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Second-Order Phase Transitions in Magnetic $Ca_3Al_2(SiO_4)(O_h^{10})$ and Non Magnetic Cubic ZnO

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Possible symmetry of modes those may cause transitions in magnetic and non magnetic crystals as well as lower space subgroup symmetries of the crystals have been found. The Landau-Lifshitz theory for non magnetic crystals has been reformulated for magnetic crystals and has been applied to $Ca_3Al_2(SiO_4)(O_h^{10})$. Some experimental data confirm our results.

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1. Introduction

A crystal can undergo several phases from higher to lower, and from lower to higher symmetries when temperature or pressure alters. Under sufficient high pressure wurtzite ZnO and GaN can be transformed to higher cubic symmetry structure [1]. This kind of transitions are of the first order. When temperature changes and reaches Curie temperature, the density of state changes continuously and the crystal experiences the second-order phase transition (S.O.Ph.Tr) [2].

The group of the crystal after transition is a subgroup of initial symmetry G_0 (active irreducible representations of O_h^5 group of rocksalt crystals are $\Gamma_{1-}, \Gamma_{2\pm}, \Gamma_{3-}, \Gamma_{4\pm}, \Gamma_{5-}$ ${}^*L_{1\pm,2\pm,3\pm}$ ${}^*X_{1-,2\pm,3\pm,4-,5-}$ ${}^*W_{1,2,3,4}$). The Landau-Lifshitz (L–L) [3] theory provides possible subgroups after transition and phonon symmetries [(active irreducible representaions (irreps) of G_0]. The theory is well established and can be found in many text books [4].

In magnetic crystals the states are classified according to irreducible corepresentations (coreps) [5].

Therefore, the phase transitions in these crystals are supposed to be analysed in terms of active coreps of phonons. Consequently the L–L theory for non magnetic crystals must be reformulated to magnetic compounds. The L–L criteria have been re-written for magnetic compounds by Cracknell [4]. However the modified L–L criteria has never been applied to any magnetic phase transitions.

Generally, the description of transitions in terms of ordinary L–L theory was applied to magnetic media. The question is whether such approach by irreps instead of coreps is adequate or not.

Here we investigate transitions in magnetic calcium aluminium thosilicate in terms of our modified L–L theory using corep methods , as well as traditional irrep theory. By comparison of results of two different methods we are able to show that the corep method yields much richer phonon properties.

The reason we considered ZnO cubic is to see whether S.O.Ph.Tr can bring it to hexagonal structure from which cubic ZnO originates.

2. Structural transitions in cubic non magnetic ZnO and GaN of O_h^5 symmetry

The main aim of L–L theory is to find the exact symmetries of active phonons (active irreps or coreps) those cause transitions and bring a crystal to a certain space subgroup. Apart from L–L approach we have used our computerized method for finding all possible space subgroups of the initial space groups O_h^5 and O_h^{10} listed in Tables I and II.

From L–L method we have found particular subgroups obtained for particular symmetry of phonons of $ZnO(O_h^5)$ (see Table III). For example, considering phonon of Γ_{3+} symmetry we note that only symmetry operators 1–4, 13–16, 25–28, 37–40 (see Table IV), together with matrices E and B do not change the basis φ_4 and φ_5.

Therefore the set of these operators form the subgroups of O_h^5: D_{4h}^1, D_{4h}^{17} and C_{4v}^9 also listed in Table I, obtained by other method.

3. Second-order phase transitions in magnetic crystal $Ca_3Al_2(SiO_4)$ of $Ia'3d$ and non magnetic crystals of O_h^{10} symmetry

In magnetic crystals vibrating atoms or ions are carrying appreciable magnetic moment and modes are classified according to irreducible corepresentations of their magnetic group.

The modified L–L criteria for phase changes are: (1)the magnetic space group M must be a subgroup of $M_0(Ia'3d)$ which is the initial group, (2) symmetrized cube of corep $[CD]_3$ must not contain identity corep CD_1, (3)the antisymmetrized square $\{CD\}_2$ must not contain the corep to which a polar vector belongs.

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TABLE I

Space subgroups of space factor G^k/T, (O_h^5/T, Fm3m,225): Symmetry operators

Initial space group		Symmetry operators			
O_h^5.Fm3m.**225**		1–12	13–24	25–36	37–48
	Subgroups				
Cubic.I	T_d^3.I$\bar{4}$3m.**217**	1–12			37–48
	O^5.I432.**211**	1–12	13–24		
	T_h^5.Im3.**204**	1–12		25–36	
	T^3.I23.**197**	1–12			
Cubic.F	T_d^2.F$\bar{4}$3m.**216**	1–12			37–48
	O^3.F432.**209**	1–12	13–24		
	T_h^3,Fm3.**202**	1–12		25–36	
	T^2.F23.**196**	1–12			
Cubic.P	O^1.P432.**207**	1–12	13–24		
	T_h^1.Pm3.**200**	1–12		25–36	
	T^1.P23.**195**	1–12			
	T_d^1.P43m.**215**	1–12			37–48
Tetragonal.I	D_{4h}^{17}.I4/mmm.**139**	1–4	13–16	25–28	37–40
	D_{2d}^{11}.I$\bar{4}$2m.**121**	1–4			37–40
	D_{2d}^{9}.I$\bar{4}$m2.**119**	1–4			37–40
	C_{4v}^{9}.I4mm.**102**	1–4	13–16	25–28	37–40
	C_{4h}^{5}.I4/m.**87**	1,4	14,15	25,28	38,39
	S_4^4.I4.**82**	1,4	14,15		
	C_4^5.I4.**79**	1,4	14,15		
Tetragonal.P	D_{4h}^{1}.P$\bar{4}$mmm.**123**	1–4	13–16	25–28	37–40
	D_{2d}^{1}.P$\bar{4}$2m.**111**	1–4			37–40
	C_{4v}^{1}P4mm.**99**	1,4	14,15	26,27	37,40
	D_4^1.P422.**89**	1–4	13–16		
	C_{4h}^{1}.P4/m.**83**	1,4	14,15	25,28	38,39
Orthorhombic.P	D_{2h}^{1}.Pmmm.**47**	1–4		25–28	
	C_{2v}^{1}.Pmm2.**25**	1,4		26,27	
Orthorhombic.F	C_{2v}^{1}8.Fmm2.**42**	1,4		26,27	
Orthorhombic.C	D_{2h}^{19}.Cmmm.**65**	1–4		25–28	
	C_{2v}^{14}.C2mm.**38**	1,4		26,27	
	C_{2v}^{11}.Cmm2.**35**	1,4		26,27	
	D_{2h}^{25}.Immm.**71**	1–4		25–28	
	D_{2h}^{23}.Fmmm.**69**	1–4	25–28		
	C_{2v}^{2}0.Imm2.**44**	1,4		26,27	
Monoclinic	D_2^8.I222.**23**	1–4			
	D_2^6.C222.**21**	1–4			
	C_{2h}^{3}.C2/m.**13**	1,4		25,28	
	C_{2h}^{1}.P2/m.**10**	1,4		25,28	
	C_2^1.P2.**3**	1,4			
	C_s^3.Cm.**8**	1		28	

TABLE II

Space subgroups of space factor G^k/T, (O_h^{10}/T, Ia3d,230): Symmetry operators

Initial space group	Symmetry operators			
O_h^{10}.Ia3d.**230**	1–12.1	13.4–24.5	25–36.1	37.4–48.5
Subgroups				
T_d^6. (I43d.**220**)	1–12.1			37.4–48.5
T_h^7.(Ia3.**206**)	1–12.1		25–36.1	
T^5.($I2_13$.**204**)	1–12		25–36.1	
T^3.(I23.**199**)	1–12.1			
D_{2h}^{17}.(Cmcm.**63**)	1–4.1		25–28.1	
O^8.($I4_132$.**214**)	1–12.1	13.4–24.5		
D_2^9.($I2_12_12_1$.**24**)	1–4.1			

TABLE III

Soft modes of r-ZnO and r-GaN involved in lowering symmetry

$O_h^5 \xrightarrow{\Gamma}_{1-}$ O^1, O^3, O^5; $O_h^5 \xrightarrow{\Gamma}_{2-}$ T_d^1, T_d^2, T_d^3

$O_h^5 \xrightarrow{\Gamma}_{2+}$ T_h^1, T_h^2, T_h^3; $O_h^5 \xrightarrow{\Gamma}_{3+}$ D_{4h}^1, D_{4h}^{17}, C_{4v}^9

$O_h^5 \xrightarrow{\Gamma}_{3-}$ D_{2d}^1, D_{2d}^9, D_{2d}^{11}

TABLE IV

Irreps of Γ point

	1–12	13–24	25–36	37–48
$\Gamma_{1-}(\varphi_1)$	+1	+1	−1	−1
$\Gamma_{2+}(\varphi_2)$	+1	−1	+1	−1
$\Gamma_{2-}(\varphi_3)$	+1	−1	−1	+1

	1–4	5–8	9–12	13–16	17–20	21–24	25–28	29–32	33–36	37–40	41–44	45–48
$\Gamma_{3+}(\varphi_4,\varphi_5)$	E	A	A*	B	C	C*	E	A	A*	B	C	C*
$\Gamma_{3-}(\varphi_6,\varphi_7)$	E	A	A*	–B	–C	–C*	–E	–A	–A*	B	C	C*

where $E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ $A = \begin{pmatrix} w^* & 0 \\ 0 & w \end{pmatrix}$

$B = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $C = \begin{pmatrix} 0 & w^* \\ w & 0 \end{pmatrix}$

The coreps involved in transitions of magnetic group $Ia'3d$ originating from irreps of O_h^{10} symmetry have been calculated (see Table V). In order to determine the phase transitions, we calculated the coreps using Wigner [5] and Bradley-Davies [6] theories. We listed them in Table V.

Consequently, using Luybarskii [7] and our method we have found particular active coreps of phonons which bring the crystals to lower magnetic symmetries listed in Table VI.

Applying the traditional L–L theory in terms of irreps to magnetic crystals $Ca_3Al_2(SiO_4)(O_h^{10})$, we have found certain irreps (symmetries of phonons) which bring the crystals to lower symmetries (see Table III).

4. Discussion

Concerning transitions in non magnetic cubic ZnO, we

TABLE V

Corepresentation $C\Gamma_3$ of O_h^{10} magnetic.

	1–4.1	5–8.1	9–12.5	37–40.1	41–44.1	45–48.1
$C\Gamma_{1-}$	+1	+1	+1	–1	–1	–1
$C\Gamma_{2-}$	+1	+1	+1	–1	–1	–1
$C\Gamma_{3-}$(c)	$\begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix}$	$\begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix}$	$\begin{pmatrix} P^* & 0 \\ 0 & P^* \end{pmatrix}$	$\begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}$	$\begin{pmatrix} Q & 0 \\ 0 & Q \end{pmatrix}$	$\begin{pmatrix} Q^* & 0 \\ 0 & Q^* \end{pmatrix}$
	$\theta 13$–$\theta 16.1$	$\theta 17$–$\theta 20.1$	$\theta 21$–$\theta 24$	$\theta 25$–$\theta 28.1$	$\theta 29$–$\theta 32.1$	$\theta 33$–$\theta 36.1$
$C\Gamma_{1-}$	+1	+1	+1	–1	–1	–1
$C\Gamma_{2-}$	–1	–1	–1	+1	+1	+1
$C\Gamma_{3-}$(c)	$\begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & Q^* \\ Q & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & Q \\ Q^* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & Q^* \\ Q^* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & Q \\ Q & 0 \end{pmatrix}$

where $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$ $\begin{pmatrix} w & 0 \\ 0 & w^* \end{pmatrix} = P$ $\begin{pmatrix} 0 & w \\ w^* & 0 \end{pmatrix} = Q$ $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = I$

TABLE VI

Soft modes of O_h^{10} magnetic involved S.O.Ph.Tr

$Ia'3d \xrightarrow{C\Gamma_{1-}} I4_1'3'2'$	from O^8
$Ia'3d \xrightarrow{C\Gamma_{2-}} I43'2$	from T_d^6
$Ia'3d \xrightarrow{C\Gamma_{3-}} Ia3'$	from T_h^7

have found that the transition is not reversible to hexagonal structure.

The magnetic $\mathrm{Ca_3Al_2(SiO_4)}$ crystal treated by ordinary L–L theory using irreps, results in the following active phonons: $\Gamma_{1-}, \Gamma_{2\pm}$ and $\Gamma_{3\pm}$ (see irreps list from Sect. 1). When treated by our modified L–L theory, this results in the following correps $C\Gamma_{1-}, C\Gamma_{2-}$ and $C\Gamma_{3-}$.

The irrep Γ_{3-} is of 2×2 dimension, while the corep $C\Gamma_{3-}$ is of 4×4 dimension. Clearly, the degeneracy of the phonon is twice of the phonon Γ_{3-}. It means that due to external or internal perturbation, the $C\Gamma_{3-}$ phonon may split into four phonons while phonon Γ_{3-} only into two. The effect can be measured by Raman spectroscopy.

5. Conclusion

There is no reversible transition from cubic to hexagonal structure in ZnO. The phonon degeneracies in magnetic and non magnetic crystals differ.Consequently, the phonon dispersion curves of magnetic and non magnetic crystals will be different and have an impact on thermal expansion coefficients. Also the electronic band structure of magnetic crystals will change essentially by increasing the degeneracy of particles.

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