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Local configurational instability of Cr^{3+} in PbTiO_3

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Abstract. The ESR spectra of Cr^{3+} impurity in PbTiO_3 single crystals are studied in the 4.2–300 K temperature range. It is shown that Cr^{3+} substitutes for Ti^{4+} with a charge compensation in distant spheres. The axial-symmetry crystal-field parameter b_2^0 is negative and exhibits unusual (for a deep tetragonal phase) temperature behaviour: $|b_2^0|$ increases linearly as the temperature is reduced to $T_0 = 170$ –180 K and then for $T < T_0$ its value strongly decreases. It is shown that the reason for this decreasing is the displacement of Cr^{3+} from the central position in the oxygen cage which is occupied by Cr^{3+} for $T > T_0$. A possible connection of this phenomenon with a small lattice distortion at $T = 170$ –180 K, which was observed earlier, is discussed.

1. Introduction

Lead titanate is a model crystal of the perovskite family, which has been considered as a displacive-type ferroelectric. At $T_c = 763$ K, PbTiO_3 undergoes a first-order transition from a paraelectric cubic to a ferroelectric tetragonal phase. It has been shown [1] that both Pb and Ti host atoms are displaced from their corresponding oxygen planes by 0.047 and 0.030 nm at $T = 300$ K, the ratio of the lattice constants being $c/a = 1.065$. Contrary to the case for BaTiO_3 , the oxygen octahedron is not distorted in PbTiO_3 during this phase transition. A schematic representation of the ferroelectric phase symmetry is shown in figure 1.

The extensive applications of PbTiO_3 ceramics have led to their intensive investigation. As in the case of PbTiO_3 single crystal, these studies are less numerous than one might expect due to the difficulties experienced in fabrication. This makes it difficult to resolve questions concerning the structure and properties of PbTiO_3 , including the strong influence of impurities and lattice defects. Many studies (see [2] and references therein) have been devoted to deciding whether the PbTiO_3 tetragonal phase transforms into other symmetry phases. Some evidence in favour of the existence of a new phase near $T = 170$ K was reported in reference [3] for the first time. Later, precise x-ray measurements of the temperature dependence of the lattice constants [2] led to the conclusion that there is a structural phase transition in PbTiO_3 single crystal at $T \approx 170$ –180 K. At this temperature, a very small reduction in lattice symmetry to an orthorhombic or monoclinic one was observed. The measurements of optical birefringence also support the possibility of a phase transition at $T = 180$ K [4]. However, no definite conclusion can be drawn as yet. Another important problem is that of establishing the local position of the impurity ions. One has

to establish whether they follow the host-lattice-ion displacement in the ferroelectric phase or not. That is why it is important to investigate PbTiO_3 single crystal by the ESR method, which is known to be very sensitive to both small lattice symmetry distortions and ion displacements.

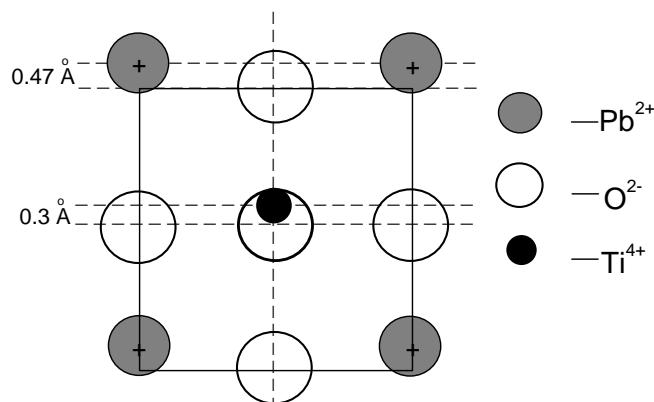


Figure 1. A schematic representation of the ionic displacements in the PbTiO_3 ferroelectric phase.

Previously we have investigated 3d-metal paramagnetic impurities in nominally pure PbTiO_3 single crystal [5]. We focused our attention mainly on the study of the structure of paramagnetic centres and ion displacements at high temperatures ($T > 300$ K). The present work is devoted to a detailed ESR investigation of PbTiO_3 single crystal doped with chromium at low temperatures (4.2–300 K). The small Cr^{3+} ESR linewidth (several gauss) makes it possible for one to study the temperature dependence of the spin-Hamiltonian parameters, i.e. to study crystalline fields, with high accuracy. In particular, an anomaly was observed in the temperature dependence of the tetragonal-symmetry crystalline-field constant b_2^0 for $T < 170$ K. The calculation of $b_2^0(T)$ within the framework of the superposition Newman model shows that the observed anomaly may be the result of spontaneous displacement of Cr^{3+} ions at $T < 170$ K from the centre of the oxygen octahedron. The possible reasons for such behaviour and its connection with the slight lattice distortion are discussed.

2. Experiments

2.1. Experimental procedure

The PbTiO_3 samples were grown by cooling a B_2O_3 – PbO melt containing stoichiometric amounts of PbCO_3 and TiO_2 . The crystals were doped with small amounts of chromium (about 200 ppm). The light-green specimens obtained were in the form of thin ($5 \times 5 \times 0.2$ mm³) plates. They had mainly c -direction domains, with the c -axis perpendicular to the crystal surface. Their domain structure was checked using a polarization microscope. The ESR spectra were recorded in the X-band radio-frequency region over the temperature interval 4.2–300 K. The Oxford Instruments ESR-9 cryosystem was used.

2.2. Experimental results

Since we mainly measured PbTiO_3 single crystals with c -direction domains (the proportion of other domain types was comparatively small, about 20%), all of the ESR spectra had axial symmetry, with the principal magnetic axis along the c -direction.

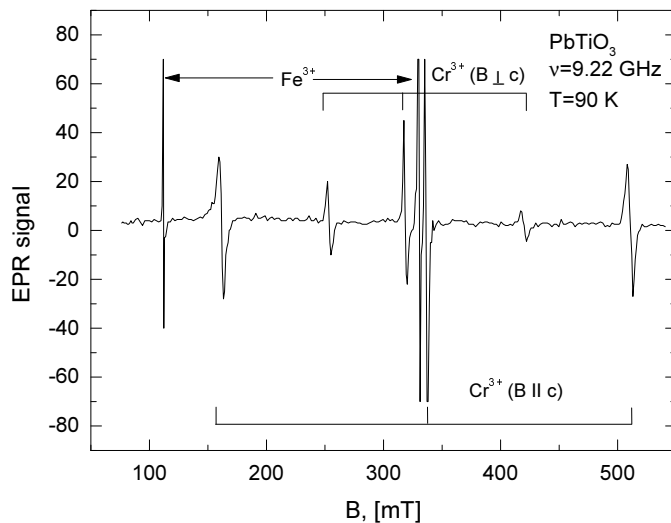


Figure 2. ESR spectra of Cr^{3+} and Fe^{3+} ions in PbTiO_3 .

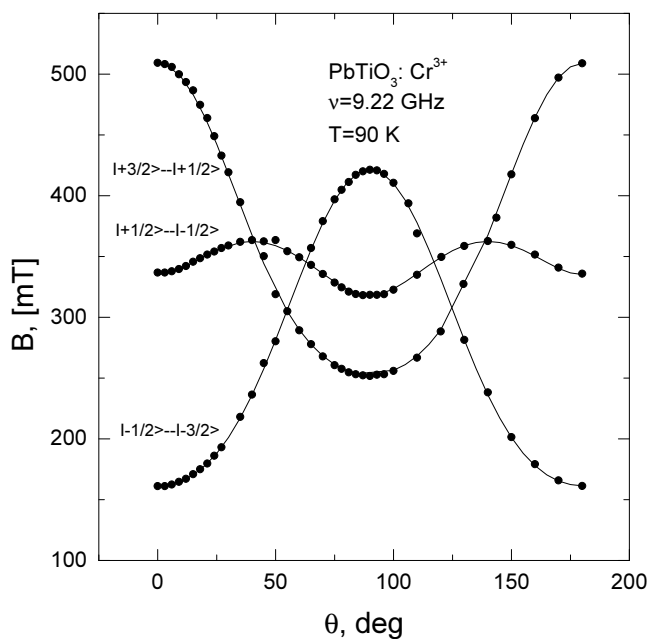


Figure 3. The angular dependence of the Cr^{3+} resonance fields in PbTiO_3 . Symbols denote experimental data, while smooth lines denote calculated results.

At low temperatures we observed the ESR spectrum to consist of two different groups of lines. The spectrum is presented in figure 2. One of the groups of lines is due to Fe^{3+} paramagnetic centres which are present in the crystal as unavoidable impurities. This spectrum, of axial symmetry, is typical for $3d^5$ ions with spin $S = 5/2$ when the external magnetic field is much smaller than the axial-symmetry crystal-field constant ($b_2^0 \gg g\beta B$). The spectrum taken at $T = 20$ K can be described by the following parameters: $g_{\parallel} = 2.000(3)$, $g_{\perp} = 1.998(5)$, $b_2^0 = 1.080(5) \text{ cm}^{-1}$, $b_4^0 = -0.004(1) \text{ cm}^{-1}$, and $b_4^4 = 0.102(1) \text{ cm}^{-1}$. This spectrum was described earlier [5]. Thus, our attention was concentrated mainly on the ESR lines of the second group, due to Cr^{3+} ($S = 3/2$). The angular dependence of the Cr^{3+} line positions is presented in figure 3. It consists of three lines corresponding to three different magnetic transitions of the ion with spin $S = 3/2$. The dependence of the observed ESR line positions on the external magnetic field orientation was fitted using a spin Hamiltonian of axial symmetry with the magnetic axis along the c -direction and $S = 3/2$:

$$\hat{H} = \beta \hat{S} \mathbf{g} \mathbf{B} + b_2^0 \left[\hat{S}_z^2 - \frac{1}{2} S(S+1) \right]. \quad (2.1)$$

The parameters of the spin Hamiltonian (2.1) are the following: $g_{\parallel} = 1.9687(1)$, $g_{\perp} = 1.9700(2)$, and $b_2^0 = -0.0865(1) \text{ cm}^{-1}$ at $T = 90$ K. The well known relation $2b_2^0 = \lambda(g_{\parallel} - g_{\perp})$ [6] (λ is a spin-orbit coupling constant) shows that the constant b_2^0 is negative, because $g_{\parallel} < g_{\perp}$ for all of the temperatures under consideration. The ESR lines were strongly saturated for $T < 15$ K. Thus, it is impossible to determine the sign of the axial constant from the relative intensity change of the fine transition lines at low temperatures. Note that the Cr^{3+} spin-Hamiltonian parameters obtained are close to those of Cr-doped PbTiO_3 ceramic samples at $T = 300$ K [7]: $g = 1.97$ and $|b_2^0| = 0.0875 \text{ cm}^{-1}$.

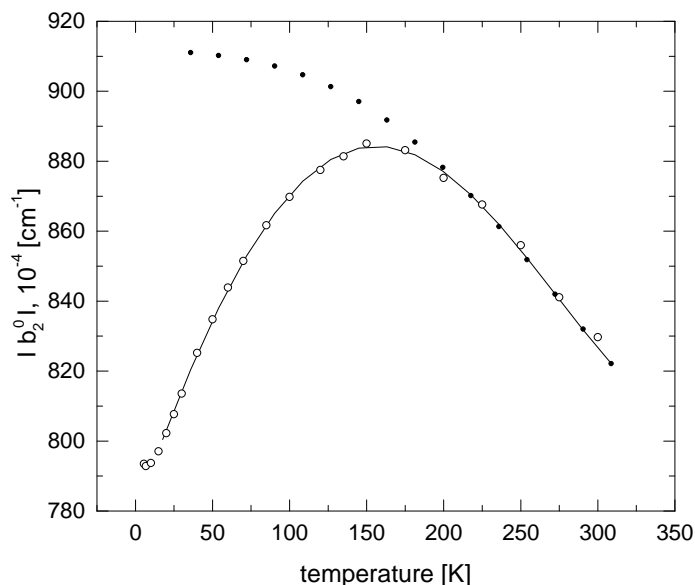


Figure 4. The temperature dependence of $|b_2^0|$ for Cr^{3+} in PbTiO_3 . Open circles: experimental data; solid line and points: calculations with and without Cr^{3+} displacement, respectively.

The temperature dependence of the crystal-field constant b_2^0 is depicted in figure 4. It differs strongly from its expected form for $T \ll T_c$. In fact, in spite of the variations

of the lattice constants being small for $T < 160$ K, the value of $|b_2^0|$ decreases strongly, the decrease being larger than that for higher temperature ($T > 160$ K), where there is significant variation of the lattice constants. Nothing similar was observed for other paramagnetic impurities (such as Fe^{3+} or Mn^{4+} [5]). This favours the supposition that the observed anomalies of b_2^0 may be the consequence of the changes in the local symmetry of the impurity rather than that of host lattice. To clarify this point, one has to know whether or not the impurity follows the displacement of the substituted host-lattice ion for $T < T_c$. Therefore we have to investigate the local position of the Cr^{3+} ions in PbTiO_3 over the entire temperature range.

3. The local position of Cr^{3+} in tetragonal PbTiO_3

The determination of the local position of the impurity in the host lattice is one of the most important problems requiring the ESR investigation of the phase transitions in solids. In fact, only impurities following the displacements of the substituted host ions are able to 'feel' lattice structure variations. The latter depend both on the host lattice and the type of impurity. For example, the paramagnetic ions Fe^{3+} and Cr^{3+} , when substituted for Ti^{4+} in a BaTiO_3 lattice, almost maintain their positions at the centres of the oxygen octahedra in all ferroelectric phases of BaTiO_3 [8]. On the other hand, Mn^{4+} has been shown to follow the Ti^{4+} -ion displacement, while the Fe^{3+} impurity ion maintains its centred position up to liquid helium temperatures in PbTiO_3 [5]. It is obvious that when the impurity-ion and substituted host-lattice-ion charges are not similar, it is important to know what the mechanism of the excessive charge compensation is. This compensation (with the help of extra impurity-ion or lattice-ion vacancies in the nearest neighbourhood of a paramagnetic centre) may result in significant complication of the structure of paramagnetic centres and a reduction in its ability to follow the host-lattice-ion position changes during phase transition.

The Cr^{3+} charge state could substitute for either Pb^{2+} or Ti^{4+} . However, the ionic radius of Cr^{3+} is closer to that of Ti^{4+} ; therefore a B-cation lattice site seems to be more probable. In addition, the observed g -factor values are close to those found for the Cr^{3+} ion in the octahedral environment of other perovskites: for example, SrTiO_3 ($g = 1.978$) [9] and BaTiO_3 ($g = 1.975$) [8]. Consequently, one can conclude that Cr^{3+} substitutes at Ti^{4+} lattice sites. Additional information about the structure of paramagnetic centres can be obtained from analysis of the crystal-field parameter $b_2^0(T)$. Because the magnetic axis of the paramagnetic centre is oriented along the tetragonal crystal axis c , we can assume that the axiality of the Cr^{3+} centre is due only to the crystal tetragonal distortion, and reflects the crystal symmetry. To verify this statement, we have calculated the crystal-field parameters within the framework of the Newman superposition model. The comparison of the experimental crystal-field parameter b_2^0 for a Cr^{3+} paramagnetic probe with that calculated in the Newman model permits us to form a model for the paramagnetic centre (i.e. the local positioning of the impurity ions and the mechanism of the charge compensation).

We have used the superposition Newman model [10] in its truncated form [11]. According to this, the axial constant b_2^0 can be represented in the form

$$b_2^0 = \frac{3}{2} \bar{b}_2(R_0) \sum_i \left(\frac{R_0}{R_i} \right)^{t_2} \left(\cos^2 \theta_i - \frac{1}{3} \right). \quad (3.1)$$

Here, R_0 is the reference point, R_i is the distance between the i th ligand and the paramagnetic ion, and θ_i is the angle between \mathbf{R}_i and the principal ESR axis of the paramagnetic centre. The axial model function $\bar{b}_2(R)$ for PbTiO_3 is not known. However,

on the basis of the similarity of the structures of PbTiO_3 and SrTiO_3 we took $\bar{b}_2(R)$ in the form of Lennard-Jones-type potentials, the parameters of which have been derived from uniaxial-stress experiments for Cr^{3+} ions in SrTiO_3 [12]. It was found that the function $\bar{b}_2(R)$ is given by

$$\bar{b}_2(R) = -A \left(\frac{R_0}{R} \right)^n + B \left(\frac{R_0}{R} \right)^m. \quad (3.2)$$

Here $A = -10.6 \text{ cm}^{-1}$, $B = -8.2 \text{ cm}^{-1}$, $R_0 = 0.1952 \text{ nm}$, $n = 10$, and $m = 13$.

The following calculations were carried out by practically the same method as was used for Cr^{3+} in BaTiO_3 [8]. $\bar{b}_2(R)$ near to the new reference point $R_0 = c/2$ was approximated by a power-law expression: $\bar{b}_2(R_0)(R_0/R)^{t_2}$ (see equation (3.1)). But unlike in the case for BaTiO_3 , where $B - A$ was used for $\bar{b}_2(R_0)$, we have taken the value calculated in accordance with (3.2), with the aforementioned parameters A , B , and R_0 . This appeared necessary because the reference radius $R_0 = c/2$ in PbTiO_3 is larger than that in SrTiO_3 and BaTiO_3 . The transfer of the reference point decreases the accuracy of the b_2^0 -calculation, because the value $B - A$ was obtained with more accuracy than the values of A and B . Nevertheless, it appeared possible to obtain good agreement with experimental data by variation of just one parameter, t_2 , in equation (3.1). Like for BaTiO_3 , the parameter t_2 is positive; its value, $+0.34$, was obtained from the fitting of calculated and measured b_2^0 -values in the temperature region $T > 180 \text{ K}$, where substantial variation of the lattice constants occurs.

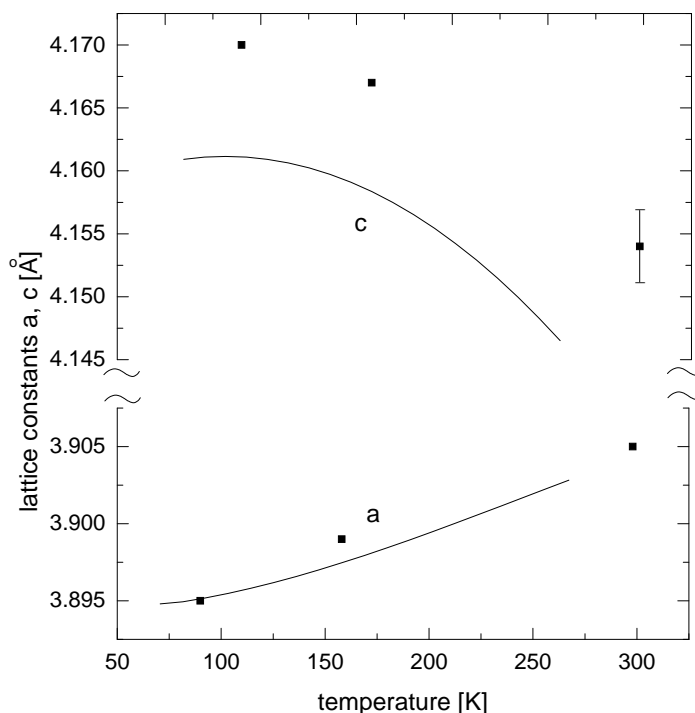


Figure 5. The temperature dependence of the lattice constants a and c for PbTiO_3 . Solid line: data from reference [2]; squares: data from reference [13].

The temperature dependences of the lattice constants a and c were taken from structural data measured accurately in [2] at low temperatures, and these are shown in figure 5. We

depict there also the data from the measurements made in [13], where the lattice constant c is approximately 0.01 \AA larger. The origin of this discrepancy is not clear. However, in our calculations it will lead to only a 2% increase of the b_2^0 -value. The character of its temperature dependence remains the same.

We have calculated the axial-symmetry crystal-field parameter b_2^0 for Cr^{3+} at the Ti^{4+} position, at both centre and off-centre positions in the oxygen cage, as well as with and without an oxygen vacancy in the ion's nearest neighbourhood. For the paramagnetic centre $\text{Cr}^{3+}-\text{V}_\text{O}$ (with the oxygen vacancy V_O as a charge compensator in the sphere nearest to the impurity ion), we have obtained a large (in comparison with the experimental one) negative value of $b_2^0 = -0.21 \text{ cm}^{-1}$. Assuming that the charge compensation takes place in remote spheres, and assuming a centred position of Cr^{3+} in the oxygen cage, we have obtained values of $b_2^0(T)$ very close to the experimental ones for $T > 180 \text{ K}$ (figure 4). In contrast, if the displacement of the Cr^{3+} is equal to that of the Ti^{4+} , the value of $b_2^0 = +0.33 \text{ cm}^{-1}$. This is much larger than the experimental value, and has the opposite sign.

It can be seen from figure 4 that the model with a central position of Cr^{3+} gives a good description of the experimental data only for $T > 180 \text{ K}$. For $T < 180 \text{ K}$ the calculated and measured b_2^0 -values begin to depart from each other. The calculated value slightly increases, while the measured one decreases. X-ray data show that at these low temperatures (at least up to $T = 77 \text{ K}$) there are no major anomalies in the behaviour of the lattice constants. The slight rhombicity, observed in [2] at $T \approx 180 \text{ K}$, cannot change the b_2^0 -value significantly. Therefore we come to the conclusion that the only reason for the unusual behaviour of $b_2^0(T)$ is the displacement of Cr^{3+} along the c -axis from the centre of the oxygen octahedron, which starts to occur at $T \approx 180 \text{ K}$. Another possible model is based on the displacement of oxygen ions along the c -axis. It is impossible to decide between these two models on the basis of ESR data. However, oxygen-ion displacement seems to be less probable, because it leads to substantial lattice perturbations.

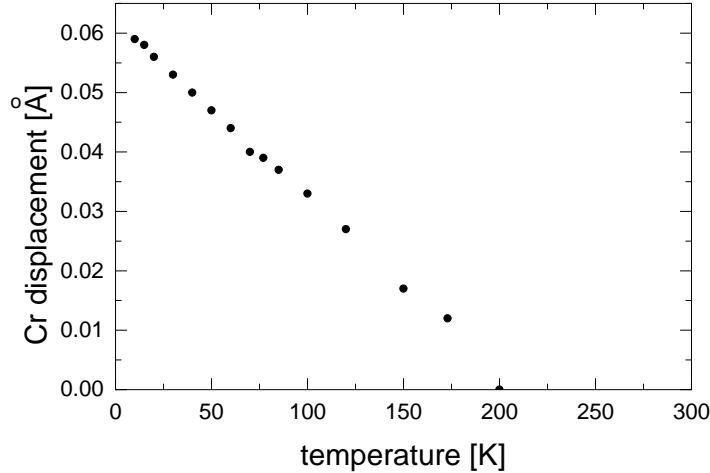


Figure 6. The temperature dependence of the displacement of Cr^{3+} in PbTiO_3 .

Introducing a temperature-dependent displacement of Cr^{3+} relative to the oxygen cage centre, we have fitted the experimental data for b_2^0 for all temperatures fairly well. The calculated Cr^{3+} displacement (d_{Cr}) is presented in figure 6. It is seen that the displacement of Cr^{3+} is about 0.06 \AA at $T = 10 \text{ K}$. Thus, it is approximately equal to the difference

between the ionic radii of Ti^{4+} and Cr^{3+} ($R_{\text{Ti}^{4+}} - R_{\text{Cr}^{3+}} \approx 0.05 \text{ \AA}$).

Note that the temperature dependence of b_2^0 , observed earlier for Cr^{3+} in BaTiO_3 [8], where the impurity also maintains its central position in the tetragonal phase, looks like that of Cr^{3+} in PbTiO_3 . To explain this dependence, the authors of [8] considered two contributions to b_2^0 ; the first one is proportional to the square of the polarization and the second one is linear in T . The existence of the latter contribution is evidence of large thermal fluctuations of the Cr^{3+} ions; their contribution is described by the spin-phonon interaction, assuming a Debye phonon spectrum. An attempt to describe our experimental data in the same way failed. The main reason for this is the following. Spin-phonon interaction has to lead to a temperature-independent b_2^0 -value in the quantum region $T < (0.2-0.3)T_D$ (T_D is the Debye temperature). This behaviour was actually observed for BaTiO_3 for $T < 60 \text{ K}$ [8]; however, there is nothing of this kind for PbTiO_3 (see figure 4).

4. Discussion and conclusions

Spontaneous displacement of impurity at some temperature T_0 is usually called a local phase transition or a local configurational instability. A mechanism for the local phase transition was proposed in [14] and [15]. The experimental manifestation of this transition has been observed for several ionic crystals with cubic symmetry: $\text{KCl}:\text{Mn}^{1+}$ [16], $\text{SrF}_2:\text{Mn}^{1+}$ [17], and $\text{BaF}_2:\text{Mn}^{2+}$ [18]. These impurities become off-centre ones for $T < T_0$, with transformation of their potential from a single-well to a multi-well one. The high symmetry of the cubic lattice was shown to play an important role in the explanation of these phenomena [15]. From this point of view it is worth emphasizing that we observed a Cr^{3+} local phase transition in the tetragonal ferroelectric phase of PbTiO_3 with two possible orientations of the spontaneous polarization along the $\pm c$ -axes. In this ferroelectric phase, the Ti^{4+} ion is known to be shifted relatively to the oxygen cage centre, the value of this shift being 0.3 \AA (see figure 1). Meanwhile, a Cr^{3+} impurity ion substituting for Ti^{4+} maintains its centred position at least at high temperatures. As the temperature is reduced, the displacement of the Cr^{3+} from its central position for $T < 180 \text{ K}$ may be the result of the interaction of the ion with lattice phonons, i.e. the formation of the local configurational instability may be connected with lattice phonon instability. This conclusion follows from the coincidence of T_0 with small temperature anomalies of the birefringence [4], thermal strains, and lattice constants [2]. Slight changes of the crystal structure at $T = 170-180 \text{ K}$ can lead to an increase of the sensitivity of the lattice to any lattice perturbation. On the other hand, this may result in local potential deformation by the impurity, and, thus, in a local phase transition. Several theoretical investigations have been devoted to the problem of changes in the defect structure near the temperatures at which the lattice instabilities occur (see, e.g., [19]). The results of the present investigation provide direct evidence of the appearance of configurational local instability even in the low-symmetry environments of the impurities.

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