

## Evidence for an Order-Order Transition on the Ge(111) Surface near 1050 K from High-Resolution Helium Atom Scattering Experiments

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Helium atom scattering has been used to investigate the Ge(111) surface phase transition at  $T_c = 1050$  K. The *elastically* scattered helium atoms show sharp, integral-order diffraction peaks that change only in their relative amplitudes at  $T_c$  and persist up to 1160 K, the highest temperature studied. Contrary to previous reports based on low-energy electron and x-ray diffraction, ion backscattering, and a recent theoretical study, the present findings show that the surface remains highly ordered above  $T_c$ , with a reduced height of the top bilayer, and that it may be metallic as was recently observed in electron energy loss spectroscopy.

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The determination of the surface structures of the group IV semiconductors, notably Si, but to an increasing extent Ge, has been one of the central problems of surface science. With changing temperature the faces of these semiconductors exhibit a variety of reconstructions. The first diffraction experiments on Ge(111) ( $T_m = 1210$  K) at high temperatures were performed by McRae and Malic [1,2] using low-energy electron diffraction (LEED); these showed a threefold decrease in the intensity of the first-order diffraction peaks around 1050 K, but no significant change in the specular peak intensity up to 1100 K. The model proposed to explain these results was the strain-induced formation of domains with disorder in only the outer bilayer, while models based on surface melting or surface roughening were ruled out. Since the LEED study, electron energy loss spectroscopy (EELS) [3] and spectroscopic ellipsometry [4] have shown changes in the electronic properties of Ge(111) around 1050 K, possibly indicating an amorphous surface. The results of medium-energy ion scattering (MEIS) experiments [5] were interpreted to indicate that above  $T_c$  the first bilayer disorders laterally without disordering normally to the surface ("layered liquid" model). In contrast, an x-ray diffraction study [6] indicated that no positional disordering and no phase transition occurs, but that there is a continuous change in surface structure involving the formation of vacancies. In a later x-ray study [7], evidence was given against bilayer vacancies and for a positionally disordered surface above 1050 K. More recently, a theoretical study found the first bilayer to be dynamically disordered and metallic [8], and an EELS experiment showed an abrupt increase in conductivity at  $T_c$  [9].

In this Letter we present the results of high-resolution helium atom scattering (HAS) from Ge(111) at high temperatures. Because HAS is only sensitive to the structure

and dynamics of the outermost surface layer, it is an ideal complement to the techniques used previously [10]. Elastic angular distributions show unusual, perhaps unprecedented, twofold to sixfold increases in the intensity of the specular peak, as well as sharp drops and rises in the first-order diffraction peaks around 1050 K. The observation of only sharp, integral-order diffraction features above  $T_c$  indicates the persistence of long-range ( $1 \times 1$ ) order in the first bilayer.

The HAS time-of-flight (TOF) spectrometer had a fixed angle of  $90^\circ$  between the incident and detected beams [11]. At a beam energy of 22 meV (incident wave vector  $k_i = 6.6 \text{ \AA}^{-1}$ ) the energy resolution was ca. 2%. The angular resolution was ca.  $0.1^\circ$  and the TOF channel width  $2 \mu\text{s}$  with a flight time for the elastically scattered He atoms of 1.83 ms. The Ge(111) crystal (*n*-type, Sb doped,  $1.3 \Omega \text{ cm}$ ,  $11.5 \text{ mm} \times 5.0 \text{ mm} \times 0.25 \text{ mm}$ ; commercially grown, cut, and polished; miscut  $0.2^\circ \pm 0.1^\circ$ ) was mounted between two Ta clips and resistively heated. The surface was prepared *in situ* by cycles of Ar-ion bombardment ( $1 \text{ keV}$  ions,  $5.7 \times 10^{11} \text{ Ar}^+$  ions/ $\text{mm}^2 \text{ s}$ , normal incidence) for 2 h at 300 K followed by a 1 h anneal at 1065 K until the Auger signal indicated a clean surface. The surface temperature was measured to within  $\pm 5$  K by an external optical pyrometer that was calibrated by melting the crystal after the experiments. The base pressure of the chamber was  $< 2 \times 10^{-10}$  Torr with the target at 300 K, but rose as high as  $5 \times 10^{-10}$  Torr with the target at 1100 K. All results reported here were reproducible over several weeks and all temperature changes reversible, indicating that the surface was stable.

Figure 1(a) shows measurements of the angular distribution of the total intensity at 1071 K, well above  $T_c$ . Only a weak hint of a few diffraction peaks superimposed on a large background is seen. The inset in Fig. 1(a)

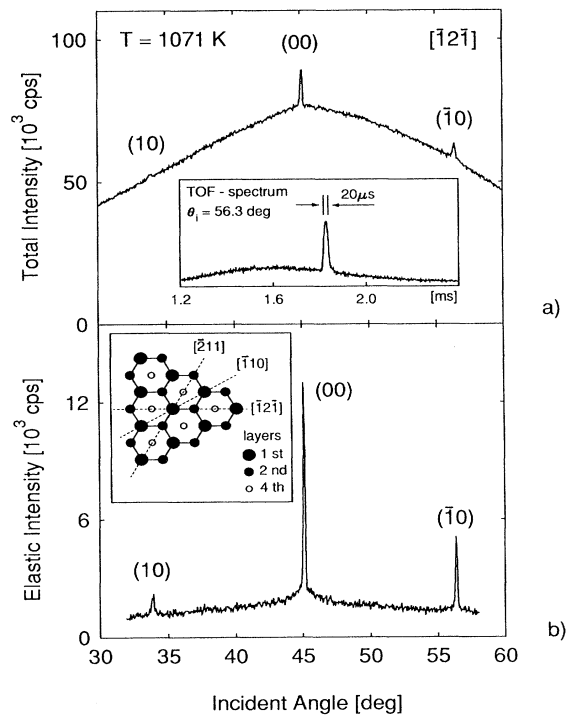


FIG. 1. Principle of method of obtaining elastic scattering. (a) Angular distribution (step width  $0.05^\circ$ , collection time  $0.5$  s per step) of total in-plane scattered He atoms; incident He energy  $22$  meV ( $k_i = 6.6 \text{ \AA}^{-1}$ ). Inset shows time-of-flight distribution at  $\theta_i = 56.3^\circ$ , and  $20 \mu\text{s}$  interval defined as elastic window. (b) Same as (a) except  $5$  s per step and plotting only He signal within elastic window. Inset shows top view of the (111) surface of Ge (diamond lattice) having structure of bulk.

shows how the “elastic” angular distributions are obtained; only the intensity in a window  $20 \mu\text{s}$  wide and equal to the FWHM of the elastic TOF peak is integrated to extract the intensity of the elastic angular distribution shown in Fig. 1(b). Very sharp diffraction peaks with widths identical to those at lower temperatures against a greatly reduced background are now apparent. Angular distributions of the total scattered intensity at  $300$  K and the elastic fraction at three elevated temperatures are shown in Fig. 2 for in-plane scattering of He atoms along the principal crystallographic directions  $[\bar{1}10]$  and  $[\bar{1}2\bar{1}]$ . At  $300$  K, half-order diffraction features due to the low-temperature  $c(2 \times 8)$  reconstruction [12] are sharp and strong. The angular distributions along the  $[\bar{1}10]$  direction are symmetric about the specular angle ( $\theta_i = 45^\circ$ ), but the distributions along the  $[\bar{1}2\bar{1}]$  direction are strongly asymmetric, being very nearly mirror images of those along the  $[\bar{2}11]$  (not shown). Because of the symmetry of the bilayer structure, changing the azimuthal angle  $\phi$  by  $60^\circ$  to change the in-plane orientation from  $[\bar{1}2\bar{1}]$  to  $[\bar{2}11]$  is equivalent to a mirror reflection of the bilayer perpendicular to the in-plane orientation, which leads to a mirror reflection of the diffraction pattern.

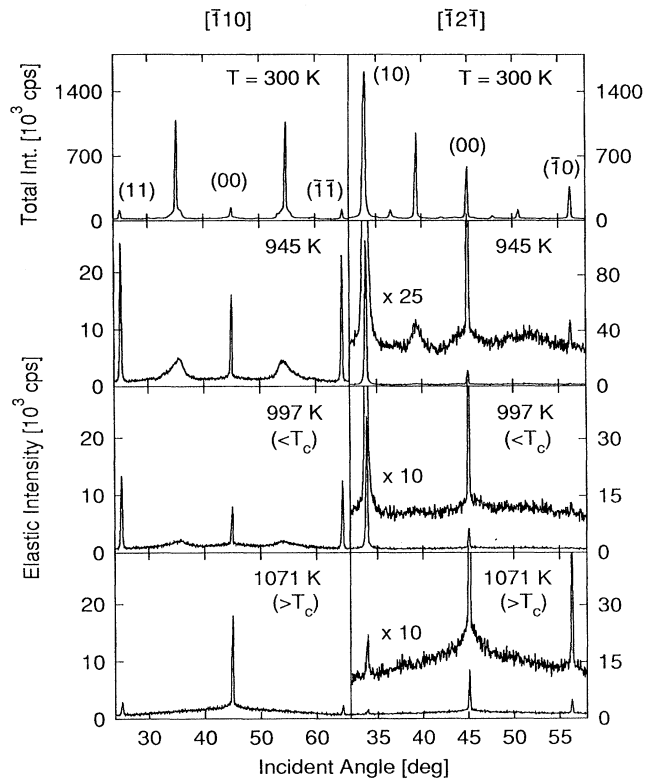


FIG. 2. Angular scans of He scattered from Ge(111) along two principal directions at temperatures below and above  $T_c = 1050$  K; He energy  $22$  meV ( $k_i = 6.6 \text{ \AA}^{-1}$ ). Orders of peaks given in parentheses using reciprocal lattice vectors.

As the surface temperature increases, the diffraction peak intensities show the usual Debye-Waller exponential decrease due to thermal attenuation. The specular and first-order diffraction peaks are visible up to  $1160$  K, while broadened and distorted half-order peaks persist up to  $1000$  K, more strongly in the  $[\bar{1}10]$  scan, but are invisible above  $1050$  K. The measured integral-order peaks did not broaden, and no peak shoulders were observed, indicating an insignificant concentration of domains with a maximum length scale smaller than the coherence scale of the apparatus (approximately  $450 \text{ \AA}$ ). The temperature dependence of the intensities of the specular and first-order elastic peaks are shown in Fig. 3 for the  $[\bar{1}10]$ ,  $[\bar{1}2\bar{1}]$ , and  $[\bar{2}11]$  in-plane azimuthal orientations. Near  $1040$  K the specular peak increases significantly in all three azimuthal orientations [13]. Sharp increases in the  $(\bar{1}0)$  peak in the  $[\bar{1}2\bar{1}]$  direction and the  $(01)$  peak in the  $[\bar{2}11]$  direction are also seen, whereas sharp decreases are observed in the other first-order peaks. The two second-order peaks measured in the  $[\bar{1}2\bar{1}]$  direction, which are not shown here, disappear above  $T_c$ . The inset in Fig. 3(b) shows the temperature dependence of the incoherent elastic intensity at  $52.5^\circ$  between the diffraction peaks. This signal, which is

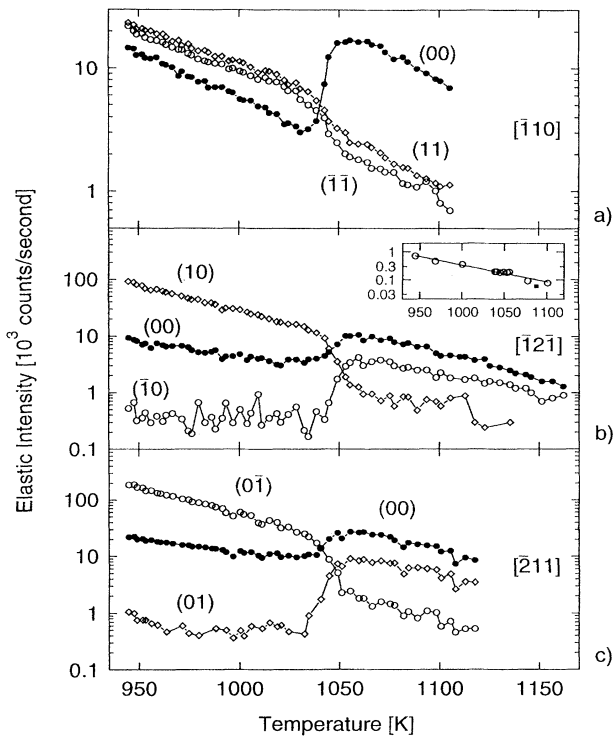


FIG. 3. Temperature dependence of areas measured for specular (00) peak at  $45^\circ$  and for first-order diffraction peaks for He scattered elastically from Ge(111) scanned along three principal directions; He energy 22 meV ( $k_i = 6.6 \text{ \AA}^{-1}$ ); symbols:  $\bullet$   $45.0^\circ$  in (a)–(c);  $\diamond$   $25.3^\circ$ ,  $\circ$   $64.7^\circ$  in (a);  $\diamond$   $33.7^\circ$ ,  $\circ$   $56.3^\circ$  in (b) and (c). Inset in (b) shows temperature dependence of incoherent elastic intensity measured at  $\theta_i = 52.5^\circ$ .

particularly sensitive to the concentration of surface defects and steps [14], shows the typical Debye-Waller attenuation. No hysteresis was observed in measurements taken with increasing and decreasing temperature.

The persistence of all, and the strengthening of some, first-order diffraction peaks, the lack of shoulders on the diffraction peaks, the monotonic Debye-Waller attenuation of the intensities of the diffraction peaks, and the behavior of the incoherent elastic peak below and above  $T_c$  rule out all models based on disorder. For example, vacancy proliferation would lead to a strong attenuation of the specular peak [15] and an increase in the incoherent elastic intensity [14] which was not observed [see inset in Fig. 3(b)]. The recent theoretical prediction of a melted surface layer [8] can be excluded because a top bilayer with liquidlike diffusion would also result in a significant loss of intensity and broadening of all the diffraction peaks including the specular one. This theory may apply, however, to the Ge surface at temperatures still closer to the melting point; a transition to what appears to be a more disordered surface has recently been observed on Si(111) near 1490 K ( $T_m = 1683 \text{ K}$ ) [16].

The significant increase of the specular intensity we see at  $T_c$  is consistent with the steplike increase in metallization of the surface bilayer at  $T_c$  recently found [9]. The presence of diffraction peaks and their intensities indicate a substantial corrugation both below and above  $T_c$ . This suggests that the metallic state is localized at the surface; if it were to extend farther into the bulk, the surface would be smoother, as seen in HAS diffraction studies of numerous (111) metal surfaces [17].

These changes at  $T_c$  may well be due to the delocalization of the adatoms [8]. At lower temperatures the adatoms stabilize the atoms of the first layer in a bulk-like structure (see Fig. 1) with almost regular tetrahedral bonds. But the disappearance of the half-order peaks just below 1050 K (see Fig. 2) shows that the adatoms are no longer regularly arranged on the surface. The first layer becomes a  $(1 \times 1)$  array of atoms, each having an unpaired electron that may be expected to change from tetrahedral or  $sp^3$  bonding to a flatter structure approaching a planar one with  $sp^2$  bonding, like that of graphite, with a possible increase in conductivity. Support for this suggestion comes from the theoretical work of Stumpf and Marcus [18] on the relaxations of the analogous (111)- $(1 \times 1)$  faces of the diamond structure for both C and Si. They found that there is almost no change in the surface layers from the bulk structure, except for a decrease in spacing of the top bilayer of 45% for C and 22% for Si and small increases in the lengths of the bonds between the bilayer and the third layer. Similar but somewhat smaller changes of the same kind may be expected for Ge, tending to make its surface become more like that of graphite. Another reason for expecting that a flattening of the top bilayer, with its attendant decreased interatomic distances, would lead to an increase in its conductivity comes from a comparison with Sn, the next heavier element in group IV. The change in the Ge surface may foreshadow the much more drastic bulk phase change at 286 K in Sn where the alpha (grey, cubic, and semiconducting) form changes to the beta (white, tetragonal, metallic, and denser) form with long-range order preserved.

We conclude that at 1050 K the top layer of Ge(111) shows an order-order transition to a bilayer with spacing reduced by about 10%. This is consistent with all the evidence available. In the LEED experiment on Ge(111) [1,2] each first-order diffraction peak was measured using the incident beam energy for which it was maximized at low temperatures, so a bilayer shrinkage would shift the  $I$ - $V$  curves and thus could lead to the observed decreases in all the diffraction peaks. Ion scattering results rely on the shadowing of deeper bilayers by the top bilayer [5]. Thus for an incident beam not normal to the surface, like that used, a change in the top bilayer spacing would be expected to produce an increase in scattering corresponding to that of 1 or 2 monolayers, just the amount seen. The observed increases in the first- and second-order x-ray diffraction peaks are consistent with

order [6], but with altered diffraction probabilities due to a change in the relative positions of the atoms in the first few layers. In summary, our results provide the first direct and consistent evidence for an order-order transition to a high temperature phase which has no observable increase in the density of defects, has a reduced top bilayer spacing, and may be metallic.

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