Elastic anomalies due to structural phase transitions in mechanoluminescent $\text{SrAl}_2\text{O}_4\text{:Eu}$

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Elastic and anelastic properties of a ceramic sample of elasticoluminescent $\text{SrAl}_2\text{O}_4\text{:Eu}$ have been characterized as a function of temperature by resonant ultrasound spectroscopy. Both the bulk (K) and shear (G) moduli show changes attributable to the influence of the $P6_322 \rightarrow P6_3 (\sqrt{3}A) \rightarrow P2_1$ sequence of structural phase transitions. Softening of K and stiffening of G at the $P6_322 \rightarrow P6_3 (\sqrt{3}A)$ transition ($T_c \approx 1135$ K) is consistent with weak strain/order parameter coupling and tricritical character. In marked contrast, the first order $P6_3 (\sqrt{3}A) \rightarrow P2_1$ transition near 930 K is accompanied by stiffening such that G is $\sim 50\%$ larger at room temperature than the value for a $P6_322$ structure extrapolated directly from high temperatures and K is $\sim 15\%$ larger. Softening of G at high temperatures is consistent with the existence of a soft acoustic mode. Both the $P6_3 (\sqrt{3}A)$ and $P6_322$ phases show an increasing acoustic dissipation with increasing temperature and there is an additional peak in the dissipation behavior below ~ 650 K. Landau theory has been used to analyze the overall strain and elastic behavior of $\text{SrAl}_2\text{O}_4\text{:Eu}$. The stability of the $P2_1$ structure is considered in terms of coupling between order parameters with Γ_6 and M_2 symmetry, though it could also be stabilized by pairwise coupling of order parameters corresponding to irreps $\Gamma_4 + M_2$, $\Gamma_4 + M_3$, $\Gamma_6 + M_3$, and $M_2 + M_3$. Twin walls in this material should have interesting properties, which are quite distinct from those of the bulk material and could contribute differently to the elasticoluminescent properties. © 2010 American Institute of Physics.

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I. INTRODUCTION

Stuffed tridymite structures can be prepared with a wide range of chemical compositions and are well known for their tendency to undergo structural phase transitions. These two characteristics lead to possibilities for developing materials with a diversity of ferroic properties relevant for technological applications. Eu^{2+} -doped SrAl_2O_4 is just such a material and has attracted attention for its elasticoluminescence behavior—emission of visible light induced by a weak elastic stress.^{1–7} The mechanoelectro-optical properties of interest are associated with changes in the local electronic structure due to strain fields induced by the application of an external stress or electric field.^{2,3,6,7} In this context, strain and elastic properties of the host SrAl_2O_4 must have a significant bearing on the overall optical behavior.^{7–9} The purpose of the present study was to determine the temperature dependence of bulk and shear moduli of a ceramic sample of $\text{SrAl}_2\text{O}_4\text{:Eu}$ and their sensitivity to the structural phase transitions which occur near ~ 950 and ~ 1130 K.

At room temperature, SrAl_2O_4 is monoclinic, with $P2_1$ space group,^{10,11} and at high temperatures, it is hexagonal, with $P6_322$ space group.¹² Structural phase transitions occur between these two structure types during cooling.^{7,12–16} Fol-

lowing the report of an intermediate structure with $P6_3$ space group and unit cell with a -dimension $\sqrt{3}$ times that of the $P6_322$ parent structure,¹⁷ Avdeev *et al.*¹⁶ determined the transition sequence with falling temperature to be $P6_322 \rightarrow P6_3 (\sqrt{3}A) \rightarrow P2_1$. The first transition is at ~ 1130 K and appears to be continuous, while the second, near ~ 950 K, is first order in character. The latter is marked by a field of two-phase coexistence and significant hysteresis. We make use of resonant ultrasound spectroscopy (RUS) to measure the elastic and anelastic properties as a function of temperature through these transitions and Landau theory to relate the observed elastic anomalies to strain and order parameter variations.

II. SAMPLE PREPARATION

Strontium aluminate powders were synthesized using a modified base-catalyzed sol-gel process. The composition was $\text{Sr}_{0.99}\text{Eu}_{0.01}\text{Al}_2\text{O}_4$. 163.40 g of aluminum triisopropoxide $[\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3]$, 84.64 g of $\text{Sr}(\text{NO}_3)_3$, and 1.56 g of $\text{Eu}(\text{NO}_3)_3 \cdot 2.9\text{H}_2\text{O}$ were dissolved in 400 ml of 0.5M dilute ammonium hydroxide. $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$ slowly hydrolyzed at 40 °C under the action of the base catalysis and formed $\text{Al}(\text{OR})_{3-x}(\text{OH})_x (\text{R}=i\text{-C}_3\text{H}_7)$. This condensation reaction led to the formation of a polymeric local structure within the sol particles with a $\text{Sr}(\text{Eu})\text{--O--Al}$ bond. Subsequently, 200 ml of N,N -dimethylformamide was added to

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FIG. 1. Dielectric permittivity of $\text{Sr}_{0.99}\text{Eu}_{0.01}\text{Al}_2\text{O}_4$ measured at 1 kHz, 1 V during heating.

the sol solution to coat the sol particles, vary their surface activity, and effectively control the particle growth. The resultant sol solution was then heated at 148 °C and dried at 200 °C before completely gelling, giving homogeneous small gel particles with an organic coating. These dry gel particles were heat treated in air at 700 °C to remove the organic and inorganic groups, followed by sintering at 1300 °C for 2 h in a reducing atmosphere of 5% H_2 – N_2 to crystallize and form the luminescent centers. On the basis of scanning electron microscopy observation, the size of the particles prepared using this process was approximately 1–2 μm . The particles were finally pressed into a pellet and resintered at 1300–1400 °C.

III. DIELECTRIC PERMITTIVITY

The final pressed pellet was polished and coated with platinum paste to form a parallel plate capacitor. The dielectric permittivity of the resultant $\text{Sr}_{0.99}\text{Eu}_{0.01}\text{Al}_2\text{O}_4$ sample was then measured as a function of temperature using a computer controlled system, including a TH2816 LCR meter (Tonghui Electronic Instrument Corp. China), an SRS PS350 high voltage generator (Stanford Research System Corp., USA), a Delta Design 9023 environmental box (Delta Design Corp., USA), a self-designed high voltage protection circuit, and an IEEE 488 bus (IEEE standard) for interconnection. The measured dielectric permittivity at 1 kHz and 1 V, as obtained during a heating sequence, is shown in Fig. 1. The main features are a peak between ~850 and ~1000 K with its maximum at 931 K, in the vicinity of the known first order phase transition of pure SrAl_2O_4 ,^{13,14,16} and a weaker anomaly at ~650 K.

IV. RESONANT ULTRASOUND SPECTROSCOPY

A. Experimental

Part of the original pressed SrAl_2O_4 :Eu pellet was sawn into a rectangular parallelepiped with dimensions of $2.157 \times 4.118 \times 4.602 \text{ mm}^3$ using a high precision annular diamond saw. Its mass was 0.1215 g, giving a calculated density of 2.972 g cm^{-3} . The theoretical density based on the composition $\text{Sr}_{0.99}\text{Eu}_{0.01}\text{Al}_2\text{O}_4$ and room temperature lattice parameters of Avdeev *et al.*¹⁶ is 3.493 g cm^{-3} , implying a porosity of ~18%. The sample had a pale green/yellow color at

the start. After RUS data collection at high temperatures, which involved heating in air up to 1353 K, it was white.

The high temperature RUS equipment used for data collection has been described in detail by McKnight *et al.*¹⁸ The SrAl_2O_4 :Eu sample was mounted across its corners between the tips of horizontally mounted alumina rods within a Netsch 1600 °C furnace. Lead-zirconate-titanate (PZT) transducers for generating the acoustic signal and detecting resonances of the sample were attached to the ends of the rods outside the furnace. Temperature was recorded using a thermocouple located a few millimeters away from the sample and a small correction applied to this, based on calibration against the α - β transition point in quartz.¹⁹ Spectra were collected using dynamic resonance system M³odulus II electronics.

Room temperature values of bulk (K) and shear (G) moduli were obtained by fitting to the frequencies of 25 resonance peaks using the software described by Migliori *et al.*²⁰ This gave $K=44.7$, $G=27.7 \text{ GPa}$, with a rms error of 0.6%. Chi-squared values increased by 2% following changes in the values of K and G by ~0.6 and 0.06 GPa, respectively. These values of K and G give Young's modulus and Poisson's ratio values of 68.9 GPa and 0.24, respectively. The high porosity of the sample accounts for the relatively low values of K , in comparison with the value of 86 GPa calculated by Yamada and Xu,⁸ and Young's modulus, in comparison with 102 GPa measured by Nanko *et al.*⁹ for a dense ceramic (3.5 g cm^{-3}). The value of Poisson's ratio is within the experimental uncertainty of the value given by Nanko *et al.*⁹ (0.23).

High temperature spectra were collected in the frequency range 50–1200 kHz, with a resolution in frequency of 0.023 kHz (50 000 data points). On the basis of the transition temperatures reported by Avdeev *et al.*,¹⁶ automated heating and cooling sequences were chosen such that the spectra were collected at 30 K intervals from room temperature to ~914 K, at 5 K intervals in the range of 914–964, at 15 K intervals for 964–1003 K, at 5 K intervals for 1003–1161 K, and at 15 K intervals for 1161–1358 K. 15 min was allowed for thermal equilibration before data collection at each temperature. All spectra were transferred to the software package IGOR PRO (Wavemetrics) for analysis. Experience of the high temperature RUS instrument has shown that the strongest resonance peaks are obtained after the sample has reached its highest temperature. This is presumably due to improved mechanical contact between a parallelepiped and the alumina rods as a consequence of some slight rounding of its corners. The spectra collected during cooling were selected for a detailed analysis, therefore.

The frequencies of 20–25 peaks could be obtained by inspection from each spectrum collected between room temperature and 1060 K in the cooling sequence. These were used to obtain fit values for K and G , with rms errors for the full fits of ~0.6%–0.7%. No adjustment was made for thermal expansion on the dimensions of the parallelepiped when making the fits, but any changes in the values obtained would be small in comparison with the changes in elastic properties due to the phase transitions. The frequencies of only eight peaks could be measured at the three highest tem-

FIG. 2. (a) Resonance frequencies, f , and (b) inverse mechanical quality factor, Q^{-1} , as a function of temperature for three resonances in the spectra collected during cooling from 1355 K to room temperature.

peratures. Values of K obtained from these were clearly anomalous, but the values of G appeared to be consistent with all the other data and the rms errors were no worse. Between ~ 1060 and ~ 1300 K, the number of measurable peaks declined from 20 to 9, but the values obtained for both G and K appeared to be consistent with the results from fits using 20–25 peak frequencies, and the highest rms error was 0.8%. In all cases, G was more tightly constrained than K , owing to the fact that most of the resonances were predominantly shear modes. Three peaks in the frequency range of ~ 200 – 500 kHz from all the spectra in the cooling sequence were also fitted with an asymmetric Lorentzian function,¹⁹ in order to determine their frequency, f , and width at half maximum height, Δf . The mechanical quality factor Q was determined as $Q = f/\Delta f$. The software for calculating the resonance behavior indicated that these peaks are determined by $\sim 100\%$ G for the lowest frequency peak, $\sim 50\%$ $G + \sim 50\%$ K for the middle peak, and $\sim 80\%$ $G + \sim 20\%$ K for the highest frequency peak of the three.

B. Results

Several distinctive features were immediately apparent from the raw spectra. With falling temperature, a slight shift in peak frequencies to higher values started to develop below ~ 1100 K and a substantially greater increase in frequencies occurred below ~ 930 K. Peak widths clearly reduced from the highest temperatures down to ~ 1100 K but significant peak broadening was then apparent also below ~ 600 K. The change in trend for frequencies at ~ 1100 K was too subtle to allow the determination of whether there was any hysteresis. These qualitative observations were confirmed for the cooling sequence by the frequency [Fig. 2(a)] and Q^{-1} [Fig. 2(b)]

FIG. 3. Variations in K and G , obtained by fitting of up to 25 resonance frequencies. The three highest temperature data points are unreliable as they were determined from only eight frequencies. Straight lines are fits to data in the stability field of the $P6_322$ structure to estimate the bulk and shear moduli variations (K_0, G_0) if no phase transitions occurred. G_0 shows a slight softening with falling temperature consistent with it containing contributions from a soft acoustic mode.

variations for three peaks. The measured frequencies reveal an additional, more subtle change in trend below ~ 600 K.

Values of K and G obtained by fitting to the resonance frequencies are shown as a function of temperature in Fig. 3. Data for K at the three highest temperatures are unreliable, owing to the small number of peak frequencies used to achieve the fit, but below 1320 K, they show a well-defined pattern. Slight stiffening, linear with temperature, occurs down to ~ 1135 K whereupon softening by up to $\sim 8\%$ takes place. A return of gradual stiffening continues down to ~ 930 K, where a much steeper and apparently continuous change occurs. At room temperature, the value of K is $\sim 15\%$ greater than the value which would be obtained by a linear extrapolation of data from the interval of 1135–1320 K.

The shear modulus decreases slightly in a linear manner (within experimental error) with falling temperature between 1320 and 1135 K, before showing a slight, nonlinear stiffening of up to $\sim 5\%$ by 930 K. Below 930 K, the pattern of stiffening is essentially the same as for the bulk modulus, though the room temperature value is $\sim 50\%$ larger than the value extrapolated directly from the data in the temperature interval of 1135–1320 K. There is also a subtle but distinct break in slope at ~ 600 K, which is not apparent in the data for K .

Relatively high attenuation ($Q^{-1} \approx 0.006$ – 0.012) occurred at the highest temperatures and reduced steadily with falling temperature [Fig. 2(b)]. A steady low level (~ 0.001) was reached at ~ 900 K and the data then show an increase below ~ 650 K. The low temperature anomaly peaks at ~ 0.005 – 0.010 between 350 and 400 K. Superimposed on this general trend appear to be peaks at and just below ~ 1130 K. They coincide with the break in slope shown by the elastic properties but should be regarded with some skepticism because the resonance peaks in this part of the spectra at these temperatures overlap with noise peaks from the alumina rods in the RUS instrument.

The most obvious changes in the trend of the bulk and shear moduli observed in the present study correlate with the

FIG. 4. Schematic form of the anomalies expected to occur in a single crystal elastic constant, C , as a consequence of strain/order parameter coupling or of some Debye relaxation process. (a) Single crystal elastic constant due to strain coupling of the form λeq^2 at a second order transition, (b) λeq^2 coupling, tricritical transition, (c) λeq coupling, first order transition. (d) Debye-type anomaly in C and Q^{-1} , due to interaction between a dynamic stress and defects (usually shown as a function of frequency rather than temperature).

transition temperatures reported by Avdeev *et al.*¹⁶ ~ 1133 K for the $P6_322 \leftrightarrow P6_3 (\sqrt{3}A)$ transition and a two-phase field between 945 and 957 K during cooling through the $P6_3 (\sqrt{3}A) \leftrightarrow P2_1$ transition. Henderson and Taylor¹³ reported a two-phase field between 968 and 928 K, which overlaps with the temperature of the steep increase in K and G observed here. Presumably, there are differences between samples due to crystallinity, grain size, defect content, etc., as well as between experimental heating/cooling rates, which are sufficient to change the precise transition temperatures.

V. ANALYSIS

Rodehorst *et al.*¹⁵ were the first to point out that a direct phase transition from a structure with $P6_322$ space group to one with $P2_1$ space group (and with the 2_1 axis oriented perpendicular to the former 6_3 axis) cannot occur by the normal operation of a single order parameter. They suggested that an intermediate structure with space group $C2$ might be stable between ~ 500 K and the hexagonal $\leftrightarrow$ monoclinic transition at ~ 960 K. The lower temperature was proposed on the basis of the observed anomalies in powder absorption IR spectra between ~ 450 and 600 K at Ba-rich compositions in the SrAl_2O_4 – BaAl_2O_4 solid solution and a smaller anomaly in SrAl_2O_4 near 550 K. The RUS data for K and G clearly match up with the later diffraction results of Avdeev *et al.*,¹⁶ but also confirm that there is indeed some additional relaxation process occurring in SrAl_2O_4 at about the temperature suggested by Rodehorst *et al.*¹⁵ The pattern of elastic behavior is considered here in terms of the light of both sets of observations, dividing into four temperature intervals: 1320–1130, 1130–930, 930–650, and 650–300 K. For comparative purposes, Fig. 4 shows some characteristic patterns of elastic anomalies, which can occur in single crystal elastic constants as a consequence of strain/order parameter coupling at displacive phase transitions, which are second order and improper ferroelastic or coelastic in character [Fig. 4(a)], tricritical and improper ferroelastic or coelastic [Fig. 4(b)], or first order and pseudoproper ferroelastic [Fig. 4(c)] (see Refs. 21–23, for example). The distinct pattern of attenuation and

stiffening that accompanies a Debye relaxation process,²⁴ without a change in the equilibrium structure, is shown in Fig. 4(d).

A. 1320–1130 K

The small increase in bulk modulus with falling temperature above ~ 1130 K is consistent with the normal effects of the thermal expansion. The $P2_1$ phase that appears at lower temperatures is a proper ferroelastic material, however, and bilinear coupling between the symmetry breaking strain, e_4 , and the driving order parameter responsible for its stability would be expected to give rise to softening of an acoustic mode as the transition point is approached from above. The relevant elastic constant is C_{44} , which would contribute to the shear modulus. A small degree of softening of the shear modulus is observed in the stability field of the $P6_322$ structure, consistent with this being the para phase of the $P2_1$ ferroelastic phase, as proposed by Perez-Mato *et al.*²⁵

Increasing dissipation at high temperatures [Fig. 2(b)] can arise simply by anelastic motion of grain boundaries.²⁶ This would not necessarily be detectable at frequencies as high as ~ 1 MHz and the onset of increased attenuation for the case of ceramic SrAl_2O_4 :Eu coincides almost exactly with the phase transition at ~ 930 K. As discussed below, a more likely explanation is a dissipation mechanism that involves dynamic coupling of strain with defects or some collective atomic motions.

B. 1130–930 K

Softening of K and stiffening of G below ~ 1130 K are taken to be due to the $P6_322 \leftrightarrow P6_3 (\sqrt{3}A)$ transition. The driving order parameter is associated with irrep K_2 of the $P6_322$ space group, and the full Landau expansion derived using ISOTROPY (Ref. 27) would be

$$G = \frac{1}{2}a(T - T_c)(q_1^2 + q_2^2) + \frac{1}{4}b(q_1^2 + q_2^2)^2 + \frac{1}{6}c(q_1^2 + q_2^2)^3 + \frac{1}{6}c'(11q_1^6 + 15q_1^4q_2^2 + 45q_1^2q_2^4 + 9q_2^6) + \lambda_1(e_1 + e_2) \times (q_1^2 + q_2^2) + \lambda_3e_3(q_1^2 + q_2^2) + \lambda_4(e_4^2 + e_5^2)(q_1^2 + q_2^2) + \lambda_5[(e_1 - e_2)^2 + e_6^2](q_1^2 + q_2^2) + \frac{1}{4}(C_{11}^0 + C_{12}^0)(e_1 + e_2)^2 + \frac{1}{4}(C_{11}^0 - C_{12}^0)(e_1 - e_2)^2 + C_{13}^0(e_1 + e_2)e_3 + \frac{1}{2}C_{33}^0e_3^2 + \frac{1}{2}C_{44}^0(e_4^2 + e_5^2) + \frac{1}{2}C_{66}^0e_6^2, \quad (1)$$

where the order parameter components $q_1 \neq 0$, $q_2 = 0$ give the $P6_3 (\sqrt{3}A)$ structure, e_1 – e_6 are spontaneous strains, λ_1 – λ_5 are coupling coefficients, and C_{ik}^0 are elastic constants of the parent $P6_322$ structure. Standard manipulations (e.g., Refs. 23 and 28) give nonzero strains scaling with q_1 and q_2 according to

$$(e_1 + e_2) = \left[\frac{2\lambda_3C_{13}^0 - 2\lambda_1C_{33}^0}{(C_{11}^0 + C_{12}^0)C_{33}^0 - 2C_{13}^0{}^2} \right] (q_1^2 + q_2^2), \quad (2)$$

$$e_3 = \left[\frac{2\lambda_1 C_{13}^0 - \lambda_3 (C_{11}^0 + C_{12}^0)}{(C_{11}^0 + C_{12}^0) C_{33}^0 - 2C_{13}^0} \right] (q_1^2 + q_2^2). \quad (3)$$

The elastic constants of the $P6_3$ ($\sqrt{3}A$) structure would be expected to evolve as

$$C_{11} = C_{22} = (C_{11}^0 + 2\lambda_5 q_1^2) - 4\lambda_1^2 q_1^2 \left(\frac{\partial^2 G}{\partial q_1^2} \right)^{-1}, \quad (4)$$

$$C_{33} = C_{33}^0 - 4\lambda_3^2 q_1^2 \left(\frac{\partial^2 G}{\partial q_1^2} \right)^{-1}, \quad (5)$$

$$C_{12} = (C_{12}^0 - 2\lambda_5 q_1^2) - 4\lambda_1^2 q_1^2 \left(\frac{\partial^2 G}{\partial q_1^2} \right)^{-1}, \quad (6)$$

$$C_{13} = C_{23} = C_{13}^0 - 4\lambda_1 \lambda_3 q_1^2 \left(\frac{\partial^2 G}{\partial q_1^2} \right)^{-1}, \quad (7)$$

$$C_{44} = C_{55} = C_{44}^0 + 2\lambda_4 q_1^2, \quad (8)$$

$$(C_{11} - C_{12}) = 2C_{66} = (C_{11}^0 - C_{12}^0) + 4\lambda_5 q_1^2. \quad (9)$$

The lattice parameter data of Avdeev *et al.*¹⁶ for the stability field of the $P6_3$ ($\sqrt{3}A$) structure (a, c) show nonlinear deviations from the linear trends established in the stability field of the $P6_322$ structure (a_0, c_0). These give a volume strain ($V_s = 2e_1 + e_3$) at ~ 950 K of ~ -0.002 , which arises primarily from a contraction along the direction of the crystallographic c -axis ($e_3 = (c - c_0)/c_0 \approx -0.0028$) and a small extension in the (001) plane ($e_1 = e_2 = (a - a_0)/a_0 \approx 0.0003$). The nonlinear strain evolution with temperature is confirmed by dilatometric data also given by Avdeev *et al.*,¹⁶ and the nonlinearity implies that order parameter evolution includes some contribution from the q_1^6 terms. The bulk modulus depends on contributions from C_{11} , C_{22} , C_{12} , and C_{13} , and the observed variation (Fig. 3) has the form shown for tricritical character in Fig. 4(b). The shear modulus of both structures depends substantially on C_{44} and C_{66} , so that the difference, $(G - G_0)$, where G is the shear modulus of the $P6_3$ ($\sqrt{3}A$) structure and G_0 is the shear modulus of the $P6_322$ structure (Fig. 3), is expected to include significant contributions which scale with q_1^2 . In this case, $(G - G_0)^2 (\propto q_1^4)$ would be proportional to $(T_c - T)$ for a tricritical transition, and this provides an adequate description of the data ($T_c \approx 1118$ K; Fig. 5). The $P6_322 \leftrightarrow P6_3$ ($\sqrt{3}A$) transition thus appears to be entirely consistent with the behavior expected for a displacive transition which is close to tricritical in character and has weak coupling of the order parameter to the strain.

Neither of the $P6_322$ or $P6_3$ ($\sqrt{3}A$) structures is expected to contain a microstructure, such as ferroelastic twin walls, which would be displaced by the application of an external stress. The increase in dissipation with increasing temperature from ~ 930 K must be due to coupling between the applied stress and other defects or some collective atomic displacements within the two structures. [Note that the anomaly below ~ 1130 K, which is additional to the general trend could be an artifact and its magnitude is certainly not as great as implied by the results shown in Fig. 2(b)]. A feature common to both structures is the tilting of AlO_4 tet-

FIG. 5. $(G - G_0)^2$ varies linearly with temperature between ~ 930 and 1118 K, where G is the measured shear modulus of the $P6_3$ ($\sqrt{3}A$) structure and G_0 is the value for the $P6_322$ structure extrapolated to lower temperatures (see Fig. 3). If $(G - G_0)$ scales with q_1^2 , the result implies $q_1^4 \propto (T_c - T)$, i.e., close to tricritical character, for a $P6_322 \leftrightarrow P6_3$ ($\sqrt{3}A$) transition with $T_c = 1118$ K.

rahedra such that the apical oxygen between successive sheets is located away from the three-fold symmetry axis (e.g., see Fig. 9 of Ref. 16). The phase transition can then be understood in terms of ordering of the tilt axes such that the apical oxygen is ordered at one of the three possible off-axis positions below T_c and disordered between three positions above T_c . The energy barrier between these three positions is likely to be small so that flipping between sites might occur through application of an external stress at RUS frequencies. With falling temperature, the thermal energy available to overcome the barrier reduces, and the off-axis positions might be effectively locked in once the symmetry is reduced by the $P2_1$ order parameters.

C. 930–650 K

Perez-Mato *et al.*²⁵ analyzed the structure relations among SrAl_2O_4 polymorphs from a group theoretical point of view. They determined that $P6_3$ ($\sqrt{3}A$) is not a supergroup of $P2_1$ and that the para phase, when considering the development of order parameters in the $P2_1$ structure, should be taken as $P6_322$. Table I lists all the irreps and nonzero order parameter components for the relevant $P2_1$ structure, which retains only the screw diad parallel to hexagonal $[210]$, i.e.,

TABLE I. All order parameters and their individual symmetries within $P2_1$ space group for basis vectors $(0, -1, 0)$, $(2, 1, 0)$, $(0, 0, 1)$ and origin $(0, -1/4, 1/4)$ with respect to a parent structure with $P6_322$ space group. Non-zero tensor properties are indicated by the nonzero basis functions.

Irrep	Order parameter components (Γ_6)	Subgroup	Nonzero basis functions
Γ_1	(a)	$P6_322$	$x^2 + y^2; z^2$
Γ_4	(a)	$P312$	
Γ_5	$(a, 0)$	$C222_1$	$x^2 - y^2$
Γ_6	$(a, 0)$	$C2$	$x; S_x; yz$
M_2	$(a, 0, 0)$	$P2_12_12_1$	
M_3	$(a, 0, 0)$	$P2_12_12$	

TABLE II. Order parameter components relating to irreps Γ_6 and M_2 of $P6_322$ space group using the notation of ISOTROPY. Note that there are two different structures with $C2$ space group and three with $P2_1$ space group. SrAl_2O_4 has $(a,0)$ for its Γ_6 order parameter.

Subgroup	Continuous	Order parameter components (Γ_6)	Order parameter components (M_2)	Basis vectors	Origin
$C2$	No	$(a,0)$	$(0,0,0)$	$(0,-1,0), (2,1,0), (0,0,1)$	$(0,0,1/4)$
$C2$	No	$(0,a)$	$(0,0,0)$	$(2,1,0), (0,1,0), (0,0,1)$	$(0,0,0)$
$P1$	No	(a,b)	$(0,0,0)$	$(1,0,0), (0,1,0), (0,0,1)$	$(0,0,0)$
$P2_12_12_1$	Allowed	$(0,0)$	$(a,0,0)$	$(2,1,0), (0,1,0), (0,0,1)$	$(1/2, 1/4, 1/4)$
$C222_1$	No	$(0,0)$	$(a,a,0)$	$(2,0,0), (2,4,0), (0,0,1)$	$(0,1,0)$
$P6_3$	Allowed	$(0,0)$	(a,a,a)	$(2,0,0), (0,2,0), (0,0,1)$	$(0,0,0)$
$P2_1$	No	$(0,0)$	(a,b,c)	$(0,2,0), (0,0,1), (2,0,0)$	$(0,0,0)$
$P2_1$		$(a,0)$	$(b,0,0)$	$(0,-1,0), (2,1,0), (0,0,1)$	$(0,-1/4, 1/4)$
$P2_1$		$(0,a)$	$(b,0,0)$	$(2,1,0), (0,1,0), (0,0,1)$	$(1/2, 1/4, 0)$
$P1$		(a,b)	$(c,0,0)$	$(2,0,0), (0,1,0), (0,0,1)$	$(0,0,0)$
$C2$		$(a,0)$	$(0,b,b)$	$(0,-2,0), (4,2,0), (0,0,1)$	$(1,0, 1/4)$
$C2$		$(0,a)$	$(0,b,b)$	$(4,2,0), (0,2,0), (0,0,1)$	$(1,1,0)$
$P1$		(a,b)	(c,d,e)	$(2,0,0), (0,2,0), (0,0,1)$	$(0,0,0)$

perpendicular to both c - and a -axes of the hexagonal parent. Perez-Mato *et al.*²⁵ further showed that the largest displacements are those associated with irreps Γ_6 and M_2 . Here, the symmetry reduction is therefore assumed to be due to the combined operation of order parameter components associ-

ated with irreps Γ_6 and M_2 , with Γ_1 , Γ_4 , Γ_5 , and M_3 developing by coupling with these. The full Landau expansion for Γ_6 and M_2 as driving order parameters and coupling with strains, as obtained using ISOTROPY,²⁷ is

$$\begin{aligned}
 G = & \frac{1}{2}a_{\Gamma}(T - T_{c\Gamma})(q_{\Gamma 1}^2 + q_{\Gamma 2}^2) + \frac{1}{4}b_{\Gamma}(q_{\Gamma 1}^2 + q_{\Gamma 2}^2)^2 + g_1\left(\frac{\partial q_{\Gamma 1}}{\partial x} + \frac{\partial q_{\Gamma 2}}{\partial y}\right) + g_2\left(q_{\Gamma 1}\frac{\partial q_{\Gamma 2}}{\partial z} - q_{\Gamma 2}\frac{\partial q_{\Gamma 1}}{\partial z}\right) + \lambda_{\Gamma 1}(e_1 + e_2)(q_{\Gamma 1}^2 + q_{\Gamma 2}^2) \\
 & + \lambda_{\Gamma 2}e_3(q_{\Gamma 1}^2 + q_{\Gamma 2}^2) + \lambda_{\Gamma 3}[(e_1 - e_2)(q_{\Gamma 1}^2 - q_{\Gamma 2}^2) + 4e_6q_{\Gamma 1}q_{\Gamma 2}] + \lambda_{\Gamma 4}(e_4q_{\Gamma 1} - e_5q_{\Gamma 2}) + \frac{1}{2}a_M(T - T_{cM})(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2) \\
 & + \frac{1}{4}b_M(q_{M 1}^4 + q_{M 2}^4 + q_{M 3}^4) + \frac{1}{4}b'_M(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2)^2 + \lambda_{M 1}(e_1 + e_2)(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2) + \lambda_{M 2}e_3(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2) \\
 & + \lambda_{M 3}\left[(e_1 - e_2)\left(q_{M 1}^2 - \frac{1}{2}q_{M 2}^2 - \frac{1}{2}q_{M 3}^2\right) + \frac{\sqrt{3}}{2}e_6(q_{M 3}^2 - q_{M 2}^2)\right] + \lambda_{M 4}(e_4^2 + e_5^2)(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2) + \lambda_{M 5}\left[e_4^2\left(q_{M 1}^2 + \frac{1}{4}q_{M 2}^2\right.\right. \\
 & \left. + \frac{1}{4}q_{M 3}^2\right) + \frac{\sqrt{3}}{2}e_4e_5(q_{M 2}^2 - q_{M 3}^2) + \frac{3}{4}e_5^2(q_{M 2}^2 + q_{M 3}^2)\left. + \lambda_q(q_{\Gamma 1}^2 + q_{\Gamma 2}^2)(q_{M 1}^2 + q_{M 2}^2 + q_{M 3}^2) + \lambda'_q\left[q_{\Gamma 1}^2\left(q_{M 1}^2 + \frac{1}{4}q_{M 2}^2 + \frac{1}{4}q_{M 3}^2\right)\right.\right. \\
 & \left. + \frac{\sqrt{3}}{2}q_{\Gamma 1}q_{\Gamma 2}(q_{M 3}^2 - q_{M 2}^2) + \frac{3}{4}q_{\Gamma 2}^2(q_{M 2}^2 + q_{M 3}^2)\right] + \frac{1}{4}(C_{11}^0 + C_{12}^0)(e_1 + e_2)^2 + \frac{1}{4}(C_{11}^0 - C_{12}^0)(e_1 - e_2)^2 + C_{13}^0(e_1 + e_2)e_3 \\
 & + \frac{1}{2}C_{33}^0e_3^2 + \frac{1}{2}C_{44}^0(e_4^2 + e_5^2) + \frac{1}{2}C_{66}^0e_6^2.
 \end{aligned} \tag{10}$$

The subscript Γ indicates parameters related to irrep Γ_6 and subscript M indicates parameters related to irrep M_2 . Gradient terms are permitted by symmetry for order parameter components belonging to Γ_6 and have been given coefficients g_1, g_2 .

The sequence of structure types in a transformation hierarchy will depend, in the first instance, on the relative temperatures of the two primary instabilities. All possibilities are

given in the form of different subgroups and nonzero order parameters components in Table II. A transformation hierarchy between these is given in Fig. 6. Considering only pathways which lead to the reported $P2_1$ structure, with $(a,0)$ for the Γ_6 order parameter, the sequence would be $P6_322 \leftrightarrow C2 \leftrightarrow P2_1$ if the Γ_6 instability occurs first or $P6_322 \leftrightarrow P2_12_12_1 \leftrightarrow P2_1$ if the M_2 instability comes first. In the improbable event that both instabilities occurred at pre-

cisely the same temperature, the transition would be directly from $P6_322$ to $P2_1$. Strong coupling between the two order parameters (large λ_q, λ'_q) would also reduce the stability field of the intermediate phase. The diffraction results of Avdeev *et al.*¹⁶ show $P6_3$ ($\sqrt{3}A$), giving way to $P2_1$ without evidence for a stability field for either the $C2$ structure or the $P2_12_12_1$ structure, however. If one of these can be stable with respect to the $P6_322$ structure, it must always be metastable with respect to the $P6_3$ ($\sqrt{3}A$) structure, therefore. A $P6_322 \leftrightarrow C2$ transition is required to be first order in character due to the existence of gradient terms in the excess free energy, and would be strongly first order if the fourth order Landau coefficient is negative.

The choice of orientation applied here for the observed $P2_1$ structure ($q_{\Gamma 1} \neq q_{M1} \neq 0$, $q_{\Gamma 2} = q_{M2} = q_{M3} = 0$) has $a_m \approx a_h$, $b_m \approx \sqrt{3}a_h$, $c_m \approx c_h$, with b_m and c_m parallel to the X and Z axes, respectively, of the reference system (subscripts m and h refer to monoclinic and hexagonal unit cells). Strain/order parameter relationships for nonzero strains in the $P2_1$ structure obtained by setting $\partial G / \partial e = 0$ in the usual way, give

$$(e_1 + e_2) = \frac{(2\lambda_{\Gamma 2} C_{13}^0 - 2\lambda_{\Gamma 1} C_{33}^0)q_{\Gamma 1}^2 + (2\lambda_{M2} C_{13}^0 - 2\lambda_{M1} C_{33}^0)q_{M1}^2}{(C_{11}^0 + C_{12}^0)C_{13}^0 - 2C_{13}^0{}^2}, \quad (11)$$

$$e_3 = \frac{(2\lambda_{\Gamma 1} C_{13}^0 - \lambda_{\Gamma 2}(C_{11}^0 + C_{12}^0))q_{\Gamma 1}^2 + (2\lambda_{M1} C_{13}^0 - \lambda_{M2}(C_{11}^0 + C_{12}^0))q_{M1}^2}{(C_{11}^0 + C_{12}^0)C_{33}^0 - 2C_{13}^0{}^2}, \quad (12)$$

$$(e_1 - e_2) = \frac{-(\lambda_{\Gamma 3} q_{\Gamma 1}^2 + \lambda_{M3} q_{M1}^2)}{\frac{1}{2}(C_{11}^0 - C_{12}^0)}, \quad (13)$$

$$e_4 = \frac{-\lambda_{\Gamma 4} q_{\Gamma 1}}{C_{44}^0 + 2(\lambda_{M4} + \lambda_{M5})q_{M1}^2}, \quad (14)$$

$$e_5 = e_6 = 0. \quad (15)$$

For the chosen orientation relationship, the shear strains depend on lattice parameters according to

$$(e_1 - e_2) = \frac{\frac{b_m}{\sqrt{3}} - a_m}{a_o}, \quad (16)$$

$$e_4 = \frac{c_m \cos \beta_m}{c_o} \approx \cos \beta_m, \quad (17)$$

where a_o and c_o are lattice parameters of the hexagonal ($P6_322$) phase extrapolated into the stability field of the monoclinic phase. In the limit of strong coupling between the order parameters from the two irreps [and $C_{44}^0 \gg 2(\lambda_{M4} + \lambda_{M5})q_{M1}^2$], q_{M1} would be expected to vary linearly with $q_{\Gamma 1}$ and, hence $(e_1 - e_2)$ would be expected to vary linearly with e_4^2 . The relatively low resolution lattice parameter data of Henderson and Taylor¹³ are consistent with this relationship

FIG. 6. Transformation hierarchy for a parent structure with $P6_322$ symmetry in which the order parameter(s) are associated with irreps Γ_6 and M_2 . The solid lines show group/subgroup relationships where the transition could be second order in character; the dashed lines show group/subgroup relationships where the transition can only be first order in character.

between the shear strains¹⁵ but more recent data of Yamada *et al.*⁷ for $\text{SrAl}_2\text{O}_4:\text{Eu}$ suggest that it is valid only down to ~ 600 K (Fig. 7). Linear extrapolation of a fit to data points between ~ 675 and ~ 925 K gives $(e_1 - e_2)$ having a small negative value when $e_4 = 0$. This would imply that the metastable structural sequence is $P6_322 \leftrightarrow P2_12_12_1 \leftrightarrow P2_1$, but the extrapolation is also within reasonable experimental error of passing through the origin (which would imply $P6_322 \leftrightarrow P2_1$ directly). Between ~ 675 and ~ 575 K there is then a marked deviation from this trend, which is certainly greater than the experimental uncertainty.

A complete description of the anomalies in the single crystal elastic constants which could result from the hexagonal $\rightarrow$ monoclinic sequence can be obtained in the usual way by applying

$$C_{ij} = C_{ij}^0 - \sum_{k,l} \frac{\partial^2 G}{\partial e_i \partial q_k} \cdot R_{kl} \cdot \frac{\partial^2 G}{\partial e_j \partial q_l} \quad (18)$$

from Slonczewski and Thomas²⁹ to Eq. (10), where the matrix R_{kl} is the inverse of the matrix, $\partial^2 G / \partial q_l \partial q_m$. For present purposes, it is sufficient to point out again that coupling terms of the form $\lambda e q^2$ are expected to give rise to a discontinuous softening with falling temperature through the transition point [as shown in Figs. 4(a) and 4(b) for second order and tricritical transitions]. The bulk modulus would be dominated by single crystal elastic constants, which depend on

FIG. 7. Variation in shear strains ($e_1 - e_2$) and e_4 for Eu-doped SrAl_2O_4 from Yamada *et al.* (Ref. 7). In the limit of strong coupling between Γ_6 and M_2 order parameter components, ($e_1 - e_2$) would be expected to scale with e_4^2 ; the straight line fit to high temperature data points is consistent with this, though it does not quite extrapolate through the origin. Below ~ 600 K, there is a distinct break in slope, however, which appears to be due to an increase in ($e_1 - e_2$).

this coupling but, instead of softening, shows a marked stiffening of the $P2_1$ structure with respect to the $P6_322$ structure. Implicit in the application of Eq. (18) is the assumption that relaxation of the order parameter in response to a strain induced by some external stress can occur within the time scale over which the stress is applied. If this does not occur, changes in the elastic properties would be determined by coupling terms of the form $\lambda e^2 q^2$, which are always allowed by symmetry. These imply that softening or stiffening (depending on the sign of the coupling coefficient) becomes an excess property which scales with q^2 , as in Eqs. (8) and (9). On this basis linear fits to data for G and K shown in Fig. 3 represent the properties of the $P6_322$ structure (G_o, K_o) and the differences, ($G - G_o$) and ($K - K_o$) (Fig. 8) below ~ 930 K are the changes in stiffness due to the $P6_322 \leftrightarrow P2_1$ transition. Away from the two-phase field of coexisting $P6_3$ ($\sqrt{3}A$) and $P2_1$ structures, the variation in ($K - K_o$) is indistinguishable from the variation in e_4^2 and, hence $(K - K_o) \propto q_{T1}^2$.

The bilinear coupling term $\lambda_{\Gamma_4 e_4 q_{\Gamma_1}}$ in Eq. (10) is expected to give rise to softening as the transition point is approached from above, followed by stiffening with further temperature reduction, a characteristic of proper or pseudoproper ferroelastic transitions. For a first order transition there would be a discontinuous stiffening at the transition point [Fig. 4(c)]. The shear modulus also includes ($C_{11} - C_{12}$), C_{44} and C_{66} (together with some other contributions) which could each scale with q^2 , so that variation in ($G - G_o$) will be more complicated than ($K - K_o$). The observation that ($G - G_o$) does not scale with e_4^2 (Fig. 8) is at least consistent with this qualitative result. As with the bulk modulus, the observed shear modulus will appear to be continuous through the transition point itself due to the two-phase field in which the proportions of coexisting phases themselves change continuously.

Ferroelastic twin walls have been observed by transmission electron microscopy in SrAl_2O_4 .¹⁵ Even at megahertz frequencies the motion of such twins under applied stress in perovskites can give rise to a substantial anelastic dissipation

FIG. 8. The variation in ($K - K_o$) (from Fig. 3) matches closely the variation of e_4^2 (data from Ref. 7), consistent with the change in bulk modulus behaving as an excess property that scales with q^2 for the $P6_322 \leftrightarrow P2_1$ transition. ($G - G_o$) does not scale with e_4^2 and shows an additional anomaly below ~ 600 K. Apparently continuous variations in G and K through the $P6_3$ ($\sqrt{3}A$) $\leftrightarrow P2_1$ transition at ~ 930 K are due to the existence of a two-phase field in which the proportions of coexisting phases change continuously with temperature. The vertical broken lines are shown at 600, 930, and 1118 K.

(e.g. Refs. 20 and 30–32). Between ~ 930 and 650 K, Q^{-1} remains small, signifying that no such dissipation occurs in SrAl_2O_4 . At least in the frequency range of ~ 0.2 –1 MHz, the twin walls are presumed to remain immobile.

D. 650–300 K

The RUS data show a marked increase in dissipation below ~ 650 K [Fig. 2(b)] and a small increase in the shear modulus starting at about the same temperature (Figs. 3 and 8). If this was due simply to a Debye-type coupling between the applied stress and defects, with the standard pattern schematically illustrated in Fig. 4(d), it would not be accompanied by variations of equilibrium properties such as spontaneous strain. There is a clear break in slope between ~ 575 and ~ 675 K in the strain data of Yamada *et al.*⁷ (Fig. 7), however, indicating that the changes in elastic properties must be due to some adjustment within the $P2_1$ structure. Changes in the coupling of order parameters with ($e_1 - e_2$) or e_4 would be expected to give rise to changes in the temperature evolution of ($C_{11} - C_{12}$) and C_{44} , and hence of the shear modulus. Thus, there are correlated changes in strain, elastic, and anelastic properties which suggest some significant change in the structural evolution of SrAl_2O_4 near ~ 600 –650 K. These correlate, further, with a change in the dielectric permittivity (Fig. 1) and an anomaly in the evolution of frequency with temperature of an IR absorption band (Rodehorst *et al.*¹⁵). Anomalies in other IR absorption bands that occur at about the same temperature across the SrAl_2O_4 – BaAl_2O_4 solid solution observed by Rodehorst *et al.*¹⁵ could be related to the improper ferroelectric transition that is known to occur in BaAl_2O_4 .^{14,33–39} Detailed structure refinements from diffraction data collected *in situ* at high temperatures, together with measurements of the frequency dependence of the dielectric properties, are needed to establish the nature of the structural changes involved. These might also give clues as to the acoustic dissipation mecha-

nism below ~ 650 K and, in particular, whether it depends on mobility of defects such as domain walls.

DISCUSSION

Although the sample used in the present study was lightly doped with Eu, the observed anomalies in elastic properties match up, at least in terms of the temperatures at which they occur and their thermodynamic character, with diffraction data from the literature for pure SrAl_2O_4 . The change in color between the start and finish of the experiment is presumed to be due to oxidation of Eu^{2+} to Eu^{3+} but, again, there is no direct evidence that this had any influence on the transformation behaviour of the bulk phase. The $P6_322 \leftrightarrow P6_3 (\sqrt{3}A)$ transition behaves in respect of its strain and elastic relaxation as a normal displacive transition which is close to tricritical in character. In marked contrast, the $P2_1$ structure has a shear modulus which is up to $\sim 50\%$ larger than its para phase and bulk modulus up to $\sim 15\%$ larger. The absence of any softening suggests that the normal strain/order parameter relaxation mechanism for displacive transitions may not operate in monoclinic SrAl_2O_4 , at least on the time scale of $\sim 10^{-6}$ s. A qualitatively similar result has been obtained for the $Pnma$ structure of perovskites,^{19,40} and the feature in common appears to be that the low symmetry phase contains atomic displacements related to two order parameters associated with different irreps. Further elasticity measurements at low frequencies of applied stress are required to confirm that the issue is not simply one of relaxation time, but at this stage it appears that the additional stiffness of the $P2_1$ phase of SrAl_2O_4 could be due to interaction between at least two sets of irreps, which does not allow relaxation of the order parameters under the influence of an external stress.

The Landau expansion developed here to account for the strain and elastic behavior is not unique in the sense that there are, in fact, five separate order parameters which could have independent instabilities. These are associated with the Γ_4 , Γ_5 , Γ_6 , M_2 , and M_3 irreps. The pairwise combination of $\Gamma_6 + M_2$ used here [Eq. (10)] would give changes in M_3 order parameter components by biquadratic coupling. On the other hand, the use of ISOTROPY shows that the $P2_1$ structure can also be generated by the combinations $\Gamma_4 + M_2$, $\Gamma_4 + M_3$, $\Gamma_6 + M_3$, and $M_2 + M_3$, with Γ_5 being generated automatically as a secondary order parameter in each case. The simplest description, which depends on only two driving the overall $P6_322 \rightarrow P2_1$ transition, needs to be tested by mode decomposition analysis of structural data obtained at a range of high temperatures. In the event that $\Gamma_6 + M_3$ was the driving combination, Equation (10) would have the same form, with three M_3 order parameter components replacing the three M_2 components. A more complete description of the strain evolution than is implied by Eqs. (11)–(16) would have coupling between five separate sets of order parameters, each with their own temperature dependence. Γ_4 can probably be ruled out, however, in the light of the result of the mode decomposition analysis of Perez-Mato *et al.*²⁵ which showed that the amplitudes of displacements with this symmetry are negligible. The additional anomaly in elastic, anelastic and spec-

troscopic properties near 600 K is then likely to be due to a change in the evolution of four order parameters when a third or fourth instability starts to influence the structural evolution. Given that the symmetry is already broken by the first two, this does not require an additional discrete phase transition.

The role of gradient terms in the transformation behavior has not been explored here. These can stabilize order parameter inhomogeneities, though no incommensurate structures have yet been observed in SrAl_2O_4 . For the $P2_1$ structure, the only nonzero gradient term from Eq. (10) would be $\partial q_{\Gamma_1} / \partial x$, indicating that spatial variations would be allowed in one direction. Gradient effects must also be important at twin walls or antiphase boundaries which, by definition, involve steep variations in the absolute values of the order parameters. With four separate order parameters involved, there is a potential for twin walls and antiphase boundaries to have quite different and interesting structural differences from the homogeneous, average structure identified by refinement of diffraction data.

From the present study, it is clear that the elastic and anelastic properties of $\text{SrAl}_2\text{O}_4:\text{Eu}$, in the $P2_1$ form which has the properties of current interest for elasticoluminescence, are dominated by the influence of phase transitions. Through the Γ_6 order parameter, the $P2_1$ structure is polar, proper- or pseudoproper-ferroelastic and should be optically active. Through the Γ_5 order parameter, SrAl_2O_4 is also an improper ferroelastic. It must be further anticipated that twin walls and antiphase boundaries will have quite distinct local structures determined by an unusual combination of order parameter gradients and that defects or dopant ions located within them could give rise to quite different luminescence from those located in the homogenous bulk. Another possibility for exploring variations in the luminescence behavior would be to investigate different bulk compositions of the host stuffed tridymite structure in order to test whether alternative structural pathways can be induced through the full transformation hierarchy shown in Fig. 6.

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