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Self-Ordered Second-Component Nb Clusters in $KNb_xTa_{1-x}O_3$ Solid Solutions and Their Physical Properties

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Semi-empirical Hartree-Fock calculations using the intermediate neglect of the differential overlap (INDO) method, for self-ordered cubic symmetry clusters of seven Nb ions in $KTaO_3$ are performed with the aim of verifying the cluster model [1] of second component-induced phase transitions in ferroelectric perovskite matrices. It is shown that a seven-particle cluster in $KTaO_3$: Nb has two types of states with different nature. Namely, a state with a dilatation combined with an off-center displacement of the central Nb ion in [111] directions in the cluster, and a state with a full-symmetric compression without any off-center effect. The consequences of such cluster structures on the multi-well potential are discussed. In particular, the resonance tunneling between cluster excited states characterized by low frequency on-center vibrations, on the one hand, and excited states of off-center cluster vibrations, on the other, gives rise to low lying tunnel states. The latter states interact with soft TO modes and form the displacive type ferroelectric phase transition induced by impurities. This new type of displacive-like ordering co-exists with order–disorder effects with development of the central peak. All these results are in agreement with experimental data on $KTaO_3$ with Nb impurities. The results of the semi-empirical INDO calculations for seven Nb ions forming an impurity cluster in $KTaO_3$ confirm the key assumptions of the cluster model of induced phase transitions.

1. Introduction

Ab initio methods are still cumbersome and time-consuming in the treatment of the electronic and spatial structure of complex systems, especially those with partially covalent chemical bonding, like the perovskites. In order to be able to study the relatively complicated case of perovskite solid solutions, there is a need to close the gap between accurate but time consuming ab initio methods and widely used, simple but not so reliable ad hoc parameter-dependent phenomenological approaches, such as the shell model. One possible compromise is to use a semiempirical quantum chemical method that is parameter-dependent, but has parameters which are more or less transferable, for the specific chemical constituents given, and is not subject to adjustment for each new compound in question. An example of such a method is the updated Intermediate Neglect of the Differential Overlap (INDO) method [2,4,5,6,7], which is a semi-empirical ver-

sion of the Hartree-Fock method. In recent years, the INDO method has been applied very succesfully for the study of defects, both in bulk and on surfaces, e.g. in many oxide materials [4,5,6,8,9,10], as well as semiconductors [11,12]. We recently applied this method to the study of phase transitions and frozen phonons in $KNbO_3$ [7], pure and Li-doped $KTaO_3$ [13], and F centers in $KNbO_3$ [14].

Taking into account the increasing number of successful INDO applications during recent years, we have chosen this method for the study of self-ordered cubic symmetry clusters of seven Nb ions in $KTaO_3$ with the aim of verifying the cluster model [1] using an $4\times4\times4$ times extended large unit cell (LUC) containing 320 atoms.

For the interpretation of the impurity-induced ferroelectric phase transition by on-center impurities (like Ba^{2+} impurities in the incipient ferroelectric $SrTiO_3$) or by weak off-center impurities (like Nb^{5+} impurities in the incipient ferroelectric $KTaO_3$, and Ca^{2+} impurities in $SrTiO_3$) a model had been proposed [1] on the basis of the self-ordered cluster model. The main assumption of this model is the following: Clusters of the second component atoms are formed and they are self-ordered. These self-ordered clusters in ferroelectric perovskites have their own degrees of freedom (of order–disorder as well as of displacive types). The percolation of the corresponding local order parameters as well as the dynamical percolation of soft, low-frequency local vibrations leads to a cooperative behaviour which finally (at a specific concentration of the second component) induces the ferroelectric phase transition. The actual mechanisms of the existence of self-ordered high symmetry clusters, as well as their soft internal degrees of freedom have been developed in Ref. [1] on the basis of a definite model in which the impurity ions interact with the lattice.

It would be very useful to use first-principles calculations to verify the two main features of the model: (i) the existence of self-ordered high-symmetry clusters with rather high bonding energy in spite of the absence of a threshold of solubility for the solid solutions under consideration, and (ii) the existence of soft internal degrees of freedom of such clusters. Such an investigation is performed in the present article, but with a simpler semi-empirical approach. The seven-impurities Nb clusters in $KTaO_3$ of cubic point symmetry are considered as an example.

It will be shown that the developed model involves the possibility of a new displacive-type dynamics mechanism which induces a ferroelectric phase transition. This type of behaviour is in agreement with experimental measurements for $KTaO_3$: Nb.

2. The Method of Cluster Calculations

The Fock matrix elements in the modified INDO approximation [4,5,6] contain a number of semiempirical parameters. The orbital exponent ζ enters the radial part of Slater-type atomic orbitals:

$$R_{nl}(r) = (2\zeta)^{n+1/2}\,[(2n)!]^{-1/2}\,r^{n-1}\exp(-\zeta r)\,, \tag{1}$$

where n is the main quantum number of the valence shell. We used a valence basis set including 4s, 4p atomic orbitals (AO) for K; 2s, 2p for O; 5s, 5p, 4d for Nb, and 6s, 6p, 5d for the Ta atom. The diagonal matrix elements of the interaction of an electron occupying the μ-th valence AO on atom A with its own core are taken as

$$U^A_{\mu\mu} = -E^A_{\mathrm{neg}}(\mu) - \sum_{\nu\in A}\left(P^{(0)A}_{\nu\nu}\gamma_{\mu\nu} - \tfrac{1}{2}P^{(0)A}_{\nu\nu}K_{\mu\nu}\right), \tag{2}$$

where $P_{\mu\mu}^{(0)A}$ are the diagonal elements (initial guess) of the density matrix, $\gamma_{\mu\nu}$ and $K_{\mu\nu}$ are one-centre Coulomb and exchange integrals, respectively. $E_{\text{neg}}^{A}(\mu)$ is the initial guess of the μ-th AO energy. The matrix elements of interaction of an electron on the μ-th AO belonging to the atom A with the core of another atom B are calculated as follows:

$$V_{\mu}^{B} = Z_B\{1/R_{AB} + [\langle\mu\mu \,|\, \nu\nu\rangle - 1/R_{AB}] \exp(-\alpha_{AB}R_{AB})\}\,, \tag{3}$$

where R_{AB} is the distance between atoms A and B, Z_B is the core charge of atom B. α_{AB} is an adjustable parameter characterizing the finite size character of the atomic core B and additionally the diffuseness of the μ-th AO. $\langle\mu\mu \,|\, \nu\nu\rangle$ is the two-center Coulomb integral. The resonance-integral parameter $\beta_{\mu\nu}$ enters the off-diagonal Fock matrix elements for the spin component u:

$$F_{\mu\nu}^{u} = \beta_{\mu\nu}S_{\mu\nu} - P_{\mu\nu}^{u}\langle\mu\mu \,|\, \nu\nu\rangle\,, \tag{4}$$

where the μ-th and ν-th AO are centered at different atoms. u is an electron subsystem with α or β spin. $S_{\mu\nu}$ is the overlap matrix between electrons on the μ-th and ν-th AOs. $P_{\mu\nu}^{u}\langle\mu\mu \,|\, \nu\nu\rangle$ is the spin-density matrix.

Thus the INDO parametrization scheme contains the following set of parameters per atom: the orbital exponent ζ describing the radial part of the μ-th Slater-type AO on the A-atom; the electronegativity of the A-atom $E_{\text{neg}}^{A}(\mu)$, defining the μ-th AO energy; the μ-th AO population $P_{\nu\nu}^{(0)A}$, i.e. the 'initial guess' for the diagonal element of the density matrix; the resonance integral $\beta_{\mu\nu}$ entering the off-diagonal Fock matrix element where the μ-th and ν-th AOs are centered at the different A- and B-atoms; and the ajustable exponent α_{AB} characterizing the extended nature of the B-atom core interaction with the electron on the μ-th AO of the A-atom. INDO parameters for Nb and Ta were optimized by us earlier, by fitting them to the results of ab initio calculations and available experimental data for $KNbO_3$ and $KTaO_3$, and are tabulated in [7,13]. In the present work we used the same set of INDO parameters as in Ref. [7,13].

3. Results: Multi-Well Cluster Potential Structure

The exploration of the Nb clusters in $KTaO_3$ was performed using the periodic LUC method that is implemented in the updated CLUSTERD [4,5,6,7] computer

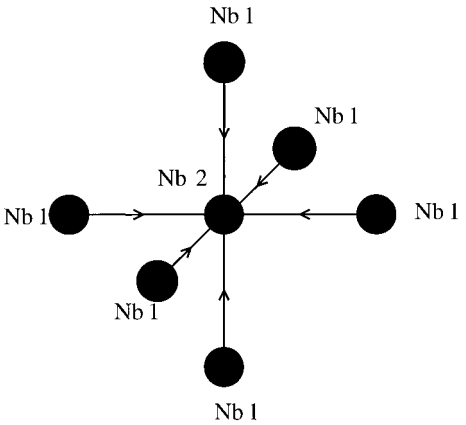

Fig. 1. Nb cluster containing seven Nb atoms inside $KTaO_3$

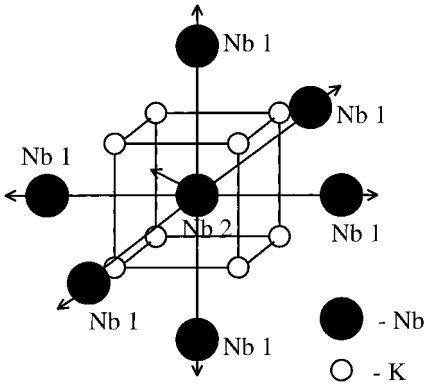

Fig. 2. Sketch of the symmetric repulsion of six Nb atoms outwards from the central Nb atom, which, as a consequence, is off-center then both in [100] and [111] directions

code. We extended our primitive $KTaO_3$ unit cell $4 \times 4 \times 4$, i.e. 64 times, which is equivalent to a bandstructure calculation at 64**k** points in the Brillouin zone. In order to calculate the Nb clusters in $KTaO_3$, we replaced in our extended unit cell, containing 320 atoms, seven Ta atoms by seven Nb atoms, as schematically shown in Fig. 1. In order to find the energy minimum of this Nb cluster in $KTaO_3$, we allowed the six Nb atoms to relax towards the central Nb atom (see Fig. 1). The positions of the K and O atoms were kept fixed. The results of our calculations show that the total energy per LUC is lowered by 0.088 eV when the six Nb atoms shift symmetrically by 0.187 Å towards the central Nb atom. Moreover, a uniform outward displacement of the six Nb atoms from the central Nb (see Fig. 2) by 0.073 Å is also favorable and lowers the energy by approximately 0.03 eV (see Fig. 3). In the case, when the six Nb atoms are shifted outwards from the central Nb

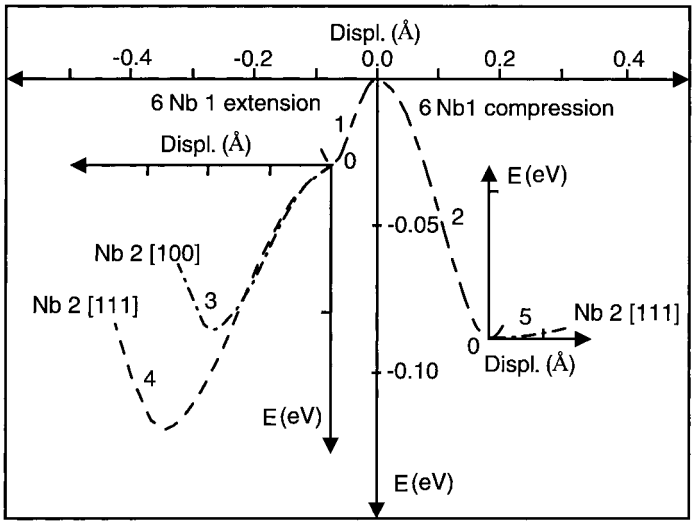

Fig. 3. Displacement energy of six Nb atoms relaxed outwards (curve 1) and inwards (curve 2) as is shown schematically in Fig. 2 and Fig. 1, respectively. The central Nb atom is off-center in the [100] and [111] direction, curves (3 and 4), in the case of a symmetric expansion of the cluster, but is on-center (curve 5), in the case of a compression of the cluster

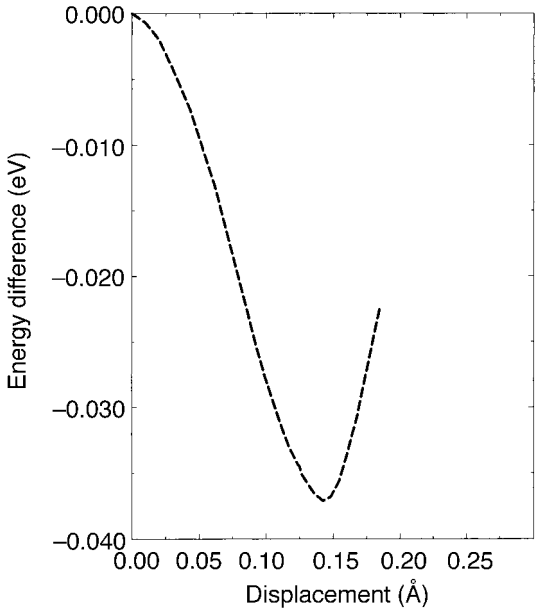

Fig. 4. The off-center behaviour of a single Nb impurity in $KTaO_3$ (with [111] equilibrium displacement)

atom, but the latter moves off-center by 0.27 Å in the [111] direction, a further lowering of 0.09 eV is found to give an overall total energy lowering of approximately 0.12 eV. These configurations correspond to a ground-state vibronic multiplet. The central Nb atom reveals also an instability in the [100] direction with a shift of 0.192 Å with an additional energy lowering of 0.056 eV after the six Nb atoms were shifted outwards from the central Nb atom. According to our calculations the central Nb atom exibits an on-center behaviour (see Fig. 3) in the case when the six Nb atoms move towards the central Nb atom (excited state). It should

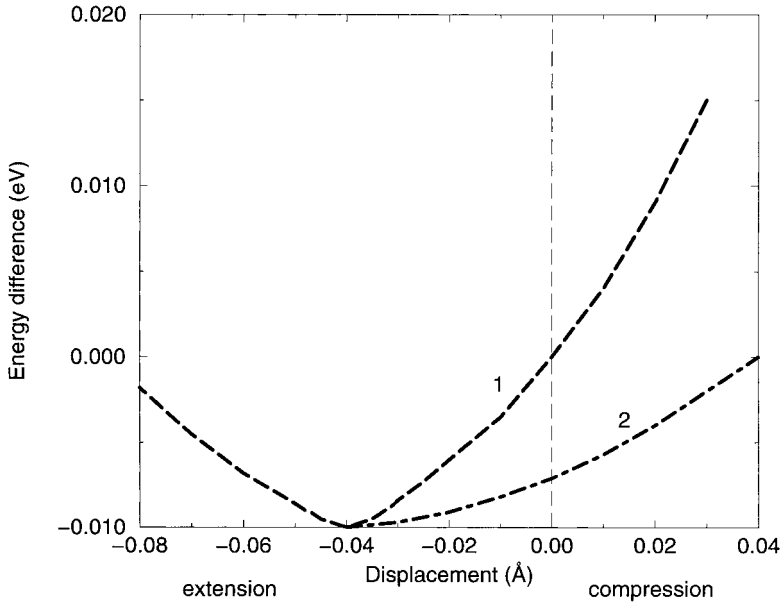

Fig. 5. Total energy vs. displacement of six nearest-neighbour Ta atoms in $KNbO_3$ (see Fig. 2 and Fig. 1) which are relaxed outwards and inwards with respect to the Ta atom at the origin (curve 1). Curve 2 shows the additional effect of the central Ta atom being displaced along the [111] direction while the other six Ta atoms are fixed at the optimised configuration corresponding to the minimum in curve 1

be emphasized that in this case the polar distortion dependence of the cluster energy is very smooth. This circumstance can lead to a rather soft polar quasilocal cluster frequency on the one hand, and to the possibility of a defect-induced dipole instability and weak off-center displacements on the other.

Fig. 4. shows the total energy for a 135-atom cluster modelling an *isolated* Nb impurity as a function of its [111] off-center displacement. The calculated displacement of 0.146 Å is very close to the experimental XAFS finding at 70 K [3]. The relevant energy gain is very small, approximately 0.0375 eV, which is a typical value for a Nb displacement as calculated earlier for different ferroelectric phases of $KNbO_3$ [7].

We have also studied the inverted impurity case: when seven Ta impurities replace seven Nb atoms in $KNbO_3$ a different behaviour is found, as in case, when seven Nb atoms replace seven Ta atoms in $KTaO_3$. The total energy minimum of the former case corresponds to the by 0.04 Å symmetrically extended configuration of the six Ta ions, while the central Ta ion retains its on-center position (see Fig. 5). In this case we have no dipole-type order–disorder degrees of freedom, but rather a soft dipole quasilocal vibration of such a cluster which can take part in a displacive type ferroelectric phase transition in $KNb_xTa_{1-x}O_3$.

4. The Nature of the Second-Component Induced Ferroelectric Phase Transition in Solid Solution $KTaO_3$:Nb. Effect of Nb Clusters

Here we shall consider the main conclusions from the results of the cluster structure computations discussed above from the viewpoint of the possibility of second component induced ferroelectric phase transition and related phenomena.

The important feature of the clusters under consideration is the existence of rather soft quasi-local modes in the excited vibration cluster state with on-center behaviour of the central Nb ion and compression of the six other Nb ions. The appearance of such soft quasi-local modes leads to the increase in the overlap between corresponding vibration wave functions in the ground on-centre compressed state and in the excited off-

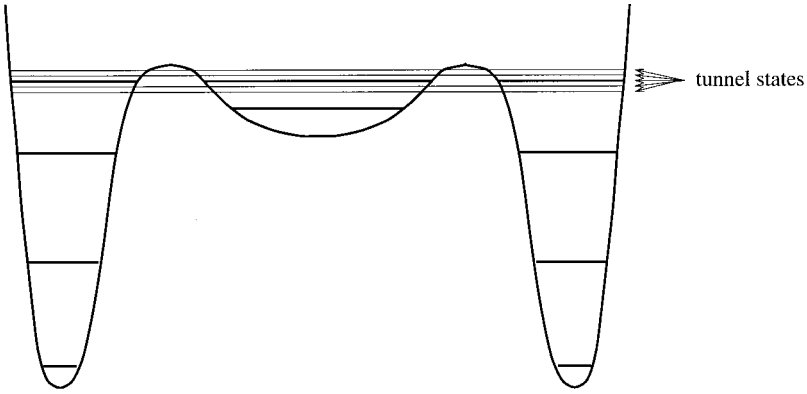

Fig. 6. The schematic form of the adiabatic potential of the cluster with seven Nb impurities. The quasi-resonance between excited vibration off-center and on-center states with a low frequency quasilocal vibration leads to the appearance of excited tunnel states

center extended states which are in the resonance conditions (Fig. 6). The latter gives rise to the well-defined tunnel states with tunnel splitting 2σ of the order of $3 \times 10^{11}\ s^{-1}$ in accordance with estimations.

We have to deal here with two principally different regimes of the co-operative behaviour induced by Nb impurities.

(i) Firstly, it is the situation which appears not very close to the soft TO-mode condensation point, where the corresponding frequency ω_{TO} is subjected to the inequality $\omega_{TO} > 2\sigma$. In this case the bilinear interaction of the polar vibration variable of the central Nb ion of the cluster on the one hand, and the soft TO polarization of the lattice on the other induces the mode-mode repulsion, which results in the softening of the central Nb-ion mode. We shall consider the case of the weak mode-mode interaction, where $2\sigma > |F| \langle Q_{TO}^2 \rangle^{1/2}$ is fulfilled, F being the mode-mode bilinear interaction parameter, $\langle Q_{TO}^2 \rangle^{1/2}$ is the average fluctuation of lattice distortion due to the soft TO mode. The above mentioned limit can take place due to the decrease of the local field factor on the central Nb ion under the conditions of realization of the extended vibration wave function. In this situation there is no resulting condensation of the central Nb ion tunnel mode, but the mode softening can correspond to a transition to the relaxation regime, $2\sigma_{result} < \tau^{-1}$, where τ^{-1} is the tunnel-lattice relaxation rate. That is why here we have to deal with the appearance of new fast relaxators (central Nb ions in clusters effected by the compression field) besides initial slow relaxators (off-center Nb ions in extension field). This case corresponds to the increase of the central peak phenomenon (see, for example, Reference [15]).

(ii) Secondly, it is the situation which rather appears near to the soft TO mode condensation point, where $\omega_{TO} < 2\sigma$. In this case the above mentioned mode-mode repulsion can lead to the condensation of the resulting soft TO mode (which is mixed with a quasilocal tunnel mode of the central Nb ion in the cluster). This is the case of ferroelectric phase transition induced by quasilocal soft cluster modes.

On the other hand, the off-center dipole type degrees of freedom of the extended cluster state obey the relaxation-type kinetics with rather small relaxation rate in comparison with the soft TO-mode frequency. This is the consequence of rather deep off-center potential wells. That is why these relaxation degrees of freedom cannot create renormalization of the soft TO-mode frequency, but can induce an important contribution to the central peak (Ref. [15]) of order parameter fluctuations. This behavior constitutes the phenomenon of the central peak in the frameworks of the considered cluster model. It should be emphasized that this origin of the central peak in doped crystals with soft phonons seems to be rather general.

Let us discuss now the principal effect in the problem considered, i.e. the impurity induced ferroelectric phase transition within the cluster model.

We shall use two assumptions within the real conditions of the physical and computation experiments. Namely, there are the following model assumptions.

(i) The equilibrium potential well of the seven Nb-impurity cluster under consideration is rather deep ($\approx$1500 K) due to lattice relaxation and is higher than the typical growth temperature ($\approx$1000 K). In this situation the non-equilibrium clusters can be realized after appropriate temperature lowering down to RT, and after subsequent temperature lowering down to the temperature of the experiment. As a result the non-equilibrium distribution between single-type Nb impurities, and Nb clusters of different types can appear. For simplicity, we shall consider the non-equilibrium co-existence of

the single-Nb impurities with concentration n, and of the self-organized seven-particle Nb clusters under consideration having the concentration N. The total concentration of Nb impurities N_1 on the sites of Ta ions is equal to $N_1 = n + 7N$ within this model. On the other hand, the concentration (N_0) of Ta ion sites is $N_0 \gg N_1$.

(ii) The energy difference Δ between the compressed equilibrium state (of the seven-particle cluster with slowly vibrating *on-centre* Nb central ion, which is involved in the resonance tunneling discussed above) and of the state with an *off-center* Nb central ion (in this cluster in the extended equilibrium case) is $\Delta > 0$ in accordance with the computer evaluation by the INDO method. But the magnitude of this energy separation is close to the precision of the computation procedure. For the following analysis we can use the noncontradictory assumption that real value of Δ is close to but less than the critical temperature (T_c) of the Nb-induced ferroelectric phase transition, i.e. $\Delta < kT_c$. The latter assumption will give the possibility to obtain an analytical solution of the problem without losing generality.

The Hamiltonian of a system of two interacting modes, i.e the tunnel mode in the excited state of the cluster and the soft TO mode can be presented in the following form:

$$\hat{H} = -2\sigma \sum_i S_i^x - \sum_{i,q} F_{i,q}^{\mathrm{TO}} S_i^z Q_q^{\mathrm{TO}} \exp\left[-iqr_i\right] + \tfrac{1}{2} \sum_q \{P_q^{\mathrm{TO}} P_{-q}^{\mathrm{TO}} + \bar{\omega}_{\mathrm{TO}}^2(q)\, Q_q^{\mathrm{TO}} Q_{-q}^{\mathrm{TO}}\}, \qquad (5)$$

where we had replaced for simplicity the real tunnel multi-level subsystem by a tunnel two level subsystem, S_i^x, S_i^z are corresponding pseudo-spin operators, Q_q^{TO}, P_q^{TO} are the TO-mode displacement and momentum normal coordinates, respectively. The resulting soft branch of the TO mode corresponds to the occupation of the above mentioned tunnel states of the cluster (with activation energy Δ), can be evaluated analogously to Ref. [16] within the random phase approximation and can be expressed in the form

$$\bar{\omega}_-^2(q) = \frac{1}{2}\left\{\bar{\omega}_{\mathrm{TO}}^2(q) + (2\sigma)^2 - \left[(\bar{\omega}_{\mathrm{TO}}^2(q) - (2\sigma)^2)^2 + 2\sigma N\varrho\, |F_q^{\mathrm{TO}}|^2 \tanh\left(\frac{\sigma}{2kT}\right)\right]^{1/2}\right\}. \qquad (6)$$

Here N is the number of the seven-particle self-organized clusters of Nb impurities, ϱ is the population of the tunnel state corresponding to the lattice extension $\varrho = \exp\left[-\Delta/kT\right]/\{2 + \exp\left[-\Delta/kT\right]\} \approx \{[3 - 2(\Delta/kT)]/\}$, where the latter simple expression is valid approximately for $\Delta/kT < 1$. It is seen that the soft mode (6) renormalized by the cluster induced mode-mode interaction has a higher condensation temperature, $\tilde{T}_c > T_c$, than the initial soft TO mode without taking into account the cluster effect. Indeed, this follows from the equation for the new soft TO-mode condensation point $\tilde{T}_c$:

$$8\bar{\omega}_{\mathrm{TO}}^2(\tilde{T}_c,\, T,\, q = 0)\, \sigma^2 = N\varrho(\tilde{T}_c)\, |F_q^{\mathrm{TO}}|^2 \tanh\left(\frac{\sigma}{2k\tilde{T}_c}\right). \qquad (7)$$

The new-soft mode frequency obeys the Cochran-type critical dependence,

$$\bar{\omega}_-^2(q = 0) = \tilde{\lambda}(T - \tilde{T}_c), \qquad (8)$$

where $\tilde{\lambda}$ is a coefficient that can be easily evaluated from the expression (6). Let us take into account the occupation of the low lying excited tunnel cluster state and the corresponding switching effect of the new soft mode (8) directly. The latter leads to the

following expression for the free energy of the crystal:

$$\delta F = N_0 M \bar{\omega}^2_{\mathrm{TO}}(q=0)\ \frac{P^2}{2} + NM\bar{\omega}^2_{-}(q=0)\ \frac{P^2}{2}\ \varrho - \frac{n(ex_0Z)^2\,P^2}{kT} + \frac{\beta}{4}\ P^4\,. \qquad (9)$$

Here $M = mV/(eZ')^2$, where m is the mass coefficent of the soft TO mode, eZ' is the effective charge of this vibration. The first term in expression (9) corresponds to soft TO-mode contribution connected with $KTaO_3$ cells of the sample, while the second one corresponds to the contribution of a new, additionally soft TO mode, connected with the above mentioned effect of Nb-cluster tunnel modes. The third term in the (9) is due to the contribution of the single Nb impurities to the resulting soft mode in the framework of the assumption of rather fast dipole reorientations and of the actual high temperature limit, and the fourth term in (9) is due to the stabilizing effect of the fourth order anharmonicity.

As follows from (8) and the Cochran-type expression for the initial soft mode frequency, the expression (9) can be rewritten in the form

$$N_0 M\lambda(T'_{\mathrm{c}} - T_{\mathrm{c}}) + N\varrho M\tilde{\lambda}(T'_{\mathrm{c}} - \tilde{T}_{\mathrm{c}}) - 2n(ex_0Z)^2\,(kT'_{\mathrm{c}})^{-1} = 0 \qquad (10)$$

in terms of the unknown value of a new critical temperature T'_{c}. Here the population ϱ is a rather smooth function of temperature as discussed above. The latter allows to use the value of this population as $\varrho \approx \varrho(\tilde{T}_{\mathrm{c}})$ solving the equation (10). As a result,

$$T'_{\mathrm{c}} = \frac{\varrho}{2} + \left\{ \left(\frac{\varrho}{2}\right)^2 + \frac{2n(ex_0Z)^2}{k} \right\}^{1/2}, \qquad (11)$$

$$\varrho = \frac{N_0 M\lambda T_{\mathrm{c}} + N\varrho M\tilde{\lambda}\tilde{T}_{\mathrm{c}}}{2}\,. \qquad (12)$$

It is seen that we have to deal with a principally new effect of an increase of the critical temperature due to the tunnel states of the Nb clusters (the second term in the numerator of expression (12)). For instance, this effect leads to the sublinear increase of the critical temperature with increasing Nb-cluster concentration. The latter is in agreement with experiment (see, for example, Ref. [17]) for Nb concentrations outside a threshold concentration, but not very close to the point of the ferroelectric phase transition induced by Nb impurities.

In the model developed here the ferroelectric phase transition induced by impurities is based on the displacive type dynamics. This circumstance is in agreement with the experimental study on $KTaO_3$: Nb.

But the soft dynamics obtained includes in a natural manner the co-existence of the renormalized soft mode of displacive type behaviour with order–disorder effects, and with central peak phenomena. Indeed, as it was underlined above the slowly relaxing order–disorder degrees of freedom of the multi-well ground state multiplet of the Nb clusters under consideration can take part in the formation of the central peak phenomenon. The latter can be an origin of long-living dynamical polar microdomains with a pronounced increase of the signal of the Second Harmonic Generation as well as the dielectric constant of the crystal.

It should be pointed out that the experimental proof of the existence of the central peak phenomena in $KTaO_3$ with Nb impurities was obtained earlier in Ref. [18].

5. Conclusions

The main result of our study is to verify the usefulness of the cluster model for induced ferroelectric transitions in perovskite solid solutions.

In addition to the above mentioned off-center effect within the cluster and the appearance of low frequency excitations, an important confirmation of the cluster model is obtained by INDO ground state energy calculations. The energy lowering induced by the cluster structure due to an outward extension of the six Nb ions and an off-center displacement of the central Nb ion, obtained in the present work ($\sim$0.12 eV), leads to a stability of such self-ordered high symmetry clusters taking into account the peculiarities of the crystal growing procedure (slow cooling from $\sim$1000 K).

A new, displacive type mechanism of the ferroelectric phase transition induced by the second component is developed. This mechanism is based on the existence of the self-organized clusters of the second component with low-frequency excitations of the tunneling type. The latter allows the *tunnel cluster mode – soft TO mode* interaction which induces the ferroelectric phase transition.

The co-existence of the displacive type dynamics discussed above in an incipient ferroelectric and impurities with central peak behaviour is obtained. The central peak effect of order parameter fluctuations of this type can be responsible for the appearance of dynamic polar microdomains. This effect can be investigated experimentally, for instance, by means of the Second Harmonic Generation technique.

On the other hand, the uncommon cluster state structure discovered here leads to the possibility of characteristic IR-absorption by the cluster states which can also serve as an experimental test of the model.

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