

## Order-to-disorder phase-transition study of Pb on Ge(111)

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X-ray standing-wave (111) and  $(11\bar{1})$  measurements have been performed on the room-temperature and high-temperature phases of a Pb layer on Ge(111). At room temperature, our results support a four-atom-unit-cell surface structure. On passing into the high-temperature phase, we find that there is an increase in the Fourier coefficient along the surface  $[11\bar{2}]$  direction for the Pb density distribution. Our model, which requires a 0.6-Å in-plane thermal vibration amplitude, is similar to one previously proposed by Hwang and Golovchenko and disagrees with a strictly two-dimensional-liquid interpretation.

In recent years, a great deal of scientific activity has focused on understanding the remarkably complex two-dimensional (2D) systems obtained by preparing a Ge(111) surface with varying coverages of Pb. In addition to harboring several surface crystal phases at different coverages, this system has been observed to undergo a temperature-driven phase transition around 175°C for coverages on the order of one monolayer, where 1 ML =  $7.22 \times 10^{14}$  atoms/cm<sup>2</sup>. In the following, we present x-ray standing-wave (XSW) results for the (111) and  $(11\bar{1})$  bulk reflections, which probe normal and surface in-plane Fourier components of the Pb density distribution. The data was analyzed in terms of the various proposed models for the structure on both sides of the phase transition. In particular, we find that it is possible to interpret the high-temperature phase transition as an order-disorder type.

The phase transitions of Pb on Ge(111) and Si(111) surfaces are considered model candidates for the study of 2D phenomena. Pb is insoluble in both bulk Ge and Si and does not alloy, intermix, or form strong chemical bonds over a wide temperature range<sup>1</sup> and can be easily evaporated and redeposited on the same substrate. The Pb surface phases have turned out to be quite rich and debate over the room-temperature (RT) structures has con-

tinued for over a decade.<sup>2-9</sup> These phases manifest themselves as three different  $\sqrt{3} \times \sqrt{3} R 30^\circ$  structures on Ge(111) (hereafter known as  $\sqrt{3}$ ): a mosaic phase ( $< 1/3$  ML), a dilute  $\alpha$  phase ( $\frac{1}{3}$  ML), and a dense  $\beta$  phase (1 ML or  $\frac{4}{3}$  ML). In addition, metastable  $(4 \times 4)$  and incommensurate phases at higher coverages have been found, although, like the mosaic phase, they have not been extensively studied.<sup>5,10</sup> While the  $\alpha$  phase is thought to consist of one  $T_4$  adatom per  $\sqrt{3}$  unit cell,<sup>7-9</sup> the atomic structure of the  $\beta$  phase has generated a good deal of controversy.<sup>5-13</sup>

The nature of the high-temperature (HT) driven structural transition of the dense phase is equally as controversial. Because of the diffuse nature of the scattering in reflection high-energy electron diffraction (RHEED) (Ref. 7) and surface x-ray diffraction (SXRD),<sup>11</sup> this phase transition was thought to be a 2D liquid. We note that the SXRD results concluded that the Pb liquid overlayer was, in addition, slightly modulated by the presence of the ideal bulklike Ge substrate. However, recent high-temperature scanning-tunneling-microscopy (STM) images from Hwang and Golovchenko<sup>12</sup> indicate that this so-called liquid phase is actually a simple Pb-terminated Ge(111)-(1 $\times$ 1) surface with the Pb atoms in a state of greatly agitated motion. A previous XSW study found

no change in the Pb density distribution across the transition, also indicating that the HT phase is at least partially ordered.<sup>14</sup> However, these XSW measurements were only performed for one temperature on either side of the transition and no RT and HT structural models were deduced.

In the following study, we present standing-wave results which help clarify the Pb/Ge(111) RT and HT structures as well as the nature of this phase transition. The XSW measurement consists of monitoring the fluorescence of the adatoms while scanning through a particular Bragg reflection of the crystal.<sup>15-17</sup> From these measurements, one can determine the phase and amplitude of the  $H$ th Fourier coefficient for the adatom distribution. The phase, or coherent position ( $P_H$ ), measures the average position of the adatom distribution along the  $H$  direction. The amplitude, or coherent fraction ( $F_H$ ), measures how sharply the adatoms are distributed about the coherent position. For a general adatom distribution,  $F_H = C a_H D_H$ , where  $C$  is the ordered fraction,  $a_H$  is the geometrical factor, and  $D_H$  is the Debye-Waller factor.<sup>16</sup>

The standing-wave experiments were performed at the X15A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. After being polished and then etched in a weak CP4 solution, the Ge(111) sample was introduced into the vacuum chamber which had a base pressure of  $1.1 \times 10^{-8}$  Pa. With  $\text{LN}_2$  flowing through the cryoshield, the sample went through a few hot sputtering ( $550^\circ\text{C}$ , 500-eV Ne at  $6.7 \times 10^{-3}$  Pa) and annealing ( $700^\circ\text{C}$ ) cycles until the low-energy-electron-diffraction (LEED) pattern (36.0 eV) showed an excellent  $c(2 \times 8)$  and the Auger spectrum indicated the sample was free from contaminants. Pd was then deposited onto the warm Ge substrate ( $\sim 200^\circ\text{C}$ ). After cooling to RT, LEED always showed a very sharp  $\sqrt{3}$  diffraction pattern. Pb deposition coverages were determined from a calibrated quartz-crystal thickness monitor. In addition, the temperature was calibrated with an Al-Cr thermocouple inserted in a Si sample and an optical pyrometer to an accuracy of  $\pm 10^\circ\text{C}$  ( $\pm 25^\circ\text{C}$ ) for temperatures above (below)  $500^\circ\text{C}$ .

The incident x-ray beam was monochromated with a Si(111) double-crystal setup to an energy of 16.3 keV. The XSW experiment consisted of recording both the Bragg reflectivity and the Pb  $L$  fluorescence from the sample. The overwhelming bulk Ge  $K_\alpha$  and  $K_\beta$  fluorescence signals saturated the Si(Li) detector, obscured the Pb  $L$  fluorescence, and created significant pileup ghost peaks. These problems were alleviated by using a 0.3-mm Al filter in front of the Si(Li) detector and pileup rejection circuitry. The coherent positions and fractions were determined from fitting the fluorescence data and both the (111) (diffracting planes parallel to surface) and the (11 $\bar{1}$ ) reflections (diffracting planes  $70.53^\circ$  to the surface) to dynamical diffraction theory.

While our results concur with the general agreement on the structure of the  $\alpha$  phase,<sup>18</sup> it is the  $\beta$  phase which has generated the most controversy and where we focused our attention. The debate over the RT  $\beta$  phase has generally centered on two groups of models whose ideal

completion coverage is either 1 ML (three atoms-unit cell) or  $\frac{4}{3}$  ML (four atoms-unit cell). Figure 1 shows a typical model from each group. Outlined in the top view are the Pb atoms (large, filled circles),  $\sqrt{3}$  unit cells, and the Ge atoms (small, open circles) in an ideal bulklike configuration. The positions of the Pb atoms with respect to the (111) and (11 $\bar{1}$ ) diffracting planes are indicated in the side view. In general, the three atom-unit-cell models consist of Pb atoms in registry with the underlying Ge(111) substrate. The consensus on the four atom-unit-cell models has been for a distorted Pb(111) overlayer,<sup>5,8,10,13</sup> although the exact atomic positions and orientations to the Ge(111) substrate are still disputed.

Figure 2 shows the XSW results for the RT  $\beta$  phase. The coherent positions and coherent fractions for both the (111) and (11 $\bar{1}$ ) reflections ( $P_{111} = 0.91 \pm 0.01$ ,  $F_{111} = 0.90 \pm 0.03$ ,  $P_{11\bar{1}} = 1.01 \pm 0.09$ , and  $F_{11\bar{1}} = 0.24 \pm 0.04$ ) were consistently obtained on several separately prepared samples with Pb coverages ranging from 1.0–1.3 ML. For each sample, the LEED pattern always showed an excellent  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  pattern consisting of sharp, bright spots on top of a low background. Auger spectroscopy confirmed the cleanliness of the Pb-terminated Ge(111) samples. The unusually large uncertainties for

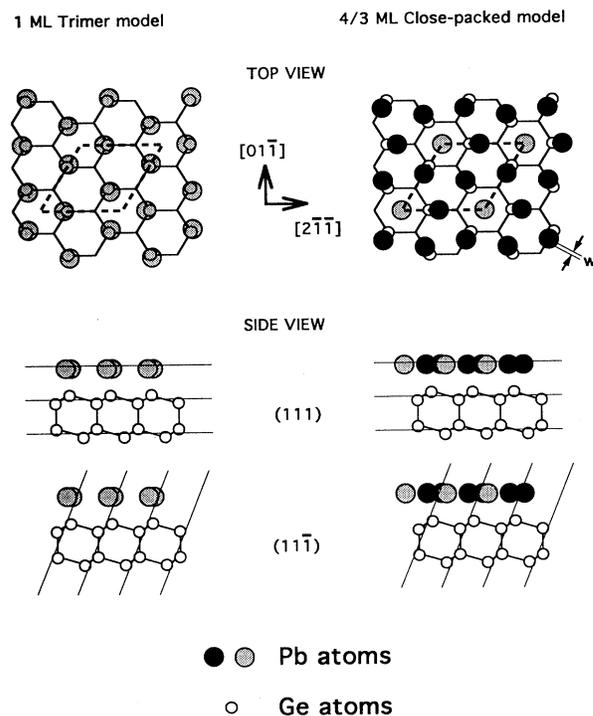


FIG. 1. Two competing structural models for the RT  $\beta$  phase. The Pb atoms in different sites are indicated by large, filled circles and the Ge atoms of the substrate are indicated by small, open circles. In the top view the  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  unit cells are indicated. The OC  $T_1$  Pb atoms in the  $\frac{4}{3}$  ML model are displaced a distance  $w$ , in units of the  $\sqrt{3}$  unit cell ( $6.95 \text{ \AA}$ ), away from the center of the bridge site and towards the  $T_1$  site. The Pb atom positions, with respect to the (111) and (11 $\bar{1}$ ) reflection planes, are also shown in a side view.

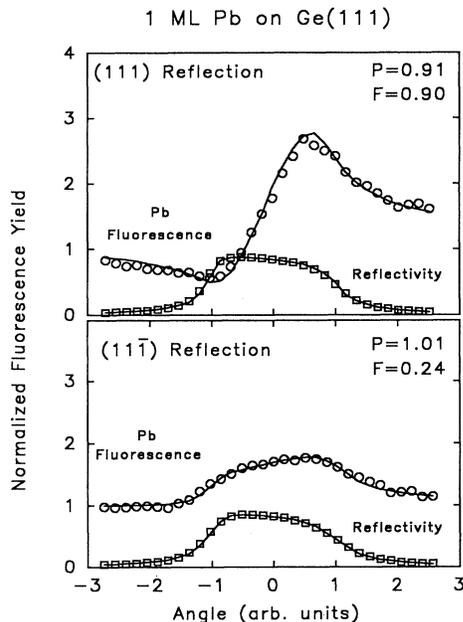


FIG. 2. The measured (111) and (11 $\bar{1}$ ) reflectivity (open squares) and the corresponding Pb  $L_{\beta}$  normalized fluorescence yields (open circles) for the 1-ML coverage of Pb/Ge(111) at room temperature. The solid lines are calculated from dynamical diffraction theory and fit to the data. The coherent position ( $P$ ) and coherent fraction ( $F$ ) were determined from the fit.

the (11 $\bar{1}$ ) measurements reflect our experimental difficulties in separating the Pb fluorescence signal from the Ge background, effective asymmetries of the (11 $\bar{1}$ ) measurements, and uncertainties in the coherent position caused by low coherent fractions. However, by reproducibly measuring the same values for  $F_{11\bar{1}}$  and  $P_{11\bar{1}}$ , we can discount any differences due to sample preparation.

The reduction of  $F_{111}$  from unity might be explained by a small amount ( $\sim 11\%$ ) of disordered Pb atoms on the surface, although LEED showed no increase in the background from the clean Ge(111)- $c$  ( $2 \times 8$ ) and we consistently measured this  $F_{111}$ . While a plausible explanation could involve the structural properties of the Pb lay-

er (i.e., a bilayer of Pb or a long-wavelength static distortion of the Pb layer) an equally valid explanation could be the influence of thermal vibrations. Assuming a value of unity for the ordered fraction of a single Pb layer, we can use our  $F_{111}$  measurement, since  $D_{111} = F_{111}$ , to estimate the surface-normal vibrational amplitude from

$$\langle u_{111}^2 \rangle = \frac{-\text{Ln}(D_{111})d_{111}^2}{2\pi^2}, \quad (1)$$

where  $d$  is the spacing between the (111) bulk Ge diffraction planes.<sup>19</sup> From Eq. (1), the mean-squared vibration amplitude,  $\langle u_{111}^2 \rangle$ , is  $0.06 \pm 0.01 \text{ \AA}^2$ . From the mass and Debye temperature of Pb ( $m_{\text{Pb}} = 207.19$ ,  $\theta_D = 81 \text{ K}$ ), the isotropic bulk Pb value for  $\langle u^2 \rangle$  is  $0.04 \text{ \AA}^2$ .<sup>20</sup> Since the surface Pb atoms are less constrained than in bulk Pb and the SXRD measurements on the  $\alpha$  and  $\beta$  phases found the Pd Debye-Waller factors in the neighborhood of their bulk values,<sup>8,21</sup> we therefore cannot rule out thermal effects. Recently, a number of thermal vibration studies have explored the vibrational amplitudes of adatoms at semiconductor surfaces.<sup>19,22</sup>

In principle, standing waves can determine the positions of the Pb atoms in the unit cell by utilizing the in-plane measurements [i.e., the (11 $\bar{1}$ ) reflection]. In general though, localizing the reconstructed surface requires more than two reflections. Due to the complicated nature of the  $\sqrt{3} \beta$  phase we cannot uniquely determine the positions of the Pb atoms in the unit cell from our two reflections. We can, however, calculate the coherent positions and geometrical factors (i.e., the structural component,  $|a_H|$ , of the coherent fraction) for existing structural models and compare them to our results.<sup>23</sup>

Table I compares our experimental results to the calculated coherent positions ( $P_H$ ) and geometrical factors ( $a_H$ ) for six existing models. Also listed for these models are the unit cell description, the Pb sites (e.g., OC  $T_1$  means off-centered  $T_1$ ), the journal reference, and the main technique used [e.g., molecular-dynamics (MD) simulation]. The postulated number of Pb atoms/unit cell was three for models 1 and 2 and four for models 3–6. Our analysis assumed three equally-populated domains, and, for models 1–3 and 5, where the perpendicular distances from the top Ge(111) layer to the Pb

TABLE I. Coherent positions and geometrical factors calculated for various RT  $\beta$ -phase models.

No.	Unit-cell Pb sites	$ a_{111} $	$P_{111}$	$ a_{11\bar{1}} $	$P_{11\bar{1}}$	Ref.
	Our experiment	[0.90–1.0] $\pm 0.02$	$0.91 \pm 0.01$	[0.24–0.27] $\pm 0.04$	$1.01 \pm 0.09$	XSW
1	1-ML Pb- $T_4$	1.0	(0.91)	1.0	0.47	6—LEED
2	1-ML Pb Trimer- OC $T_1$	1.0	(0.91)	$0.94 \pm 0.04$	$1.18 \pm 0.02$	12—STM
3	$\frac{4}{3}$ -ML Pb(111)- OC $T_4$ , $H_3$ bilayer	0.99	(0.91)	$0.48 \pm 0.13$	$1.04 \pm 0.01$	10—STM
4	$\frac{4}{3}$ -ML Pb Chain- OC $T_1$ , OC $T_4$	1.0	$0.95 \pm 0.03$	$0.30 \pm 0.02$	$1.19 \pm 0.01$	13—MD
5	$\frac{4}{3}$ -ML Pb(111)- OC $T_1$ , $H_3$	1.0	(0.91)	$0.30 \pm 0.01$	$1.06 \pm 0.01$	8—SXRD
6	$\frac{4}{3}$ -ML Pb(111)- OC $T_1$ , $H_3$ bilayer	0.92	0.90	0.29	1.09	9—LEED

atoms were not provided, we used our experimental  $P_{111}$  values (shown in parentheses). As an example, the form of the equations used to determine  $|a_H|$  and  $P_H$  for the four atom-unit cell models 3, 5, and 6 are shown below.

$$|a_{11\bar{1}}| = \frac{1}{4} [6 - 4 \cos(6\pi w) + 2 \cos(4\pi w) - 4 \cos(2\pi w)]^{1/2} \quad (2)$$

and

$$P_{11\bar{1}} = \frac{1}{2\pi} \tan^{-1} \left[ \frac{2 \sin[c(P_{111} - 3w)] - \sin[c(P_{111} + 6w)] - \sin(cP_{111})}{2 \cos[c(P_{111} - 3w)] - \cos[c(P_{111} + 6w)] - \cos(cP_{111})} \right], \quad (3)$$

where  $c = 2\pi/3$  and  $w$  is the displacement, in units of the  $\sqrt{3}$  unit cell (6.95 Å), away from the center of the bridge site (i.e., located half way between the  $T_1$  and  $T_4$  sites) and towards the  $T_1$  site as is indicated in the top view for the  $\frac{4}{3}$ -ML model in Fig. 1. Since these models all have small  $w$  values ( $< 0.1$ ), the  $|a_{11\bar{1}}|$  values (and hence,  $F_{11\bar{1}}$ ) are also small. One can easily visualize Eq. (2) using the  $(11\bar{1})$  side view in Fig. 1. At small  $w$  the Pb atoms are divided between *two* sites which are almost completely out of phase with regard to the standing-wave field. This destructive interference causes  $|a_{11\bar{1}}|$  to be quite small. This is in contrast to the situation for the 1-ML model, also seen in the  $(11\bar{1})$  side view of Fig. 1, where the Pb atoms are all closely centered about *one* site. This yields a large value for  $|a_{11\bar{1}}|$ .

Table I shows that our results are in better agreement with the four atom-unit-cell models. Of these models, the chain model 4 differs from our  $P_{11\bar{1}}$  results and model 3 has a larger  $|a_{11\bar{1}}|$  value, although, by moving the "bridge-site" Pb atoms an additional 0.4 Å towards the  $T_4$  site, we can also get reasonable agreement. Our results best agree with, but cannot distinguish between, models 5 and 6. These models differ in their  $|a_{111}|$  values where, for model 5, the Pb atoms sit in one plane while, for model 6, the Pb atoms form a bilayer.

We note that for the calculation of our experimental geometrical factor,  $a_H = F_H / (CD_H)$ , we assumed an ordered fraction of unity (i.e.,  $C = 1$ ). In addition, since SXRD results place the in-plane Pb Debye-Waller factor in the neighborhood of its bulk value, we will assume  $0.9 \leq D_{11\bar{1}} < 1.0$  (i.e., similar to our  $D_{111}$  values).<sup>8,11</sup> We have expressed the resultant  $|a_H|$  ranges within square brackets for our experimental results in Table I.

The  $\beta$  phase is known to go through a reversible phase transition, from  $\sqrt{3} \times \sqrt{3} R 30^\circ$  to  $1 \times 1$ , occurring around 175°C. In order to examine this transition, we repeated our  $F$  and  $P$  measurements for both the  $(111)$  and  $(11\bar{1})$  reflections with the sample stage at different temperatures. Before each measurement, the sample was left at the requisite temperature for two hours to reach equilibrium. Our measured positions and coherent fractions are shown in Fig. 3 for various temperatures. The solid lines through the points are guides showing the trend in each parameter. A small increase in  $F_{11\bar{1}}$  and  $P_{11\bar{1}}$  occurs

We have assumed a single domain and a single layer of Pb atoms although the more complicated three-domain and multilayer equations gave similar results. The  $(11\bar{1})$  results are

around 175°C while  $F_{111}$  and  $P_{111}$  do not appreciably move (within uncertainty).

Above the  $\sim 175^\circ\text{C}$  transition, we determined  $F_{111} = 0.88 \pm 0.02$ ,  $P_{111} = 0.92 \pm 0.01$ ,  $F_{11\bar{1}} = 0.33 \pm 0.04$ , and  $P_{11\bar{1}} = 1.06 \pm 0.09$ . The  $(111)$  results indicate that the Pb atoms remained in a highly-ordered layer, located  $3.01 \pm 0.03$  Å above the top of the bulklike Ge(111) double layer. Since this  $(111)$  measurement determined that no structural changes occurred normal to the surface, the phase transition must be truly 2D. The  $(11\bar{1})$  results show that the amplitude ( $F_{11\bar{1}}$ ) of the Fourier coefficient in the surface  $[11\bar{2}]$  direction increases. This indicates a *higher* degree of correlation with the Ge(111) substrate, although not dramatically different from the RT results. This is certainly not consistent with a strictly 2D liquid Pb overlayer where the correlation with the Ge(111) substrate should *decrease*. This suggests that the Pb overlayer is now being modulated more strongly by the Ge substrate potential in agreement with STM (Ref. 12) and SXRD.<sup>11</sup>

Presented below is one possible HT model which reconciles our results with most aspects of RHEED,<sup>6,7</sup> SXRD,<sup>11</sup> STM,<sup>10,12</sup> photoemission<sup>9</sup> and MD.<sup>13</sup> The RT models 5 and 6, which agree best with our results, both have four atoms per unit cell with three Pb atoms in OC

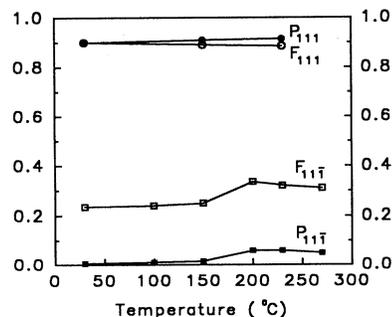


FIG. 3. The average (unitless) values of the  $(111)$  and  $(11\bar{1})$  coherent positions (squares) and coherent fractions (circles) at various temperatures for 1-ML Pb/Ge(111). The lines through the points are guides to the eye. The positions (mod 1) and fractions change slightly as they go through the phase transition ( $\sim 175^\circ\text{C}$ ).

$T_1$  sites and one Pb atom in an  $H_3$  site. For simplicity we will assume all Pb atoms are in a single layer (i.e., model 5) and have the same in-plane vibrational amplitudes. As we increase the temperature above the  $\sqrt{3} \times \sqrt{3} R 30^\circ \rightleftharpoons 1 \times 1$  phase transition, the Pb atoms in the OC  $T_1$  sites move to the  $T_1$  sites restoring the  $C_{3v}$  symmetry of the ideal Ge(111) surface. These  $T_1$  site Pb atoms have been reproducibly observed with the STM.<sup>12</sup> Above the phase transition, the Pb  $H_3$  atoms are now free to occupy any  $H_3$  site due to the restored symmetry of the surface. Since the domain sizes have decreased below the x-ray and electron coherence lengths (typically  $\sim 500$  Å), the fractional-ordered reflections should become weakly diffuse. This is what has been seen in SXRD (Ref. 11) and RHEED,<sup>7</sup> although, from a standing-waves perspective, the local structure is still well defined. This transition is represented in Fig. 4 by arrows which show the movement of the Pb atoms in OC  $T_1$  sites to  $T_1$  sites. With this increase in symmetry, the Pb atoms in the  $H_3$  sites are no longer confined to domains and randomly occupy  $H_3$  positions.

For this HT model, we calculate  $P_{11\bar{1}} = 1.12$ , which is within the uncertainty of our positional measurement. Assuming an ordered fraction of unity, the difference between the geometrical factor for this model,  $|a_{11\bar{1}}| = 0.62$ , and the measured coherent fraction,  $F_{11\bar{1}} = 0.33$ , is then solely due to the Debye-Waller contribution. From Eq. (1), we find that  $\sqrt{\langle u_{11\bar{1}}^2 \rangle} = 0.58 \pm 0.04$  Å and, assuming surface perpendicular and parallel components are independent of one another, each Pb atom has an in-plane vibrational amplitude of  $0.60 \pm 0.04$  Å. This corresponds to a Debye temperature of  $\theta_D = 32 \pm 2$  K,<sup>20</sup> which, although quite small, compares favorably with molecular dynamics theory ( $\theta_D \sim 36$  K),<sup>13</sup> photoemission ( $\theta_D = 41$  K),<sup>9</sup> and with the greatly agitated state of the Pb atoms seen in the STM topographs.<sup>12</sup> Since a majority of the Pb atoms are fluctuating about the  $T_1$  sites, our results are similar to the images of Hwang and Golovchenko<sup>12</sup> and disagree with a strictly liquid interpretation.

In summary, we have determined that the RT  $\beta$  phase has four atoms per unit cell, similar to the conclusions drawn from LEED and SXRD. The HT phase transition was found to be indicative of an order-to-disorder variety (i.e., a lattice-gas model) since the Pb atoms are modulat-

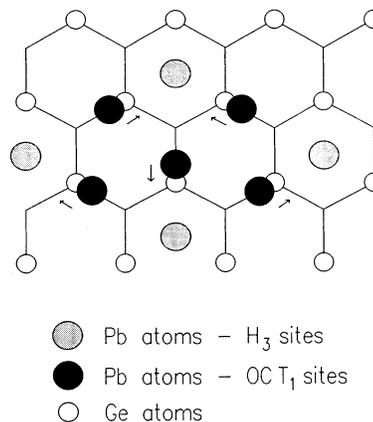


FIG. 4. A single unit cell of the  $\frac{4}{3}$ -MT RT model. The Pb atoms are shown in their  $H_3$  and OC  $T_1$  sites. The Ge atoms are shown as small, open circles. As the temperature is increased above the phase transition, the Pb atoms in OC  $T_1$  sites move in the direction of the arrows to  $T_1$  sites and the Pb atoms in  $H_3$  sites are not constrained to specific  $H_3$  sites.

ed by the underlying substrate potential and, within any given unit cell, are fluctuating about  $T_1$  and  $H_3$  high-symmetry sites. Therefore, by increasing the temperature of the Pb overlayer, we have decreased the Pb-Pb interactions so that the Ge substrate potential plays a more important role in determining the structure of the HT  $\beta$  phase.

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