_0 in (4) is temperature dependent and this dependence alone was studied in [5] to obtain a good fit to the SHG data for quantum paraelectrics. In the present work the temperature dependence of the other cofactor, $\langle s \rangle$, will be investigated.

Both quantities (the order parameter and the average cluster size) are computed for each sample and are then averaged over samples for each temperature point. The number of samples is selected so that the averages reach saturation (the maximal number of samples was 1 000).

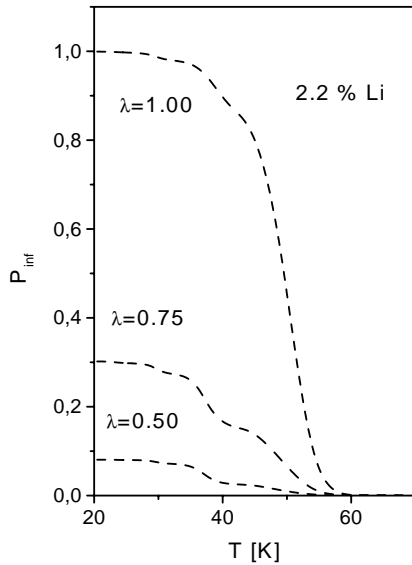


Fig. 1. The dependence of the order parameter on temperature: 2.2% Li concentration.

The cluster growth is now limited only by the cut-off radius. This is not sufficient to describe the glass-type behavior for low Li concentrations. If there are no other constraints, the system will undergo a ferroelectric-type phase transition just after reaching the percolation threshold. In order to suppress this phase transition (to decrease the order parameter) one needs to impose a constraint that does not allow large clusters to grow and become connected. A simple form of the constraint is

$$s_i s_j < B \quad (5)$$

where B is a constant. The constant is found from fitting the experimental data and takes a value of about 550. Note that similar results were obtained using a sum of the sizes instead of a product. Real constraints connected with a microscopic model will be derived later.

The proposed constraint results in saturation of the macroscopic polarization (if it appears) as well as saturation of the free cluster sizes when temperature reaches the percolation threshold. The sizes of the free clusters remain large but do not become infinite and the connected cluster does not grow upon further decrease of the temperature.

3 Some computational results

Firstly we computed the average size (which is proportional to the SHG intensity) for $\text{KTaO}_3:\text{Li}$ with Li concentration 2.2%. This concentration was chosen as it corresponds both to the spheres (with the correlation radius) just touching in the mean field approximation, and the start of the phase transition. We find in this model that the macroscopic polarization appears at 50 K. However, owing to the constraint, the saturated value of the macroscopic polarization is rather low, $P_{\text{inf}} \ll 1$, and this value

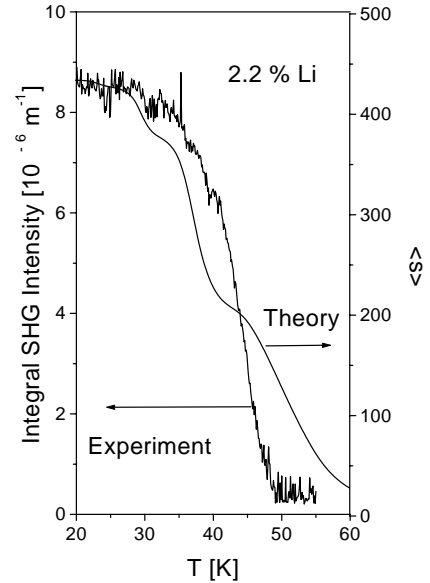


Fig. 2. The dependence of the average size on temperature. Comparison between theory and experiment [3]: 2.2% Li concentration.

remains even at zero temperature. In principle, the value of the order parameter can change upon enlarging the size of the cube and it is not possible at present to say whether a macroscopic polarization in reality exists (although very low), or not. The value of the order parameter is so small that there are many factors which can disturb this value and make it equal to zero.

To study the dependence of the average cluster size on the strength of the constraint, we introduce a phenomenological parameter, λ , in the following way

$$(1 - \lambda)s_i s_j < B. \quad (6)$$

The case $\lambda = 1$ corresponds to the complete absence of constraint, while $\lambda = 0$ gives the full constraint. Figure 1 shows the temperature dependence of the order parameter for different values of λ (the Li concentration is 2.2%). It can be seen that increasing λ leads to a large increase of the average size. This increase looks like critical behavior. The temperature dependence of the average size also looks critical. Note that, at $\lambda < 1$, the order parameter saturates at a value lower than 1 and it practically (but not completely) vanishes at $\lambda = 0$. It may be seen that the constraint suppresses the growth of the connected cluster although the percolation threshold occurs in the same temperature region.

We have also performed the computation for the temperature dependence of the average cluster size for concentration 2.2%, and for smaller (0.8%) and larger (6.3%) concentrations. The results are shown in Figures 2, 3 and 4. Experimental data are also shown in the same figures. Only temperature cooling was used although for large concentrations there is a strong hysteresis in the experimental data. From the data obtained it is apparent that the shape of the temperature dependence of the SHG intensity looks qualitatively similar to that found in the experiment. In all cases considered there is a sharp

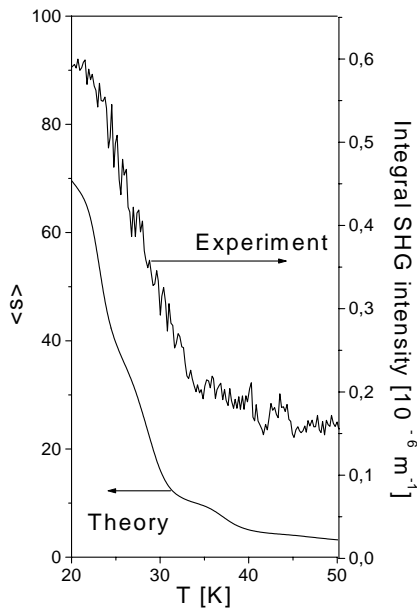


Fig. 3. The dependence of the average size on temperature. Comparison between theory and experiment [3]: 0.8% Li concentration.

increase of SHG intensity in some temperature region. The temperature at which this enhancement appears increases with Li concentration. For 0.8% Li this temperature is rather small, about 30 K. For the intermediate case, 2.2% Li, this region is between 40 and 50 K. For comparatively large Li concentration, 6%, this region is shifted to 80–100 K. It should be stressed that the shape of the temperature dependence of the SHG intensity changes. One should draw attention to the fact that the macroscopic polarization is suppressed at small Li concentrations almost completely while the macroscopic polarization is practically unsuppressed for the 6% Li concentration.

4 Discussion

It is observed that, in spite of the set of assumptions made, the proposed model can explain the SHG-experiment at least semi-quantitatively. The approach has three parameters, a , B and λ . Varying a leads to a threshold shift while the qualitative dependencies of the averages are not changed by this parameter. Hence this parameter can be used to find the suitable scale of temperatures. The values of B and λ govern the suppression of the phase transition. In fact, only the ratio $B/(1 - \lambda)$ is important. Lowering this ratio, the phase transition disappears while a large increase of cluster size near the threshold temperature remains. Hence, this value can be chosen on the basis of the coincidence of the critical concentration for the phase transition in theory and experiment. Note that here again, we have the case where the qualitative picture of the SHG intensity dependence on temperature does not change with a parameter, but rather the amplitude of the

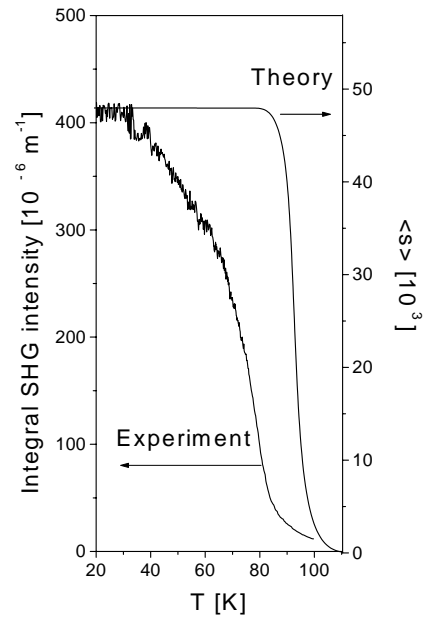


Fig. 4. The dependence of the average size on temperature. Comparison the theory and experiment [3]: 6.3% Li concentration.

SHG intensity just below threshold can be changed dramatically. The experiment [3] has shown that the step in the intensity increases critically with concentration with a large exponent (not linearly) and only at the concentration of 6% does this dependence become slow. These data are in very good agreement with the assumption that there is a constraint depressing the phase transition. A similar conclusion was made in [4] considering relaxors like PMN. In that case the constraint was connected with the random fields appearing due to the nonuniformity of the charge density. In our case the random fields can be produced by the percolation clusters. These random fields can prevent the growth of the clusters when the temperature decreases. As a result, the phase transition can be suppressed. It is evident from this that the B parameter should be connected with the dipole-dipole interaction energy of the clusters to prevent cluster flipping. The random field concept within the percolation approach for solid solutions of quantum paraelectrics will be developed elsewhere. In the present paper we consider only a simplified version of the theory where the constraint has rather a mathematical than a physical meaning.

In the standard percolation approach it is usually assumed that only the nearest neighbors interact. In the present approach the interaction radius is comparatively large, of 10 to 20 Å. It is assumed that all impurities separated by a distance less than this interact, and that these impurities are strongly correlated. Due to these strong correlations, the light from the laser is understood to be scattered by the cluster moment as a whole rather than by the separate dipole moments of the individual impurities. Nevertheless, at a small concentration the scattering by single impurities dominates as they are separated by a distance longer than the correlation radius [5].

The proposed percolation approach shows that the polarization in the solid solution of incipient ferroelectrics can be suppressed by employing a constraint. This constraint leads to a freezing of large clusters and does not allow the connected cluster to grow further. We believe that applying an external electric field will align the clusters and due to this the total polarization will increase. It implies that the nanoscale domains (clusters) can be easily oriented by employing the field-cooling procedure. However, this is true only for a comparatively small Li concentration. For larger concentrations, the macroscopic polarization appears just after the percolation threshold and the electric field cannot strongly disturb this polarization as it is already practically saturated. Hence, we believe the concentration region from 2% to 6% to be intermediate between pure ferroelectric and pure glass behavior. Inside this concentration region the zero-field saturated SHG intensity increases critically at first, while at a Li concentration of 6% it saturates.

The picture drawn above is a result of the constraint we use. This constraint does not allow large clusters to grow and owing to this, the macroscopic polarization is suppressed. Future attention will be directed towards understanding the microscopic meaning of this constraint or deriving a new one. It should be mentioned that the angular dependence of the long-range dipole-dipole interaction prevents the appearance of a ferroelectric-type transition whereas the short-range ferroelectric-type interaction facilitates the phase transition. It is clear from this consideration that the larger the dipole moments of nearest clusters, the larger the long-range interaction between them. Hence, there is a natural cause for the suppression of large cluster growth.

Another point to attract attention in the future is the connection between correlation and cut-off radii. The simplest approach with the coefficient a constant should be improved. The real relation between these two radii can be obtained from the following requirement: an impurity belongs to a cluster if the maximum interaction energy between this impurity and an impurity belonging already to the cluster exceeds some specific (for these impurities) interaction energy. A study of this complex definition will be done separately.

Finally, we draw attention to the electric field influence on the SHG intensities. The large influence of the electric field on polarization at small concentrations is believed to arise from the reorientation of the clusters (poling) in the field. This reorientation has some peculiarities which can be described in the framework of the spherical model [10]. One of the consequences of such a consideration is that the longitudinal susceptibility behaves as $E^{-1/2}$. It implies that the polarization depends on the field in the following complex form: $P_0 + AE^{1/2}$ where A is a constant and P_0 is the zero-field polarization, which appears in field cooling experiments for KTL [11]. As a result, the SHG intensity is proportional to $(P_0 + AE^{1/2})^2$ at least for small E . This analysis shows that at small E , the macroscopic polarization should increase at a rate that can be considered as softening the constraint. In reality this softening

could mean compensation, for example, because of the interaction of the electric field with the dipole moments of the clusters. This interaction is linear with the field and the sum of the cluster sizes. Probably, these arguments can be used also for relaxors where a spherical model is effective [12].

The results obtained encourage us to employ this approach for finding averages of different thermodynamic quantities. The real cluster statistics permits us to find any of the physical values. For example, a calculation of light scattering can be developed. Indeed, earlier in order to explain the temperature dependence of the SHG intensity for small Li concentrations a single impurity model was used [5]. The origin of light scattering was the single impurity surrounded by a polarization cloud. The radius of this cloud is temperature dependent (through the dependence of the correlation radius on temperature). Hence, the scattering intensity proves to be also temperature dependent. Another possibility arises if one takes into account the cluster statistics. It has been shown in the present paper that even for very small concentration of Li impurities of 0.8%, the average cluster size strongly increases at low temperature below 30 K. This large increase could also be a source for SHG intensity increase. A general theory which takes into account both factors needs to be developed.

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