Comment on "Silent soft mode in hexagonal barium titanate observed by hyper-Raman scattering"

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The soft zone-center E_{2u} mode was recently observed by means of hyper-Raman scattering by Inoue *et al.* [Phys. Rev. B **38**, 6352 (1988)]. Knowing that the E_{2u} mode drives the transition, we obtain the lower-symmetry space group of the transition, construct the free energy (including elastic coupling), and show the possible optical modes allowed by symmetry.

In a recent paper[1] Inoue *et al.* discussed a soft optical phonon that drives the second-order phase transition from hexagonal $BaTiO_3$, space group $P6_3/mmc\,(D_{6h}^4)$, to a lower-symmetry structure at $T_a=222$ K. The new phase is not ferroelectric and its structure is not known. The soft mode is Raman and infrared inactive and therefore is a so-called "silent" mode. Using hyper-Raman scattering, Inoue *et al.*[1] observed that the zone-center E_{2u} mode was underdamped and became soft as the temperature T_a was approached from above. Since it remained underdamped the phonon frequency could be followed near the transition and gave a mean-field Landau-Cochran exponent $\gamma=1$. On the basis of the E_{2u} driving mode, they indicated that the lower-symmetry phase should be of symmetry $222(D_2)$ or $mm2(C_{2v})$.

In this Comment, we use space-group theory to discuss results which follow from knowing that the zone-center E_{2u} mode is driving the transition. We obtain the lower-symmetry space group from the order parameter, we give the free energy for the structure including its elastic coupling, and we show the possible optical distortions allowed by the soft mode.

The E_{2u} mode is labeled as the Γ_5^- representation in Table I of Stokes and Hatch.[2] The onset of the order parameter of this representation brings about the symmetry reduction to the space groups $C222_1(D_2^5)$, $Cmc2_1(C_{2v}^{12})$, and $P2_1(C_2^2)$ depending upon the direction of the order parameter. The subgroup $C222_1(D_2^5)$ is improper ferroelastic and the transition from the paraphase $P6_3/mmc\,(D_{6h}^4)$ is allowed to be a continuous. The subgroup $Cmc2_1(C_{2v}^{12})$ is improper ferroelastic and improper ferroelectric. This transition from the paraphase is also allowed to be continuous. The subgroup $P2_1(C_2^2)$ is improper ferroelastic and improper ferroelectric but the transition must be discontinuous. Since the observed lower-symmetry phase is nonferroelectric,[3] the phase $C222_1(D_2^5)$ is most likely the lower-symmetry phase of hexagonal barium titanate. It is of course possible that, even though the improper ferroelectric properties are allowed by symmetry for the other two phases, they are not significant because of weak coupling. However, it is likely that the ferroelectric properties would be observed if allowed so we expect the structure below the transition to be $C222_1(D_2^5)$.

From Tables IX and X in Stokes and Hatch[2] we can obtain the free energy of the order parameter. For the Γ_5^- representation, the free energy to fourth order takes the form

$$\Delta F=\frac{1}{2!}a_1(\eta_1^2+\eta_2^2)+\frac{1}{4!}b_1(\eta_1^2+\eta_2^2)^2\ . \tag{1}$$

Notice that this free energy does not contain the additional fourth order D_n term of Yamaguchi *et al.*[4] since such a term is not allowed by the Γ_5^- representation. Since the $C222_1(D_2^5)$ phase is an improper ferroelastic, spontaneous strain can occur at the transition but would not be the driving order parameter, i.e., the strain could be coupled linearly to a power of the driving optical-order parameter. From Table IV of Stokes and Hatch[2] the strain components transform under the Γ_1^+, Γ_5^+, and Γ_6^+ representations. The strain components $(\epsilon_{11}+\epsilon_{22})$ and (ϵ_{33}) both transform under the one-dimensional Γ_1^+ representation and couple bilinearly to the primary order parameter Γ_5^-. Strain components of this form are also allowed in the higher-symmetry phase since they transform under the identity representation. Thus, these strains do not introduce new components at the transition. The strain components $(\epsilon_{11}-\epsilon_{22},\epsilon_{12})$ transform under the Γ_5^+ representation. Using the transformation matrices of the Γ_5^- and Γ_5^+ representations, it can be seen that these strain components also couple linearly to a power of the primary order parameter, and since they are not allowed in the higher-symmetry phase, they onset spontaneously at the transition. The strain components of Γ_6^+ are not allowed by the symmetry $C222_1(D_2^5)$.

Components of the piezoelectric modulus also transform under Γ_5^-, e.g., $(d_{311}-d_{322},d_{312})$. Therefore, the spontaneous onset of new piezoelectric modulus components is possible at the transition to $C222_1(D_2^5)$.

Using single-index notation for the strain components, the free energy takes the form

$$\Delta F=\frac{1}{2!}a_1(\eta_1^2+\eta_2^2)+\frac{1}{4!}b_1(\eta_1^2+\eta_2^2)^2+\frac{1}{2!}a_2(\epsilon_1^2+\epsilon_2^2)+\frac{1}{2!}a_3\epsilon_3^2$$
$$+\frac{1}{2!}a_4\epsilon_6^2+\frac{1}{2!}a_5\epsilon_1\epsilon_2+\frac{1}{2!}a_6(\epsilon_1+\epsilon_2)\epsilon_3+\lambda_1(\epsilon_1+\epsilon_2)(\eta_1^2+\eta_2^2)+\lambda_2\epsilon_3(\eta_1^2+\eta_2^2)$$
$$+\lambda_3[(\epsilon_1-\epsilon_2)(\eta_1^2-2\sqrt{3}\eta_1\eta_2-\eta_2^2)+\epsilon_6(\sqrt{3}\eta_1^2+2\eta_1\eta_2-\sqrt{3}\eta_2^2)]+\lambda_4(\eta_1q_1+\eta_2q_2)\ . \tag{2}$$

TABLE I. Modes of distortion allowed by the Γ_5^- representation of $P6_3/mmc(D_{6h}^4)$. The six inequivalent Wyckoff positions occupied by the atoms are indicated. The vector displacements of the atoms from their equilibrium positions in $P6_3/mmc(D_{6h}^4)$ are shown for each of the seven allowed doubly degenerate modes.

Atoms:	$Ti_I(2a)$					
Positions:	$(0,0,0)$,	$(0,0,\frac{1}{2})$				
Mode:	$(x,0,0)$,	$(\bar{x},0,0)$				
	$(0,y,0)$,	$(0,\bar{y},0)$				
Atoms:	$Ti_{II}(4f)$					
Positions:	$(\frac{1}{3},\frac{2}{3},z)$,	$(\frac{2}{3},\frac{1}{3},z+\frac{1}{2})$,				
	$(\frac{2}{3},\frac{1}{3},\bar{z})$,	$(\frac{1}{3},\frac{2}{3},\bar{z}+\frac{1}{2})$				
Mode:	$(x,0,0)$,	$(\bar{x},0,0)$,	$(x,0,0)$,	$(\bar{x},0,0)$		
	$(0,y,0)$,	$(0,\bar{y},0)$,	$(0,y,0)$,	$(0,\bar{y},0)$		
Atoms:	$Ba_I(2b)$					
Positions:	$(0,0,\frac{1}{4})$	$(0,0,\frac{3}{4})$				
Mode:	none					
Atoms:	$Ba_{II}(4f)$					
Positions:	$(\frac{1}{3},\frac{2}{3},z)$,	$(\frac{2}{3},\frac{1}{3},z+\frac{1}{2})$,				
	$(\frac{2}{3},\frac{1}{3},\bar{z})$,	$(\frac{1}{3},\frac{2}{3},\bar{z}+\frac{1}{2})$				
Mode:	$(x,0,0)$,	$(\bar{x},0,0)$,	$(x,0,0,)$,	$(\bar{x},0,0)$		
	$(0,y,0)$,	$(0,\bar{y},0)$,	$(0,y,0)$,	$(0,\bar{y},0)$		
Atoms:	$O_I(6h)$					
Positions:	$(x,2x,\frac{1}{4})$,	$(2\bar{x},\bar{x},\frac{1}{4})$,	$(x,\bar{x},\frac{1}{4})$,	$(\bar{x},2\bar{x},\frac{1}{4})$	$(2x,x,\frac{3}{4})$,	$(\bar{x},x,\frac{3}{4})$
Mode:	$(0,0,0)$	$(0,0,z)$	$(0,0,\bar{z})$	$(0,0,0)$,	$(0,0,z)$,	$(0,0,\bar{z})$
	$(0,0,2z)$,	$(0,0,\bar{z})$,	$(0,0,\bar{z})$	$(0,0,2z)$,	$(0,0,\bar{z})$,	$(0,0,\bar{z})$
Atoms:	$O_{II}(12k)$					
Positions:	$(x,2x,z)$,	$(2\bar{x},\bar{x},z)$,	$(x,\bar{x},z)$,	$(\bar{x},2\bar{x},z+\frac{1}{2})$	$(2x,x,z+\frac{1}{2})$,	$(\bar{x},x,z+\frac{1}{2})$
	$(2x,x,\bar{z})$	$(\bar{x},2\bar{x},\bar{z})$	$(\bar{x},x,\bar{z})$,	$(2\bar{x},\bar{x},\bar{z}+\frac{1}{2})$	$(x,2x,\bar{z}+\frac{1}{2})$,	$(x,\bar{x},\bar{z}+\frac{1}{2})$
Mode I:	$(0,0,0)$,	$(0,0,z)$,	$(0,0,\bar{z})$,	$(0,0,0)$,	$(0,0,z)$,	$(0,0,\bar{z})$,
	$(0,0,z)$,	$(0,0,0)$,	$(0,0,\bar{z})$,	$(0,0,z)$,	$(0,0,0)$,	$(0,0,\bar{z})$
	$(0,0,2z)$,	$(0,0,\bar{z})$,	$(0,0,\bar{z})$,	$(0,0,2z)$,	$(0,0,\bar{z})$,	$(0,0,\bar{z})$,
	$(0,0,\bar{z})$,	$(0,0,2z)$,	$(0,0,\bar{z})$,	$(0,0,\bar{z})$,	$(0,0,2z)$,	$(0,0,\bar{z})$
Mode II:	$(2x,0,0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}x,0)$,	$(2\bar{x},0,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}x,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}\bar{x},0)$,
	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(2x,0,0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}x,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}x,0)$,	$(2\bar{x},0,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}\bar{x},0)$
	$(0,0,0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(0,0,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}x,0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}x,0)$,
	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(0,0,0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}\bar{x},0)$,	$(\frac{1}{2}\bar{x},\frac{1}{2}\sqrt{3}x,0)$,	$(0,0,0)$,	$(\frac{1}{2}x,\frac{1}{2}\sqrt{3}x,0)$
Mode III:	$(0,0,0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}\bar{x},0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}x,0)$	$(0,0,0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}x,0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}\bar{x},0)$
	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}\bar{x},0)$	$(0,0,0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}x,0)$	$(\frac{1}{2}\sqrt{3x},\frac{1}{2}x,0)$	$(0,0,0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}\bar{x},0)$
	$(0,2x,0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}x,0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}x,0)$	$(0,2\bar{x},0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}\bar{x},0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}\bar{x},0)$
	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}x,0)$	$(0,2x,0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}x,0)$	$(\frac{1}{2}\sqrt{3}\bar{x},\frac{1}{2}\bar{x},0)$	$(0,2\bar{x},0)$	$(\frac{1}{2}\sqrt{3}x,\frac{1}{2}\bar{x},0)$

In Eq. (2), we use (q_1,q_2) to denote the term corresponding to the spontaneous piezoelectric properties. The components $(q_1,q_2)\equiv((\epsilon_1-\epsilon_2)P_3,\epsilon_6P_3)$ transform in the same manner as the Γ_5^- optical phonon. The free energy we obtain is very similar to the phenomenological free energies obtained by others.[4,5] We differ from those expressions in that we find the D_n term of Ref. 4 is not allowed by symmetry, and the form of the coupling between the primary order parameter and the spontaneous strain (the λ_3 term) is slightly different. This latter difference is because our choice of representation matrices for Γ_5^- is not the same as theirs, even though it is unitarily equivalent to their selection of matrices. We have also omitted the c_{44}^H term of Ref. 4 as well as certain terms related to the secondary parameter P_3. The elastic constant measurements of Ref. 4 show that the coupling parameters λ_1,λ_2 are negligible. Thus, only the strain contributions which are allowed by the lower-symmetry phase $C222_1(D_2^5)$ and which are not allowed in the paraphase, are significant. Yamaguchi *et al.*[4] indicate that piezoelectricity is seen experimentally in the lower-symmetry phase.

Using induced representation theory we can specify the types of modes (distortions) consistent with the symmetry change and atomic positions. Structural data[6] on the $P6_3/mmc(D_{6h}^4)$ phase indicate that there are six molecules in the primitive unit cell. The atoms are in the following special positions:

2 Ti_I at $(2a)$,

4 Ti_{II} at $(4f)$, $z=0.845$,

2 Ba_I at $(2b)$,

4 Ba_{II} at $(4f)$, $z=0.097$,

6 O_I at $(6h)$, $x=0.522$,

12 O_{II} at $(12k)$, $x=0.836$, $z=0.076$.

From induced representation theory, as discussed by Hatch *et al.*,[7] and projection-operator techniques, we obtained the modes (distortions) at the Wyckoff positions of the atoms in the unit cell allowed by the Γ_5^- representation. The results are shown in Table I. There we list the atoms, their positions in the unit cell, and the distortions associated with each of the listed positions. We obtained seven sets of doubly degenerate modes. However, linearly independent combinations of the modes also transform under the Γ_5^- representation. The physical modes cannot be obtained by symmetry arguments, but instead require more details of the microscopic mechanisms leading to the transition.

The transition at $T_c=74$ K is a ferroelectric transition.[1,8] As can be seen from Table I in Stokes and Hatch,[2] a group-subgroup transition from $C222_1(D_2^5)$ to $P2_1(C_2^2)$ is allowed by the Γ_2 representation of $C222_1(D_2^5)$. Since $P2_1(C_2^2)$ is also a subgroup of $P6_3/mmc(D_{6h}^4)$, when the order parameter is in a general direction, the possible sequence of transitions $P6_3/mmc(D_{6h}^4)$-$C222_1(D_2^5)$-$P2_1(C_2^2)$ would result from selected directions of the order parameter of a single representation Γ_5^-.

After this Comment was submitted, it was called to our attention that the lower-symmetry space group had been determined by x ray and is indeed $C222_1(D_2^5)$.[9]

[1]K. Inoue, A. Hasegawa, K. Watenabe, H. Yamaguchi, H. Uwe, and T. Sakudo, Phys. Rev. B **38**, 6352 (1988).

[2]H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1988).

[3]H. Yamaguchi, H. Uwe, T. Sakudo, and E. Sawaguchi, J. Phys. Soc. Jpn. **56**, 589 (1987).

[4]H. Yamaguchi, H. Uwe, T. Sakudo, and E. Sawaguchi, J. Phys. Soc. Jpn. **57**, 147 (1987).

[5]K. Deguchi, H. Kobayashi, E. Nakamura, H. Yamaguchi, H. Uwe, and T. Sakudo, J. Phys. Soc. Jpn. **57**, 4011 (1988).

[6]R. D. Burbank and H. T. Evans, Acta Crystallogr. **1**, 330 (1948).

[7]D. M. Hatch, H. T. Stokes, and R. M. Putnam, Phys. Rev. B **35**, 4935 (1987).

[8]E. Sawaguchi, Y. Akishige, and M. Kobayaski, J. Phys. Soc. Jpn. **54**, 480 (1985).

[9]T. Yamamoto, Y. Akishige, and E. Sawaguchi, J. Phys. Soc. Jpn. **57**, 3665 (1988).