Raman scattering study and symmetry aspects of the phase transition in ferroelastic Sb_5O_7I

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The low-frequency Raman spectra of ferroelastic Sb_5O_7I crystals have been measured for temperatures ranging from 295 K to well above the phase transition at $T_c = 481$ K. A strongly damped soft mode which is present only in the ferroelastic phase and quasielastic scattering from a central line, whose intensity peaks around T_c, are observed. A symmetry analysis shows that the instability of the hexagonal high-temperature phase may be explained by assuming a triply degenerate soft mode belonging to the star of the zone-boundary M point in the Brillouin zone. An expression for the free energy consistent with symmetry is constructed and the relation between the spontaneous elastic strain and the soft-mode amplitudes are determined. Applying this phenomenological theory it is shown that the intensities of several Raman lines, which decrease with rising temperature and vanish above T_c, are a measure of the temperature dependence of the order parameter. The experimental results indicate that the phase transition is weakly discontinuous.

I. INTRODUCTION

Antimony (III)-oxide-iodide of chemical composition Sb_5O_7I, undergoes a displacive phase transition at 481 K. In the high-temperature prototypic phase the crystal belongs to the space group $C_{6h}^2(P6_3/m)$ of the hexagonal class and has two formula units in the elementary cell. Below the transition temperature the symmetry is reduced to $C_{2h}^5(P2_1/c)$ of the monoclinic system where one of the primitive translations normal to the hexagonal axis is doubled. The crystal then contains four formula units in the cell. According to the notations of Aizu,[1] which we adopt throughout the paper, Sb_5O_7I is, in the low-temperature phase, a fully ferroelastic crystal belonging to the species $6/mF2/m$ with three different orientational states or domains of the spontaneous strain. The three fold rotations C_3 and C_3^2 contained in the prototypic point group C_{6h}, which cease to be symmetry operations in the ferroic phase, transform one domain into another. By a suitably chosen external mechanical stress, different domains may be forced to collapse into a single orientational state yielding a single-domain crystal.[2]

In a previous work we reported Raman scattering measurements of Sb_5O_7I.[3] The complete spectra in the monoclinic phase have been determined and were discussed with regard to the symmetry of the ferroic phase and the symmetry change which occurs in the course of the phase transition. By a factor group analysis the number and symmetries of zero-wave-number phonons were enumerated for both phases. The temperature dependence of the spectra has been determined up to above the transition temperature and the results were discussed by applying compatibility relations among the irreducible representations of the prototypic and ferroic structure. The most significant changes of the spectra with temperature have been found in the very-low-frequency range. In particular a strongly damped Raman-active soft mode which is present only in the ferroelastic phase has been found and three low-frequency lines were observed, whose intensities decreased strongly with increasing temperature and vanished at the phase-transition point.

The aim of this paper is to report detailed measurements of the temperature dependence of these lines and to determine a probable mechanism of the structural change of Sb_5O_7I. It is found that the phase transition of Sb_5O_7I is of first-order nature, with a very small discontinuity at T_c. As the behavior of weakly discontinuous structural transitions may be well described by the theory of Landau,[4] we will discuss our results on the basis of this classical approach. An appropriate expression of the free energy as a power series in terms of the strain and the normal coordinates of a phonon, which is assumed to become soft, is developed using standard group-theoretical methods. From this model the Raman scattering intensity as a function of temperature is derived for phonons which become Raman active when the symmetry of the crystal is lowered by the phase transition. The results are found to agree well with the experimentally determined temperature dependences.

II. CRYSTAL STRUCTURE

The structural properties of Sb_5O_7I have been determined by Krämer for both phases[5] and have been summarized in Ref. 3 in order to discuss the Raman spectra. Therefore here we will only describe the relations of the crystallographic axes and the Brillouin zones of both phases and settle a coordinate system. Figure 1 shows a cross section of the elementary cells and the Brillouin zones for both phases of Sb_5O_7I normal to the sixfold axis of the hexagonal structure. In Fig. 1(a), $\vec{a}$, $\vec{c}$, and $\vec{a}_1, \vec{a}_2$ are monoclinic and hexagonal axes, respectively, and x, y are Cartesian coordinates. In Fig. 1(b) several points of different symmetries in the Brillouin zone are indicated by the usual symbols. The change in crystal structure during the phase transition is mainly determined by internal displacements of the iodine atoms which couple to elastic deformations of the crystal lattice and yield the ferroelastic properties of the crystal. Below T_c two equivalent iodine atoms in neighboring unit cells are displaced alternately in opposite directions along one of the twofold axes of the hexagonal structure, $\vec{a}_1$, $\frac{1}{2}(\vec{a}_1 + \vec{a}_2)$, or $\vec{a}_2$. Thus, the phase transition doubles one of the primitive translations along a crystallographic axis normal to the sixfold $\vec{a}_3$ axis. In Fig. 1(a) this doubling is shown to occur parallel to $\vec{a}_2$. However, instead of $\vec{a}_2$ the primitive translations $\vec{a}_1$ or $\frac{1}{2}(\vec{a}_1 + \vec{a}_2)$ may be doubled resulting in different domains of the ferroelastic crystal. This doubling of a basic vector in the direct lattice cuts the Brillouin zone normal to the Σ axis, as shown in Fig. 1(b), and translates
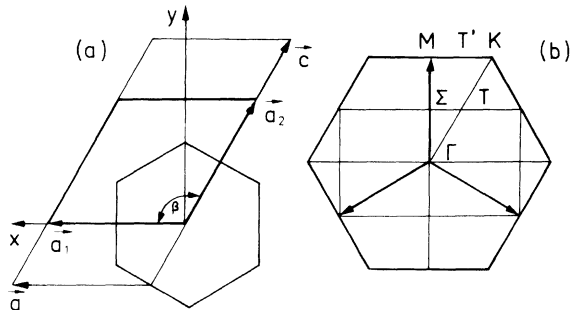
the zone-boundary M point to the center of the zone.

The significant irreducible components of the spontaneous elastic strain u_{ij}^s, which accompanies the internal displacements of the iodine atoms, are $u_{xx}^s - u_{yy}^s$ and u_{xy}^s.[6] The magnitude of these strain components at room temperature can be estimated from Krämer's crystallographic data.[5] For the orientational state of Fig. 1(a), it is found

$$u_{xx}^s - u_{yy}^s = 1.3 \times 10^{-2}, \quad u_{xy}^s = 3 \times 10^{-3}.$$

Applying the three fold rotations of the point group C_{6h}, the values of the strain components for the two other domains may easily be determined. The magnitude of the spontaneous strain[6] u^s

$$= [2(u_{xx}^s - u_{yy}^s) + 2u_{xy}^s]^{1/2} \text{ is } 1.9 \times 10^{-2}.$$

III. EXPERIMENTAL

A. Techniques

Raman scattering was excited by an argon laser at 514.5 nm. The incident laser power was approximately 100 mW. The scattered light was analyzed by a Jarrel-Ash double monochromator utilizing a FW 130 photomultiplier as a detector. The spectral resolution was 0.6 cm^{-1}. The direction of the polarization of the incoming laser beam was selected by a broadband polarization rotator and that of the scattered radiation by a Polaroid filter. Standard photon-counting techniques were applied.

Samples of approximately 3 mm length of each side were prepared and oriented as described previously.[3] The samples were placed in an electrically heated oven with windows of fused quartz. The temperature was monitored by a NiCr-Ni thermocouple mounted close to the crystal and controlled by a Thor model 3010 temperature controller. A temperature stability of about 0.5 K could be achieved. The incident laser beam was directed parallel to the z coordinate (hexagonal $\vec{a}_3$ axis or monoclinic $\vec{b}$ axis) and the scattered radiation was observed in the usual 90° configuration in the y direction.

FIG. 1. (a) Elementary cell of Sb_5O_7I: $\vec{a}_1$, $\vec{a}_2$ are hexagonal axes, $\vec{a}$, $\vec{c}$ monoclinic axes, x, y Cartesian coordinates; the hexagonal $\vec{a}_3$ axis, the monoclinic $\vec{b}$ axis, and the z coordinate are normal to the plane of the drawing; $\beta = 120°$ in the hexagonal phase. (b) Brillouin zone: points of specific symmetries of the hexagonal zone are indicated by the usual symbols. The doubling of the elementary cell folds the Brillouin zone normal to the Σ axis and translates the M point to the center. The three wave vectors of the star of the M point are indicated by arrows.

B. Results and discussion

In the ferroelastic phase Raman-active phonons belong to the irreducible representations A_g and B_g of the point group C_{2h}, whereas in the high-temperature phase Raman-active modes transform according to A_g, E_{1g}, and E_{2g} of C_{6h}.[3] In Fig. 2 the Stokes-Raman spectra between 2 and 62 cm^{-1} are shown for $z(xx)y$ and $z(xz)y$ scattering configurations corresponding to A_g and B_g representations of C_{2h}, respectively. The spectra were recorded at various temperatures up to above T_c
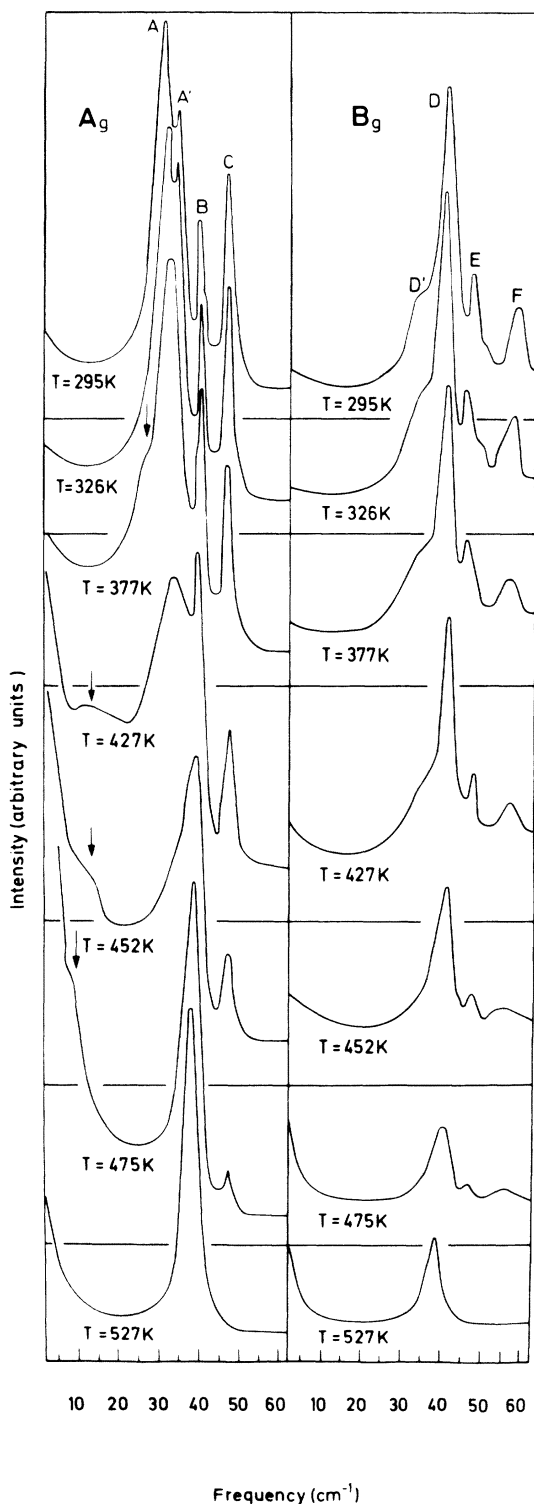
FIG. 2. Low-frequency Raman spectra of Sb_5O_7I at various temperatures below and above $T_c = 481$ K. Left side: A_g, $z(xx)y$; right side: B_g, $z(xz)y$. The strongly damped soft mode is indicated by arrows.

TABLE I. Compatibility relations between Γ- and M-point representations of C_{6h}^2 yielding Raman (R)-active modes in C_{2h}^5. P_{ij} are components of the polarizability tensor.

$\Gamma\ (C_{6h}^2)$	$\Gamma\ (C_{2h}^5)$	$M\ (C_{6h}^2)$
R-active:	R-active:	inactive:
$A_g(P_{xx}+P_{yy}, P_{zz})$		
$E_{1g}\ (P_{yz}, P_{xz})$	$A_g\ (P_{xx}, P_{yy}, P_{zz}, P_{xy})$	M_1
$E_{2g}\ (P_{xx}-P_{yy}, P_{xy})$		
inactive:	$B_g\ (P_{yz}, P_{xz})$	M_2
B_g		

and exhibit considerable temperature dependences. At 295 K there are four A_c lines: A, A', B, C and four B_g lines: D, D', E, F. At lower temperatures (100 K) the lines A, A' and D, D' are well separated.[3] Above the transition temperature only two Raman-active modes remain in the spectral range of Fig. 2, one for each scattering configuration. These modes result from the A_g modes A', B and the B_g modes D', D which coincide at T_c and become doubly degenerate modes belonging to the irreducible representations E_{2g} and E_{1g} of C_{6h}, respectively (see Table I).

With increasing temperature at the low-frequency side of the A_g spectrum a strongly damped soft mode indicated by arrows in Fig. 2 can be observed in the ferroelastic phase below T_c. It is split off from the A, A' doublet at about 420 K, decreases in frequency with increasing temperature and disappears above T_c. Because of the large width of this very-low-frequency line it was not possible to determine accurately the soft-mode frequency as a function of temperature.

The condensation of the soft mode is accompanied by the appearance of a strongly temperature-dependent central Rayleigh line whose intensity peaks around the transition temperature. Below about 400 K the soft mode and the central line are well separated. Closer to T_c the soft mode shows up as a broad shoulder on the wing of the central line. The integrated intensity of the Rayleigh scattering as a function of temperature has been determined for both scattering configurations. The data have been obtained by extrapolating the measured spectral intensity to zero frequency and to higher frequency with a Gaussian curve. The contribution of the thermal population has been removed by dividing the integrated intensities by the absolute temperature T. The results are displayed in Fig. 3 and show a distinctly dif-
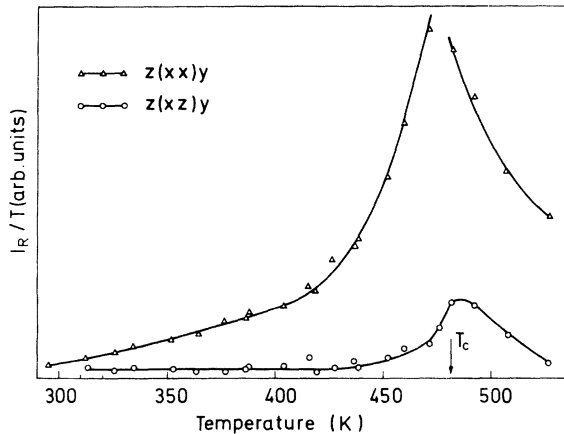
FIG. 3. Integrated intensity I_R of the central line divided by the temperature T as function of temperature for $z(xx)y$ and $z(xz)y$ scattering configurations.

ferent temperature behavior for both scattering configurations. The magnitude of the B_g scattering is constant up to approximately 450 K. We attribute this temperature-independent reduced intensity to elastic scattering by crystal imperfections. Close to T_c the scattering is enhanced. This may be due to elastic scattering by domain walls which are formed in a temperature interval of about 20–30 K below T_c. In contrast to the B_g scattering the reduced integrated intensity of the central line in the A_g spectrum increases continuously from room temperature to T_c. In the temperature range up to 20–30 K below T_c the sample used was certainly a single-domain crystal. Thus, the major part of this intensity must be of dynamical origin resulting from light scattering by phonon-density fluctuations. The extrapolated spectral intensity curve extends up to approximately 40 cm^{-1} into the Raman spectrum. In this respect the central line of Sb$_5$O$_7$I is very similar to that in SbSI observed by Steigmeier et al.[7] However, in the case of Sb$_5$O$_7$I the central line scattering is also present above T_c where no Raman-active soft mode exists, which may cause the coupling of the exciting light to phonon-density fluctuations by anharmonicity. Wehner and Klein have shown by analyzing the response function of a dielectric crystal in the hydrodynamical regime that direct coupling to phonon-density fluctuations is conceivable if second-order Raman polarizability is taken into account.[8] This process seems to play an important role in the quasielastic scattering of Sb$_5$O$_7$I.

At higher frequencies the spectra exhibit one A_g line C, and two B_g lines E and F, whose intensities strongly decrease approaching T_c and vanish above the phase transition (see Fig. 2). The re-

duced intensities [intensity divided by the Bose population factor $n(\omega) + 1$] of these lines as functions of temperature are displayed in Fig. 4. The experimentally determined values after subtracting the constant background are shown by circles and triangles. The solid lines are fitted curves and will be discussed later. The intensities of the considered lines decrease almost continuously as the temperature approaches T_c. Close to T_c the lines E and F are too weak to be measured accurately; however, the strength of line C is definitely nonzero at T_c. We will show that these intensity curves reflect the temperature dependence of the order parameter of the phase transition. Thus, we conclude that the phase transition of Sb$_5$O$_7$I is of first order, however the discontinuity of the order parameter at T_c is expected to be very small.

IV. PHENOMENOLOGICAL THEORY OF THE PHASE TRANSITION

A. Mechanism of the phase transition

Several mechanisms connected with soft phonon modes may induce a ferroelastic phase transition. If phonons of zero wave number or close to zero wave number are involved in the lattice instability two different types of crystals capable of becoming ferroelastics may be distinguished.[9] In the case of an optical-type ferroelastic the phase transition is caused by an oversoftening of a Raman-active lattice vibration. This phenomenon has recently been observed in NdP$_5$O$_{14}$ and LaP$_5$O$_{14}$,[10] which are, below 419 and 391 K, respectively, purely ferroelastic materials.[11] If the crystal is of the elastic type the phase transition results from an elastic instability or, being more precise, the group velocity at zero wave number of a certain transverse acoustic phonon vanishes at the transition temperature: $(d\omega/dq)_{q=0} = 0$. Such an instability causes the pressure-induced phase transition in TeO$_2$.[12] Neither situation applies to Sb$_5$O$_7$I. For an optical-type ferroelastic we expect a Raman-active soft mode to be present below and above T_c rather than only in the ferroelastic phase as observed in Sb$_5$O$_7$I, whereas for an elastic-type ferroelectric no optical soft mode should occur. Furthermore neither mechanism can explain the doubling of the unit cell below T_c. Guided by this latter effect it seems natural to assume a zone-boundary soft mode belonging to the wave vector $\vec{q}_M$ of the M point of the Brillouin zone. Below the transition temperature this mode is shifted to $\vec{q} = 0$ having the full symmetry of the ferroic phase and yielding the Raman scattering of the A_g soft mode which we have observed. Thus, the phase transition of Sb$_5$O$_7$I is of antiferrodis-

tortive nature like the transition of ferroelectric and ferroelastic $Gd_2(MoO_4)_3$.[13] Ferroelasticity is a subsidary effect of Sb_5O_7I being induced by a coupling of the M-point soft mode to elastic deformations of the crystal. The primary quantity is the normal coordinate of the zone-boundary soft mode and is to be regarded as the order parameter of the phase transition.

B. Active representation

The normal coordinate of the M-point soft mode in the high-temperature phase must transform according to an irreducible representation of the space group C_{6h}^2, which is an active representation in the sense of the Landau theory. This representation must contain the identity representation A_g, if the symmetry is reduced to that of the ferroelastic phase, and it has to satisfy the Landau conditions.[14] The space group C_{6h}^2 may be decomposed into left cosets of the space group $G(\vec{q}_M)$ of the wave vector $\vec{q}_M$. Written as a complex product it becomes

$$C_{6h}^2 = C_3 \times G(\vec{q}_M) , \tag{1}$$

where C_3 is the point group whose symmetry elements transform the ferroelastic domains. $G(\vec{q}_M)$ is isomorphic to the point group C_{2h}. We denote the small irreducible representations of $G(\vec{q}_M)$ by M_i, where the numbering follows the tables of Zak.[15] Though C_{6h}^2 is a nonsymmorphic space group the representations M_i are identical to those of C_{2h} because the nonprimitive translation $\vec{\tau}$ is normal to the wave vector $\vec{q}_M$: $\vec{q}_M \cdot \vec{\tau} = 0$, thus $\exp(i\vec{q}_M \cdot \vec{\tau}) = 1$. The representations M_i are all real and one dimensional. We have determined the compatibility relations between the M point and the Γ point of C_{6h}^2 and the Γ-point of C_{2h}^5.[3] The results for representations yielding Raman-active modes in the ferroelastic phase of C_{2h}^5 symmetry are reproduced in Table I, showing that only M_2 contains the identity representation A_g of the ferroic phase, if the symmetry is reduced. Thus, only M_2 can be an active representation.

The star of $\vec{q}_M$ consists of three wave vectors where each pair includes an angle of $\frac{2}{3}\pi$ in the hexagonal plane of the Brillouin zone. Therefore the irreducible representations of the entire space

group belonging to $\vec{q}_M$, which we will denote by D_i^M, are all three dimensional. They may easily be determined by the usual methods from the small representations M_i. A straightforward calculation gives the following decompositions of the antisymmetrized square $\{D\}^2$ and the symmetrized cube $[D]^3$ of D_2^M in terms of irreducible representations of C_{6h}^2:

$$\{D_2^M\}^2 = D_1^M , \quad [D_2^M]^3 = B_g + 3D_2^M . \tag{2}$$

We see that the Landau conditions are satisfied for D_2^M, since $\{D_2^M\}^2$ does not contain the vector representation $\Gamma_v = A_u + E_{1u}$ of C_{6h}^2 and $[D_2^M]^3$ has no common representation with A_g. We denote the thermal averages of the components of the M-point soft-mode normal coordinates by Q_1, Q_2, and Q_3, where each Q_μ is associated with one wave vector of the star of $\vec{q}_M$. The triply degenerate set of coordinates $\{Q_1, Q_2, Q_3\}$ constitute a basis of D_2^M. Because according to Eq. (1) the point group operations of C_3 transform one component of normal coordinates into another, we may attribute each Q_μ to one of the three orientational states of the ferroelastic crystal, which we will call S_μ.

Thus, below the transition temperature the threefold degeneracy is removed. One single component of the $\{Q_\mu\}$, depending on which domain is realized, becomes a zone-center mode and determines the crystal structure of the ferroelastic phase. The two other components remain zone-boundary modes of the low-temperature structure as can be seen from Fig. 1(b).

C. Spontaneous elastic strain

The free energy F is assumed to be expandable into a power series in terms of the soft-mode normal coordinates Q_μ and the elastic deformations u_{ij}, with coefficients depending only smoothly on the temperature T. The explicit form of the power-series expansion is determined by the requirement that F is invariant against all operations of the high-temperature space group C_{6h}^2. By applying the appropriate projection operator on powers of the required order of the variables u_{ij} and Q_μ, we find

$$F = a_1(u_{xx}+u_{yy}) + a_3 u_{zz} + \tfrac{1}{2}a_{11}(u_{xx}+u_{yy})^2 + \tfrac{1}{2}a_{33}u_{zz}^2 + a_{13}(u_{xx}+u_{yy})u_{zz} + \tfrac{1}{2}a_{66}[(u_{xx}-u_{yy})^2 + 4u_{xy}] + \tfrac{1}{2}\alpha' \sum_\mu Q_\mu^2 + \tfrac{1}{4}\beta_1' \sum_\mu Q_\mu^4$$

$$+ \tfrac{1}{4}\beta_2' \sum_{\sigma_i} [(Q_{\sigma_1}^2 + Q_{\sigma_2}^2)Q_{\sigma_3}^2] + f(Q_\mu) + [c_1(u_{xx}+u_{yy}) + c_3 u_{zz}] \sum_\mu Q_\mu^2 + d[(u_{xx}-u_{yy})(2Q_3^2 - Q_2^2 - Q_1^2) + 2\sqrt{3}\,u_{xy}(Q_2^2 - Q_1^2)] ,$$

$$\tag{3}$$

with

$$f(Q_\mu) = \tfrac{1}{6}\gamma_1 \sum_\mu Q_\mu^2 + \tfrac{1}{4} \sum_{\sigma_i} Q_{\sigma_1}^2 \{[\gamma_2(Q_{\sigma_1}^2 Q_{\sigma_2}^2 + Q_{\sigma_3}^4) + \gamma_3(Q_{\sigma_1}^2 Q_{\sigma_3}^2 + Q_{\sigma_2}^2)]\} .$$

σ_1, σ_2, σ_3 are cyclic permutations of the numbers 1, 2, 3. The elements of the strain tensor are introduced in F as linear combinations which are irreducible components of the point group C_{6h}:

$$A_g \simeq u_{xx} + u_{yy}, u_{zz}; \quad E_{2g} \simeq \{u_{xx} - u_{yy}, 2u_{xy}\}.$$

The E_{1g} terms $\{u_{yz}, u_{xz}\}$ are omitted because they do not couple to the coordinates Q_μ. The linear terms with coefficients a_i represent the thermal expansion. The a_{ij} are related to the elastic constants c_{ij} at constant Q_μ as $c_{11} = a_{11} + a_{66}$, $c_{12} = a_{11} - a_{66}$, $c_{13} = a_{13}$, and $c_{33} = a_{33}$. The c_{ij} are elastic constants of the high-temperature phase because above the phase transition $Q_\mu = 0$. The elastic constant c_{44} which is connected with u_{yz} and u_{xz} is insensitive to the phase transition. The terms with α', β_i', and γ_i give the contribution of the soft mode to the free energy. Because the phase transition in Sb_5O_7I is assumed to be of first order the power series has been developed up to sixth order in Q_μ. The coefficients c_i and d yield the coupling between the strain tensor and the soft mode. The existence of this interaction energy is essential for the crystal to become ferroelastic in the low-temperature phase. If the term containing d, which is constituted by the scalar product of the E_{2g} components of u_{ij} and $Q_\mu Q_\mu$, were forbidden by symmetry, the low-temperature phase of the crystal would be nonferroelastic. As in all antiferrodistortive phase transitions, no bilinear terms between u_{ij} and Q_μ are allowed by symmetry in F. Therefore, no anomaly in the elastic constants is expected above the transition temperature. In particular the elastic compliances will not show a Curie-Weiss behavior as is the case for normal ferroelastics of the elastic or optical type.[9] In the terminology of Aizu Sb_5O_7I is a faint ferroelastic with an index of faintness of 2.[16]

Using the equilibrium conditions at zero external stress:

$$\frac{\partial F}{\partial u_{ij}} = 0,$$

we obtain the relations between the elastic strain and the soft mode amplitudes:

$$u_{xx} + u_{yy} = A_1 + C_1 \sum_\mu Q_\mu^2,$$

$$u_{zz} = A_3 + C_3 \sum_\mu Q_\mu^2,$$

$$u_{xx} - u_{yy} = D(2Q_3^2 - Q_2^2 - Q_1^2),$$

$$2u_{xy} = D\sqrt{3}\,(Q_2^2 - Q_1^2)$$

(4)

with

$$A_i = -\tilde{a}_{i1}a_1 - \tilde{a}_{i3}a_3,$$

$$C_i = -\tilde{a}_{i1}c_1 - \tilde{a}_{i3}c_3, \quad i = 1, 3$$

$$D = -\tilde{a}_{66}d.$$

The coefficients $\tilde{a}_{ij}$ constitute the inverse matrix of a_{ij} and satisfy the same relations with the elastic compliances s_{ij} of the paraelastic phase as the coefficients a_{ij} with the elastic constants c_{ij}. By introducing Eq. (4) into the free energy we eliminate the elastic strain and get F solely as a function of Q_μ:

$$F = \alpha \sum_\mu Q_\mu^2 + \tfrac{1}{4}\beta_1 \sum_\mu Q_\mu^4$$

$$+ \tfrac{1}{4}\beta_2 \sum_{\sigma_i} [(Q_{\sigma_1}^2 + Q_{\sigma_2}^2)Q_{\sigma_3}^2] + f(Q_\mu). \quad (5)$$

The parameters α, β_1, and β_2 correspond to the primed values of Eq. (3) renormalized by the interaction between u_{ij} and Q_μ. They may easily be enumerated by a straightforward calculation, however, we will not give explicitly these rather lengthy relations. As is well known, for first-order phase transitions the parameters β_1 and γ_1 have to satisfy the conditions $\beta_1 < 0$ and $\gamma_1 > 0$.

The equilibrium values of the soft-mode amplitudes Q_μ are determined by the requirement

$$\frac{\partial F}{\partial Q_\mu} = 0, \quad (6)$$

where

$$\frac{\partial F}{\partial Q_1} = \alpha Q_1 + \beta_1 Q_1^3 + \gamma_1 Q_1^5 + \beta_2 Q_1(Q_2^2 + Q_3^2)$$

$$+ \gamma_2 Q_1(2Q_1^2 Q_2^2 + Q_3^4) + \gamma_3 Q_1(2Q_1^2 Q_3^2 + Q_2^4).$$

$\partial F/\partial Q_2$ and $\partial F/\partial Q_3$ are obtained by cyclic permutations of the indices 1, 2, and 3.

Now we make the usual assumption that the only parameter having a significant temperature dependence close to the phase transition is α, with $\alpha(T) = \alpha_0(T - T_0)$ and $\alpha_0 > 0$. T_0 is the low-temperature boundary of the stability of the prototypic phase. Above T_0 in this phase $Q_\mu = 0$ for all μ is clearly a stable solution of Eq. (6) if $\alpha_0 > 0$. Below the phase transition the equilibrium condition has the three independent solutions for the three domains S_μ as required after the discussion at the end of Sec. IV B, which we will call Q_μ^s:

$$S_1: Q_1^s = \eta(T) \neq 0, \quad Q_2^s = Q_3^s = 0;$$

$$S_2: Q_1^s = 0, \quad Q_2^s = \eta(T) \neq 0, \quad Q_3^s = 0; \quad (7)$$

$$S_3: Q_1^s = Q_2^s = 0, \quad Q_3^s = \eta(T) \neq 0.$$

The function $\eta(T)$ takes on the familiar expression of the order parameter for phase transitions of first order:

$$\eta^2(T) = -\frac{\beta_1}{2\gamma_1}\left[1 + \left(1 - \frac{4\gamma_1}{\beta_1^2}\alpha_0(T - T_0)\right)^{1/2}\right]. \quad (8)$$

If we denote by T_1 the temperature above which the ferroelastic phase cannot exist, Eq. (8) can be written as

$$\eta^2(T) = \eta^2(T_1)\{1 + [(T_1 - T)/(T_1 - T_0)]^{1/2}\}, \quad (9)$$

with

$$T_1 = T_0 + \beta_1^2/\gamma_1\alpha_0 = T_0 + \tfrac{4}{3}(T_c - T_0)$$

and

$$\eta^2(T_1) = -\tfrac{1}{2}(\beta_1/\gamma).$$

As usual T_c is defined as the temperature where both phases have the same free energy.

The thermodynamic stability of the solutions (7) requires that the matrix $(\partial^2 F/\partial Q_\mu \, \partial Q_\mu)_{Q_\mu = Q_\mu^s}$ is positive definite. It can be shown that this condition is satisfied for $T < T_1$ in the ferroelastic phase if $\gamma_1 > 0$ and the inequalities $\beta_2 > \tfrac{1}{2}(\beta_1\gamma_2/\gamma_1)$ and $\beta_2 > \tfrac{1}{2}(\beta_1\gamma_3/\gamma_1)$ are fulfilled.

Now we insert the spontaneously appearing amplitude Q_μ^s of Eq. (7) into the relations (4) and find the elastic strain in the ferroelastic phase. The A_g components are given by

$$u_{xx} + u_{yy} = A_1 + C_1\eta^2(T),$$
$$u_{zz} = A_3 + C_3\eta^2(T) \quad (10)$$

and are independent of the domains realized below the phase transition. These strain components describe the continuation of thermal expansion of the prototypic phase into the ferroelastic phase. The symmetry breaking E_{2g} components, conventionally called spontaneous strain,[6] will be denoted by the superscript s. They are different for different domains. From Eq. (4) we find for the domain S_μ

Domain	S_1	S_2	S_3
$u_{xx}^s - u_{yy}^s =$	$-D\eta^2(T)$	$-D\eta^2(T)$	$2D\eta^2(T)$
$2u_{xy}^s =$	$-\sqrt{3}\,D\eta^2(T)$	$\sqrt{3}\,D\eta^2(T)$	$0.$

(11)

Then the magnitude of the spontaneous strain is given by $u^s = \sqrt{2}\,D\eta^2(T)$.

Finally we will note that the phase transition in Sb_5O_7I may take place even if the crystal is clamped at $u_{ij} = 0$. In this case T_0 is replaced by a temperature T_0^{cl} with $T_0^{cl} = T_0 - \Theta$, where $\Theta = (2/\alpha_0)(\tilde{a}_{11}a_1c_1 + 2\tilde{a}_{13}a_1c_3 + \tilde{a}_{33}a_3c_3)$. This result shows that the transition may occur if $T_0 > \Theta$. Although the domains of the low temperature-phase now cannot differ in elastic strain, they will differ in other symmetric second-rank polar-property tensors, e.g., the dielectric constants.

V. TEMPERATURE DEPENDENCE OF THE RAMAN LINES ACTIVATED BY THE PHASE TRANSITION

In the ferroelastic phase we have observed three lines denoted in Fig. 2 by C, E, and F whose intensities decrease with rising temperature and vanish above the phase transition. According to Table I these lines may result either from zone-boundary modes of the prototypic phase belonging to the irreducible representations M_1 and M_2, which are shifted to the Γ point and become Raman active in the ferroelastic phase, or from zone-center B_g modes of C_{6h}, which are Raman inactive in the hexagonal structure and will be activated by the appearance of the spontaneous strain. In order to relate the intensities of the considered lines to the temperature-dependent order parameter $\eta(T)$ we expand the Raman polarizability $P_{ij}(\omega)$ in terms of Q_μ^s and u_{ij}^s. We denote the dynamical coordinates of the zone-boundary M_i modes of frequency ω by $Q(\omega, M_i)$ and that for the Γ-point B_g modes by $Q(\omega, B_g)$. By simple group theoretical considerations it is found that the following components of $P_{ij}(\omega)$ may be different from zero: for M_i modes,

$$P_{ij}(\omega) = P_{ij}^{(2)}Q(\omega, M_1)Q_\mu^s \quad \text{with } i = x, y \text{ and } j = z,$$
$$P_{ii}(\omega) = P_{ii}^{(2)}Q(\omega, M_2)Q_\mu^s \quad \text{with } i = x, y, z; \quad (12)$$

and for B_g-modes,

$$P_{yz}(\omega) = P_0 Q(\omega, B_g)(u_{xx}^s - u_{yy}^s),$$
$$P_{xz}(\omega) = -P_0 Q(\omega, B_g)2u_{xy}^s,$$

where $P_{ij}^{(2)}$ and P_0 are expansion coefficients which are assumed to be independent of the temperature. The Raman scattering in the ferroelastic phase by the M_i modes may be considered as two-phonon scattering: The soft-mode contributes to this second-order process with zero frequency, however it acts to compensate the wave vector $\vec{q}_M$ of the dynamical zone-boundary coordinate so that the Raman polarizability becomes a homogeneous function in space.

For the scattered intensity we can write

$$I \propto \langle |e_i^i P_{ij}(\omega)e_j^s|^2 \rangle_T,$$

where e_i^i and e_j^s are the unit vectors of the polarization of the incident and scattered radiation, respectively, and $\langle \ \rangle_T$ denotes thermal averaging. Noting that for a dynamical phonon coordinate $\langle |Q(\omega)|^2 \rangle_T$ is proportional to the Bose population factor $n(\omega) + 1$, we obtain the reduced intensity $I_{red} = I/[n(\omega) + 1]$ in the ferroelastic phase as a function of $\eta(T)$ by inserting in Eq. (12) Q_μ^s from Eq. (7) and u_{ij}^s from Eq. (11):

$$I_{red} \propto \begin{cases} \eta^2(T) & \text{for } M_i \text{ modes} \\ \eta^4(T) & \text{for } B_g \text{ modes.} \end{cases} \quad (13)$$

This shows that the temperature variation of a
mode, which is activated by the phase transition
at the zone-boundary M point is different from that
of a mode activated at the zone center.

The temperature dependences of the reduced peak
intensities of the lines C, E, and F are shown in
Fig. 4. We have fitted the measured values by us-
ing Eq. (13) and using the expression (9) for $\eta(T)$.
The temperature interval $\Delta T = T_1 - T_0$ and the pro-
portionality constant of Eq. (13) have been varied.
The results shown by the solid lines in Fig. 4
agree rather well with the experimental points.
The intensity of the A_g line C is found to be propor-
tional to $\eta^2(T)$ and, thus, line C results from an
M_2-zone-boundary phonon of the hexagonal struc-
ture. Both B_g lines E and F are best described by
$\eta^4(T)$ and are therefore Raman-inactive optical
phonons at the Γ point above the phase transition.
The temperature interval ΔT, which gives the ex-
tent of the metastability region where both phases
may coexist, turned out to be as small as 1 K.
This result agrees well with the value of ΔT, de-
rived from the temperature dependence of the op-
tical birefringence in the monoclinic plane.[17] It
can be shown that the birefringence varies like
$\eta^2(T)$.

VI. CONCLUSION

By investigating the temperature dependence of
the low-frequency Raman spectra of ferroelastic
Sb_5O_7I and discussing the symmetry properties of
the crystal we have proved that the phase transi-
tion in Sb_5O_7I is of antiferrodistortive nature. The
experimental results confirm our explanation of
the phase transition to be induced by a zone-bound-
ary mode belonging to the factor group representa-
tion M_2. On account of the knowledge of all atomic
positions in the prototypic phase[5] it was shown that
actually there exist 16 phonon modes of this sym-
metry.[3] Clearly the softening of one of these pho-
nons can only be established by inelastic neutron
scattering.

From a free-energy expansion compatible with
the symmetry of the high-temperature phase the
relation between the spontaneous strain and the
order parameter has been derived. It has been
shown that the temperature variation of the order
parameter $\eta(T)$, as determined from the intensities
of the Raman lines C, E, and F is best described
assuming that $\eta(T)$ behaves according to the Landau
theory for weakly discontinuous phase transitions.
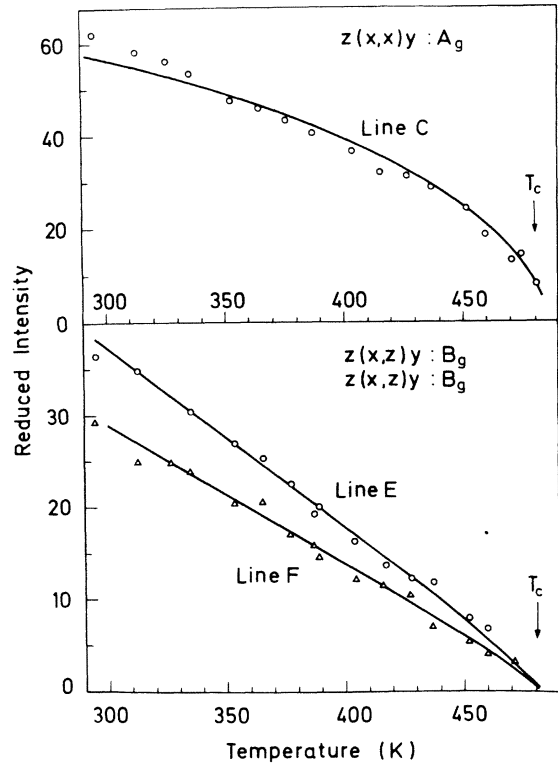A second-order transition can obviously be ruled

FIG. 4. Temperature dependence of the reduced inten-
sity $I_{red} = I/[n(\omega) + 1]$ for the lines C, E, and F. The
circles and triangles are experimentally determined
values, the full lines are best-fit curves according to
Eq. (13).

out, because the temperature dependence of line
C in particular cannot be described by $\eta^2 \propto T_c - T$
over a substantial temperature range as it would
be necessary if this were the case.

Note added. Crystallographic investigations by
V. Krämer have shown that Sb_5O_7I crystallizes in
several different crystal structures all having the
same chemical composition and being ferroelastic
in the low-temperature phase. The crystal studied
in the present work is now called α-Sb_5O_7I and is
most frequently found in the crystal growing pro-
cess employed by Krämer *et al.*[2]

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