сообщения
объединенного
института
ядерных
исследований
дубна

E17-83-624

A.Podolska-Strycharska

ON THE THEORY OF STRUCTURAL PHASE TRANSITIONS IN $RbCaF_3$

1983

1. INTRODUCTION

Transitions caused by condensation of zone boundary modes associated with rotation of BX_6 octahedra occur in a number of perovskites ABX_3. It is well established that these phase transitions are caused by the condensation of one or two normal modes and these transform like irreducible representations R_{25} and M_3. These both modes represent the rotational vibrations of BX_6 octahedra around cubic principal axes. The difference between R_{25} and M_3 is that the R_{25} represents the opposite rotation of the neighbouring BX_6 octahedra along the rotation axis, whereas the M_3 represents the rotations in the same direction.

One can find examples of these transitions in refs.[1,2]. Neutron and X-ray structure determinations[3] have shown, that for the phases which have two or more octahedral rotations the static displacements of the ions cannot be accounted for by the linear superposition of R- and M-type rotational modes alone. It was suggested in[1] that for phases in which these modes have condensed, static displacements associated with the normal mode of X-type are also present.

A structural phase transition in the perovskite ABX_3 caused by the condensation of the parallel components of the R- and M-modes with taking into account the displacements of A-ions corresponding to X-mode has been considered in ref.[4].

The purpose of the present paper is to analyze the structural phase transitions in ABX_3 corresponding to the condensation of nonparallel components of R- and M-modes. Such a transition is encountered in $RbCaF_3$, for example.

2. SYMMETRY ANALYSIS

The atomic displacements corresponding to R_{25} and M_3 modes can be described by three-dimensional irreducible representation τ_8 (through this paper, the irreducible representations will be labelled in accordance with[5]) of the one-component star $\{\vec{k}_{13}\}$ (the R-point of the Brillouin zone, $\vec{k}_R = (\pi/a)(1,1,1)$) and by the one-dimensional irreducible representation τ_5 of the three-component star $\{\vec{k}_{11}\}$ (the M-point of the Brillouin zone, $\vec{k}_{1M} = (\pi/a)(0,1,1)$, $\vec{k}_{2M} = (\pi/a)(1,0,1)$, $\vec{k}_{3M} = (\pi/a)(1,1,0)$).

As is shown in paper [1], for phases in which R- and M-modes have condensed, static displacements of A-ions associated with a normal mode with wave vector of the X-point are also present.

In phases, in which the parallel components of the R- and M-modes have condensed ($r_\alpha \neq 0$, $m_\alpha \neq 0$, $\alpha = 1,2,3$), the displacements of A-ions along the axis α take place and they transform like the one-dimensional irreducible representation τ_4 of the three-component star $\{k_{10}\}$ (the X-point of the Brillouin zone $\vec{k}_{1X} = (\pi/a)\ (1,0,0)$, $\vec{k}_{2X} = (\pi/a)\ (0,1,0)$, $\vec{k}_{3X} = (\pi/a)(0,0,1)$).

However, if the nonparallel components of R and M condense ($r_\alpha \neq 0$, $m_\beta \neq 0$, $\alpha \neq \beta$), then the A-ions are displaced along the axis of the R-type rotation, and these displacements transform like the two-dimensional irreducible representation τ_{10} of the star $\{k_{10}\}$. In this case the displacements of X-ions accompanied by the displacements of A-ions under the structural phase transitions may be described by 12-component order parameter:

$$p = \{(r_1, r_2, r_3),\ (m_1, m_2, m_3),\ (X_1^y, X_1^z, X_2^z, X_2^x, X_3^x, X_3^y)\}.$$

Following Landau's phenomenological theory of the second order phase transition, we expand the free energy of the system in terms of (r_1, r_2, r_3), (m_1, m_2, m_3), $(X_1^y, X_1^z, X_2^z, X_2^x, X_3^x, X_3^y)$ up to the fourth order

$$\begin{aligned} F = F_0 &+ \alpha_1 \sum_{i=1}^{3} r_i^2 + \beta_1 \sum_{i=1}^{3} r_i^4 + \gamma_1 \sum_{i \neq j} r_i^2 r_j^2 + \\ &+ \alpha_2 \sum_{i=1}^{3} m_i^2 + \beta_2 \sum_{i=1}^{3} m_i^4 + \gamma_2 \sum_{i \neq j} m_i^2 m_j^2 + \\ &+ A_1 \Big(\sum_{i=1}^{3} r_i^2\Big)\Big(\sum_{i=1}^{3} m_i^2\Big) + A_2 \sum_{i=1}^{3} r_i^2 m_i^2 + \\ &+ \alpha_3 \sum_{i \neq j} (X_i^j)^2 + \delta \sum_{i \neq j} r_j m_i X_i^j . \end{aligned} \qquad (1)$$

Each term is constructed so that cubic symmetry operations leave it invariant. It is assumed that only temperature dependent coefficients are α_1, α_2 and

$$\alpha_1 = \alpha_1^\circ (T - T_R^\circ), \quad \alpha_2 = \alpha_2^\circ (T - T_M^\circ),$$

where T_R°, T_M° are, respectively, the critical temperatures of (r_1, r_2, r_3) and (m_1, m_2, m_3) separately.

The expression (1) differs from the one used to describe the system in which the condensation of R_{25} and M_3 modes takes place through the inclusion of terms in X_i^j.

The equilibrium state at an arbitrary temperature should be determined by the minimization of F with respect to r_i, m_i and X_i^j, in particular

$$\frac{\delta F}{\delta X_i^j} = 2\alpha_3 X_i^j + \delta r_j m_i ; \quad X_i^j = -\frac{\delta}{2\alpha_3} r_j m_i . \qquad (2)$$

So, one can see that a particular set of non-zero components of R- and M-modes determines which of various X_i^j have non-zero values.

3. PHENOMENOLOGY OF $RbCaF_3$

The expression (1) for the free energy will be now applied to $RbCaF_3$.

Experimental work up to date indicates that it undergoes a series of structural phase transitions: the 193K transition (O_h^1 to D_{4h}^{18}) induced by the condensation of one of the components of the triply degenerated R_{25} mode [6] and the 50K transition (D_{4h}^{18} to D_{2h}^{16}) induced by the condensation of M_3 mode [7]. In the phase below 50K the rubidium displacements along |101| are observed [8].

According to Glazer's notation [9] the successive phases correspond to the following sequence of tilts:

$$\underset{D_{2h}^{16}}{a^- a^+ a^-} \quad \overset{50K}{\rightleftarrows} \quad \underset{D_{4h}^{18}}{a^\circ a^\circ c^-} \quad \overset{193K}{\rightleftarrows} \quad \underset{O_h^1}{a^\circ a^\circ a^\circ} .$$

The solution of (1) corresponding to the above tilt system is

$$r_1^2 = r_3^2 = \frac{-2\beta_2 \alpha_1 + \tilde{A}_1 \alpha_2}{2\beta_2 (2\beta_1 + \gamma_1) - 2\tilde{A}_1^2}, \qquad (3a)$$

$$m_2^2 = \frac{-\alpha_2 (2\beta_1 + \gamma_1) + 2\tilde{A}_1 \alpha_1}{2\beta_2 (2\beta_1 + \gamma_1) - 2\tilde{A}_1^2}, \qquad (3b)$$

$$X_2^z = -\frac{\delta}{2\alpha_3} r_3 m_2 , \qquad (3c)$$

$$X_2^x = -\frac{\delta}{2\alpha_3} r_1 m_2 , \qquad (3d)$$

where $\tilde{A}_1 = A_1 - \frac{\delta^2}{4a_3} \equiv A_1 - \delta'$. The stability of this phase requires

$$(4\beta_2 m_2^2 + 2\delta' r_1^2)[(4\beta_1 + 2\gamma_1) r_1^2 + \delta' m_2^2] - 4\tilde{A}_1^2 r_1^2 m_2^2 > 0 , \qquad (4a)$$

$$a_3 > 0 , \qquad (4b)$$

$$(4\beta_1 - 2\gamma_1) r_1^2 + \delta' m_2^2 > 0 . \qquad (4c)$$

Under the assumption that the structural phase transitions in $RbCaF_3$ are well described by the dynamic model/10/, we are led to:

$$\beta_1 = \beta_2 , \quad \gamma_1 = \gamma_2 ; \qquad A_1 = \gamma_1 , \quad A_2 = 6\beta_1 - \gamma_1 . \qquad (5)$$

If we furthermore take into account that $r_1^2 = m_2^2$, we can rewrite the inequality (4a) in the form

$$-(\delta')^2 + 6(\beta_1 + \gamma_1)\delta' + 2(4\beta_1^2 + 2\beta_1\gamma_1 - \gamma_1^2) > 0 . \qquad (6)$$

It yields together with inequality (4c) the following condition for the coupling constant δ':

$$2(\gamma_1 - 2\beta_1) < \delta' < 3(\beta_1 + \gamma_1) + w , \qquad (7)$$

where $w = (17\beta_1^2 + 22\beta_1\gamma_1 + 7\gamma_1^2)^{1/2}$.

It should be here noted that by considering only the R- and M-modes in the expression (1), the following stability conditions for the phase ($r_1 = r_3 \neq 0$, $m_2 \neq 0$) are readily obtained

$$\beta_1 > 0 , \qquad (8a)$$

$$4\beta_1^2 - \gamma_1^2 > 0 . \qquad (8b)$$

If the phase ($r_3 \neq 0$) is the previous to the phase mentioned above, the following condition should be satisfied additionally

$$2\beta_1 < \gamma_1 . \qquad (9)$$

One can see that the set of inequalities (8a)-(8b) is inconsistent with the inequality (9).

To the light of these results it is seen that the displacements of Rb-ions corresponding to X-mode play an important role in stabilization of the observed phases.

Comparing the free energies of the neighbouring $(a^\circ a^\circ c^-)$ and $(a^- a^+ a^-)$phases, we obtain the following expression for the critical temperature:

$$T_M = \frac{2aT_R^\circ + 2bT_M^\circ - c(T_R^\circ + T_M^\circ) - (T_R^\circ - T_M^\circ)\sqrt{c^2 - 4ab}}{2(a + b - c)} , \qquad (10)$$

where

$$a = [\beta_1(2\beta_1 - \gamma_1) - \tilde{A}_1^2](a_1^\circ)^2 ,$$

$$b = \beta_1(2\beta_1 + \gamma_1)(a_2^\circ)^2 ,$$

$$c = 4\tilde{A}_1 \beta_1 a_1^\circ a_2^\circ .$$

It is easy to check that at $T = T_M$ the squares of the order parameters r_1^2, m_2^2 are nonvanishing, hence this transition is of the first order.

ACKNOWLEDGEMENTS

I would like to thank prof. N.M.Plakida who has contributed greatly to the content of this paper through valuable discussions.

REFERENCES

1. Darlington C.N.W. phys.stat.sol. (b), 1976, 76, p. 231.
2. Fuji Y. et al. Phys.Rev.B, 1974, p. 4549.
3. Ahtee M., Glazer A.M., Megaw H.D. Phil.Mag., 1972, 26,p. 995.
4. Plakida N.M., Podolska-Strycharska A., Sikora W. Kristallogr., 1983, 28, No. 5.
5. Kovalev O.V. Irreducible Representations of the Space Groups (Academy of Sciences of the Ukrainian SSR, Kiev, 1961). English transl: Gordon and Breach Science Publishers, New York 1964.
6. Modine F.A. et al. Phys.Rev.B, 1974, 10, p. 1623.
   Ridou C. et al. Ferroelectrics (EMF Zurich) 1975.
7. Ho J., Unruh W.P. Phys.Rev.B, 1976, 13, p. 447.
8. Ridou C., Rousseau M. Ferroelectrics, 1981, 36, p. 463.
   Bulou C. et al. J.Physique, 1981, 41, p. 87.
9. Glazer A.M. Acta Crystallogr. A, 1975, 31, p. 756.
10. Konwent H., Plakida N.M. JINR, P17-82-219, P17-82-220, P17-82-438, Dubna, 1982.

Received by Publishing Department
on August 31, 1983.

Подольска-Стрыхарска А. E17-83-624

К теории структурных фазовых переходов в $RbCaF_3$

Рассматриваются структурные фазовые переходы в перовските $RbCaF_3$, индуцированные мягкими модами R_{25} и M_3. На основе симметрийного анализа получено разложение свободной энергии с учетом сопутствующих переходу $D_{4h}^{18} \to D_{2h}^{16}$ смещений ионов Rb. При анализе условия стабильности фаз, показано, что одновременная конденсация мод R_{25} и M_3 возможна лишь при определенной величине константы связи ионов Rb с решеткой.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1983

Podolska-Strycharska A. E17-83-624

On the Theory of Structural Phase Transitions in $RbCaF_3$

Structural phase transitions in prevoskite $RbCaF_3$ induced by the soft modes R_{25} and M_3 are considered. On the basis of the symmetry analysis a free energy expansion is obtained, where displacements of Rb ions are taken into account. By analyzing the stability conditions, it was shown that soft modes R_{25} and M_3 may condensate simultaneously only for a definite value of Rb-ion coupling with the lattice.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1983