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On Critical Dipole Interaction in Displacive-Type Ferroelectrics

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The $SrTiO_3$ crystal shows structural phase transition accompanied by the rotation of oxygen octahedra, which is in marked contrast to the displacive-type ferroelectrics such as $BaTiO_3$.[1] In this article the mechanism why the phase transition is ferroelectric in some case and structural in other case for the perovskite-type crystals is studied. The potential due to short range interaction acting on the Ox and Oy ions for the shifts in the direction of y and x axes respectively can be expressed as

$$U' = U_{\text{overlap}} + U_{\text{waals}},$$

where

$$\begin{aligned} U_{\text{overlap}} = {} & 2\lambda_{\text{OT}} l^{-s}\{3 - s(x^2+y^2)/(2l^2) + s(s+2)(x^4+y^4)/(8l^4)\} + 2\lambda_{\text{OO}}(\sqrt{2}l)^{-s} \\ & \times \{6 + s(s-2)(x^2+y^2)/(4l^2) - s(s+2)xy/(2l^2) + s^2(s^2-4)(x^4+y^4)/(192l^4) \\ & + s(s+2)(s^2+6s+12)x^2y^2/(32l^4) - s^2(s+2)(s+4)xy(x^2+y^2)/(48l^4)\} \\ & + 2\lambda_{\text{AO}}(\sqrt{2}l)^{-s}\{6 + s^2(x^2+y^2)/(4l^2) + s(s+2)(s^2-2s-12)(x^4+y^4)(192l^4)\} \\ & + \lambda_{\text{OO}}(2l)^{-s}\{9 + s(s-1)(x^2+y^2)/(2l^2) + s(s+2)(s^2+4s+9)(x^4+y^4)/(24l^4)\}, \end{aligned} \quad (1)$$

and for U_{waals} the quite similar equation can be obtained. Now it must be noted that the difference between the force constant for the Ba and Sr ions is considerable, namely, the value of λ_{AO} is 99.0×10^{-82} (A = Ba) and 55.6×10^{-82} (A = Sr), and also μ_{AO} is 162.0×10^{-62} (A = Ba) and 98.5×10^{-62} (A = Sr).[2] Rewriting $U_{\text{overlap}} + U_{\text{waals}}$ as

$$a(x^2+y^2) + a'xy + b(x^4+y^4) + b'x^2y^2 + b''xy(x^2+y^2), \quad (2)$$

and putting $x = y = u$, we find that the coefficient $2b + b' + 2b''$ of a u^4-term is positive while the coefficient $2a + a'$ of a u^2-term is negative. Assuming for the half lattice constant $l = 2$Å, we obtain the values -0.495×10^5 for $BaTiO_3$ and -1.142×10^5 for $SrTiO_3$, which mean the short range interaction are favorable to the shift of the O-ions in accordance with the previous report.[3] On the other hand the long range dipole interaction can be expressed as

$$U'' = cu^2 = \gamma(ne)^2u^2, \quad (3)$$

where n means the effective charge of the oxygen ions, and γ is the factor

$$(1/2)(q-p-s)\{(2l)^3 - s\alpha_0\}^{-1}, \quad (4)$$

where $q = 30.082$, $p = 8.668$, $s = 14.456$ and $\alpha_0 = 2.75 \times 10^{-24}$ cm^3. Since in the region above the structural transition point, the long range term eq. (3) (positive) overwhelms the term of u^2 in eq. (2). Then the coefficient of u^2 in the total potential $U = U' + U''$, namely, $2a + a' + c$ is positive, so the spontaneous shift is impossible. At the critical point the value of $2a + a' + c$ becomes zero, and then for the lower temperatures it becomes negative, resulting in the spontaneuos shift of the oxygen ions due to the decrease of the lattice constant and somewhat due to the change of the electronic state.[4] It may be concluded that in $SrTiO_3$ the oxygen rotational shift is much easier than in $BaTiO_3$, because the absolute value of the coefficient of u^2 in short range force for $SrTiO_3$ is about 2.3 times larger than for $BaTiO_3$. On the other hand in $BaTiO_3$ the Ti shift is much easier than in $SrTiO_3$, because the distance between Ti and oxygen ions is larger in the former than in the latter, resulting in the decrease of the short range repulsion, and then the ferroelectric phase transition can be brought about.[5]

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