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A quantitative evaluation of the dimer concentration during the (2 × 1)-(1 × 1) phase transition on Ge(0 0 1)

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Abstract

We propose a new quantitative model of the high-temperature (2 × 1)-(1 × 1) phase transition on Ge(0 0 1). We demonstrate that the transition is driven by an entropy facilitated breakup of dimers. A full quantitative description of the reversible variation of the dimer concentration requires incorporation of vibration entropy, not only of the topmost atoms, but also of those in two layers beneath. The main ingredients of our new model include the dimer formation energy and the difference in vibration entropy between the reconstructed (2 × 1) and the bulk-terminated (1 × 1)-phase. This entropy difference amounts to about 1.4 meV/K and the obtained dimer formation energy of 1.5 ± 0.2 eV is in good agreement with calculated values.
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The physical nature of the reversible (2 × 1)-(1 × 1) phase transition on Ge(0 0 1) is subject to considerable controversy. In their early X-ray diffraction study Johnson et al. [1] report that the phase transition is driven by dimer break-up, accompanied by "a corresponding loss of height–height correlation". In contrast, Lelay et al. [2] conclude from their angle-resolved photo-emission data that the number of dimers remains essentially conserved. Both sides attracted support in later studies. Cvetko et al. [3] claimed an order–disorder phase transition from their TEAS study. A similar conclusion was reached by Zeng and Elsayed-Ali [4]. Further support for Lelay et al. was provided by a more recent photo-emission study by Santoni and Dhanak [5]. In contrast, our recent low energy electron microscopy and diffraction study [6] demonstrates that heavy dimer break-up drives the reversible transition in support of Johnson et al. Asada and Miura now support that conclusion [7] after initially challenging it [8].

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The assignment of essentially conserved dimers is based on the observation of a finite density of states near the Fermi level. This is consistent with theory showing that symmetric dimers give rise to a metallic peak at the Fermi level [9,10]. Indeed it has been demonstrated recently that (2×1) domains with symmetrically appearing dimers show metallic behavior, while asymmetric dimers composing the coexisting $c(4 \times 2)$ phase do not [11]. However, we claim [12] that monomers provide metallic character too. This fact was disregarded in Lelay et al.'s paper [2] and by their supporters. Note also that the exact position of the Fermi level depends on the surface structure and thus on the dimer concentration! Lelay et al.'s paper and all subsequent supportive papers have in common that the presumed structural information is indirect and subject to interpretation.

Johnson et al.'s [1] conclusion on the breakup of dimers was based on a structural study. Recently, we could demonstrate that the integrated intensity of the $(\frac{1}{2}, 0)$ peak is an unequivocal measure of the dimer concentration [13,7]. Therefore, it is a hard structural fact that the dimer concentration varies from 100% to less than 1% during the phase transition. Unfortunately, McCoy et al. [14] did not fully appreciate this fundamental structural knowledge in their theoretical description of Johnson's experimental data.

Below we provide a new quantitative model for the varying dimer concentration during the phase transition. The transition occurs close to the melting temperature and entropy effects may thus be crucially important. As a starting point we consider a thermodynamic description of the Ge(0 0 1) surface. Following Sparnaay [15] we note that we are clearly dealing with a microcanonical ensemble. It is emphasized that surface tension and entropy are the only system variables, which are not constant as function of dimer concentration. Obviously, the surface tension depends strongly and directly on the reconstruction of the surface. Consequently, any variation of the surface tension must be compensated by a corresponding entropy change.

We consider a partly reconstructed surface with dimer concentration θ. For the surface free energy per site one obtains

$$F = -u \cdot \theta + \theta \cdot kT \cdot \left[\frac{1-\theta}{\theta} \ln(1-\theta) + \ln \theta \right]$$
$$- \theta \cdot T \cdot s_{\text{di}} - (1-\theta) \cdot T \cdot s_{\text{mo}} \tag{1}$$

The dimers are assumed non-interacting and thus placed randomly on lattice sites; u, s_{mo} and s_{di} denote the dimer formation energy and the entropy of a monomer pair and a dimer, respectively. The term in brackets, multiplied by Boltzmann's constant k, represents the configuration entropy per dimer. The equilibrium density is obtained by taking the derivative of Eq. (1) with respect to θ and putting it equal to zero. As a direct consequence of our starting point any change in u is compensated by a corresponding change in entropy, leading to

$$\frac{1}{kT} \cdot \frac{\mathrm{d}F}{\mathrm{d}\theta} = -\frac{u}{kT} + \ln \left(\frac{\theta}{1-\theta} \right) + k^{-1} \cdot (s_{\text{mo}} - s_{\text{di}})$$
$$= 0 \tag{2}$$

Eq. (2) is rewritten as

$$\theta = \frac{1}{1 + \exp\left[\left[-u + T \cdot (s_{\text{mo}} - s_{\text{di}}) \right] / kT \right]} \tag{3}$$

The consideration of possible contributions to the entropy terms leads to the conclusion that translation terms can be neglected in this 2D description and rotational contributions to $s_{\text{mo}} - s_{\text{di}}$ are assumed negligibly small. This only leaves vibration entropy as sizeable constituent in $s_{\text{mo}} - s_{\text{di}}$. Within the high-temperature approximation the Debye model yields for the vibration entropy for *one atom*:

$$s = 3 \cdot k \cdot \ln \left(\frac{T}{T_{\text{D}}} \right) \tag{4}$$

T_{D} denotes the Debye temperature, 374 K in the case of germanium [16]. The factor of three relates to the degrees of freedom for the vibrating atom. From now onwards we will take N_{a} as the effective number of atoms contributing to $s_{\text{mo}} - s_{\text{di}}$ per dimer site. N_{a} equals two would thus refer to the two atoms originally composing the dimer. With N_{a} and the dimer formation energy u as fitting parameters we obtain the fit to the experimental data shown in Fig. 1.
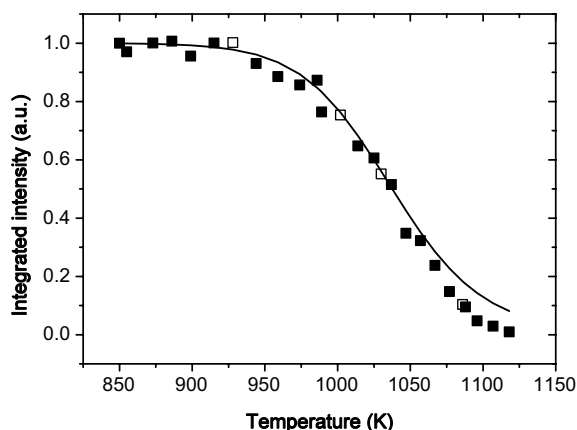
Fig. 1. Normalized 2D-integrated intensity of the $(\frac{1}{2}, 0)$-peak, corrected for linear Debye–Waller effects as a function of temperature. Full (open) data points taken with increasing (decreasing) temperature. The solid line fits to Eq. (3) with $u = 1.5$ eV and $N_a = 5.4$.

Fig. 2. *R*-factor (Eq. (5)) as a function of assumed dimer formation energy u.

The result is quite satisfactory with an *R*-factor, defined as:

$$R = \sqrt{\frac{\sum_T (I_{\text{measured},T} - I_{\text{model},T})^2}{\sum_T (I_{\text{measured},T})^2}} \quad (\text{with } T \leqslant 1080 \text{ K}) \tag{5}$$

of 0.04 and N_a equaling 5.4. N_a and u are strongly correlated. An equally good fit is obtained if one allows for enhanced vibration amplitudes of the atoms in the topmost layer. Assuming a surface Debye temperature $T_{\text{DS}} = 190$ K requires a dimer formation energy of 1.65 eV and a lesser involvement of atoms in hidden layers ($N_a \approx 4.8$). An even much better fit is achieved by taking into account inharmonic lattice vibrations. This involves an additional term in Eq. (4), which gets really active above 1080 K, with a modest ($\sim$15% at 1130 K) increase of s compared to Eq. (4). Being very close to the melting temperature the inclusion of such a term is perfectly reasonable. For simplicity, however, we choose to further apply the simple, straightforward results of Eqs. (3) and (4). This is motivated also by the increasing **relative(!)** uncertainty in the experimental data for $T \geqslant 1080$ K due to background corrections.

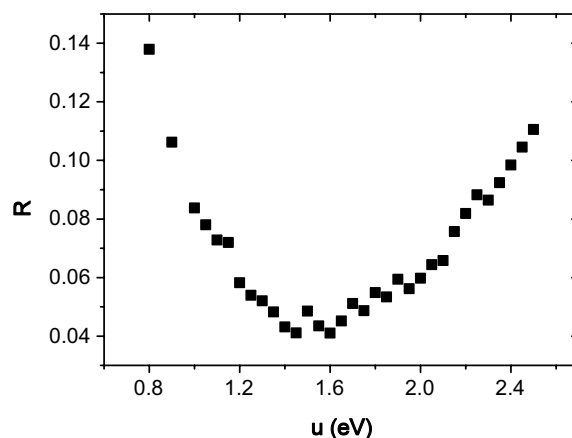Fig. 2 exhibits a plot of the *R*-factor as a function of the dimer formation energy u. These *R*-fac-

tors have been obtained by optimizing $s_{\text{mo}} - s_{\text{di}}$ for each assumed u-value. Note that $s_{\text{mo}} - s_{\text{di}}$ and u are strongly correlated. Fig. 2 shows a quite well defined minimum value of R for $u = 1.5 \pm 0.2$ eV, thus providing a meaningful experimental value for the dimer formation energy. This number is in good agreement with the value of 1.66 eV, calculated for Ge(001) by Krüger and Pollmann [17]. The corresponding optimum number for N_a suggests that per *dimer* site 5.4 atoms are involved in accommodating the vibration entropy difference. This obviously is impossible in a model restricted to one single plane. Therefore, rather three layers, i.e., the two atoms in the outermost layer and their neighboring pairs in two layers underneath are (partly) involved. This result appears perfectly reasonable after realizing that the formation of a surface dimer bond must lead to extensive lattice distortions due to the fact that the orientation of the surface dimer bond conflicts with the allowed bulk bond directions. This conflict probably imposes strong restrictions on the atomic vibrations in the nearby layer(s) when the surface atoms form a dimer. Therefore, the full vibration entropy is only available for the region beneath the dissociated dimers and not (or much less) beneath intact dimers.

We now concentrate on more details of the (2×1)-(1×1) phase transition. Fig. 3 shows the integrated intensity of both the specular beam
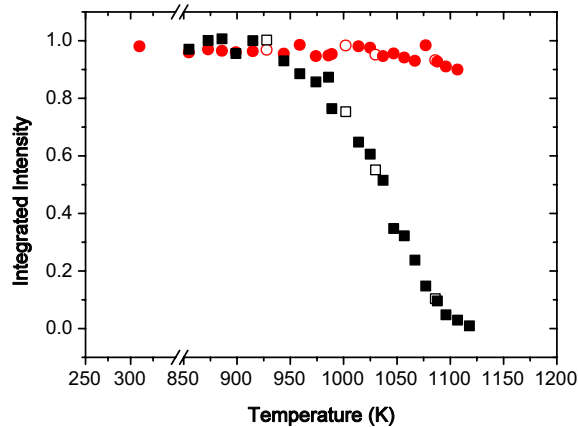
Fig. 3. Normalized integrated intensity of the $(0,0)$-beam (circles) and the $(\frac{1}{2},0)$-beam (squares). The intensities were corrected for Debye–Waller effects (see text). The filled and open symbols were taken with increasing and decreasing temperature, respectively.
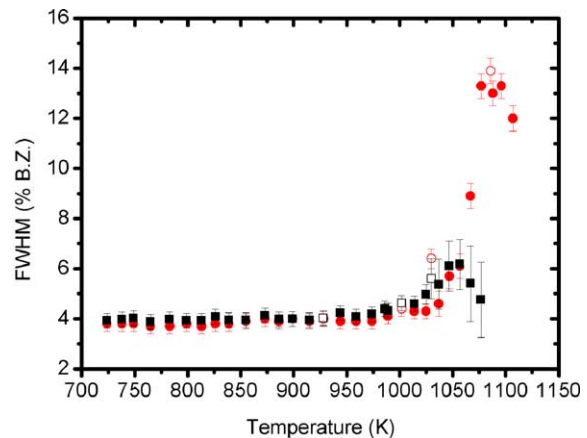

Fig. 4. The full width half maximum of the specular (circles) and the $(\frac{1}{2},0)$-order beam (squares) as a function of temperature. The full and open symbols have been acquired with increasing, respectively, decreasing temperature.

(circles) and the $(\frac{1}{2},0)$-order peak (squares). Both data sets have been corrected for linear Debye–Waller effects, i.e., the mean squared amplitude of surface vibrations is assumed proportional to temperature. By virtue of the low energy of the probing 4 eV electrons these corrections are extremely small (<15%) anyhow. The thermal behavior of the specular beam shows that no definite deviations from harmonic vibrations apply even close to the melting temperature. The data are not inconsistent either with a small anharmonicity above 1070 K, needed for a perfect fit of the $(\frac{1}{2},0)$-order diffraction data as mentioned above.

The literature dispute focuses on order–disorder considerations. To shed some more light on this matter, we have plotted the width of both the specular and the $(\frac{1}{2},0)$-order beam as a function of temperature in Fig. 4. The phase difference for scattering from adjacent terraces, separated by one layer high steps, amounts to 2.9 and 1.9 radians for the specular and the $(\frac{1}{2},0)$-order beam, respectively. We conclude that both data sets are sensitive to step proliferation with the specular beam data being most sensitive.

We also notice that, in contrast to the $(\frac{1}{2},0)$-order beam, the specular beam is not sensitive to the size of co-planar (2×1)-domains. Fig. 4 shows that the width of the specular beam increases sig-

nificantly only above about 1040 K, where the dimer concentration has decreased already by 50% or more. The increase in beam width is spectacular, indicative of substantial step proliferation during late stages of the phase transition. At 1090 the mean terrace width amounts to about 4 nm. Also the $(\frac{1}{2},0)$-order beam broadens with increasing temperature. Although its sensitivity for height differences is smaller than that of the specular beam, as outlined above, the broadening of the $(\frac{1}{2},0)$-order beam already takes off at significantly lower temperature. This reveals a decrease of the average (2×1) domain size occurs before step proliferation [6]: the breakup of dimers drives the shrinking of the (2×1) domains. The progressive dimer dissociation facilitates subsequent step meandering giving rise to shrinking mean terrace widths. This feature is in line with previously reported attractive forces between dimers [18]. The low intensity of the $\frac{1}{2}$-order peak at very high temperatures does not allow an accurate determination of the peak widths and therefore these data points have not been included in the figure. Note again that at all considered temperatures the observed behavior is fully reversible.

For completeness we remind the reader that a loss of height–height correlation not only occurs through step proliferation. A "non-reversible" planar roughening takes place above 1130 K [6], i.e.,

at very low concentrations of <1%. Then the dimers reside in their dissociated state for >99% of their time and lack in-plane binding during this time. In competition with their tendency to repeatedly form dimers with in-plane neighbors a particular surface atom has also the option to emerge from its parent terrace and become an adatom. This requires the breaking of two bonds with atoms in the layer below at a cost of the cohesive energy of 3.85 eV. In its final adatom stage the atom will regain the bonding of 3.85 eV plus about 0.2 eV assuming that the adatom is free to translate. So there is a clear incentive for atoms to stay on top caused by a 0.2 eV translation entropy driving the planar roughening. Apparently, this process occurs quite frequently at 1130 K and above leading to substantial surface roughening. Once formed this roughness does not reverse at a time scale at least two orders of magnitude larger than needed for the complete reversal of the step proliferation. For this reason we have coined this planar roughness transition as "non-reversible".

In a further contribution to solve the controversial discussion of the character of the (2×1)-(1×1) surface phase transition of Ge(001) we make below a concise comparison between present data set and that of Johnson et al. [1]. In short: We do not find any significant inconsistency between the two data sets.

The most eye catching apparent discrepancy is the difference on the temperature scale of about 100 K. The temperature measurement of semiconductor samples is notoriously troublesome. Following the procedure described in Ref. [1] (comparison of the readings of an optical pyrometer and a thermocouple) we managed to accidentally melt the crystal at about 100 K below the "anticipated melting temperature". This demonstrates that an absolute error of 100 K is easily made and the incident gave the benefit of an accurate and relevant calibration point. We consider our results close to reality and estimate our absolute temperature assignment good to 25 K. Further support for this conclusion is taken from the fact that the temperature difference between the (2×1)-(1×1) phase transition and the "irreversible" roughening is about 100 K in both experiments!

The reversible phase transition occurs in a temperature range of about 150 K. This holds also in the case of Ref. [1] assuming, as these authors do, a linear Debye–Waller correction. The seemingly more abrupt transition in Johnson et al.'s data relies heavily on a couple of very high temperature data points, which are subject to considerable uncertainty (see count rate!).

Ref. [1] reports a decay of the "X-ray reflectivity" around the phase transition as illustrated in Fig. 2c [1]. At first sight this seems at variance with our Fig. 3, which shows that the integrated intensity of the specular beam remains constant during the phase transition. Actually this latter result must be expected based on the kinematic approximation as long as the scattering density in the exposed layers remains constant (see also Ref. [19]). Note that neither our present model nor the model proposed in Ref. [1] allows for a variation of the atomic density in the exposed layers.

It is unclear how the notion "X-ray reflectivity" should be interpreted. Since the authors make a distinction between the term "integrated intensity" (in Fig. 2a [1] for the fractional order beam) and "X-ray reflectivity" (for the specular beam in panel c of Fig. 2 [1]) the latter probably refers to the height of the specular beam. In that case the difference must be attributed to the about one order of magnitude larger transfer width (sometimes confusingly referred to as coherence length) in the X-ray experiment. This leads to an earlier pickup of thermally induced broadening of the specular peak, also seen at higher temperatures in our Fig. 4. As mentioned above thermal effects, including dimer break-up, lead to enhanced step meandering, which gives rise to decreasing terrace widths and therefore increasing widths of diffraction peaks in non-Bragg positions. If, however, the decrease of the "X-ray reflectivity" as manifest in Fig. 2c of Ref. [1] has been obtained for fully angle integrated specular beams, the consideration outlined here does not apply. We emphasize that after correction for Debye–Waller effects a variation of integrated specular intensity is not anticipated within the framework of the kinematic approximation (cf. Ref. [19]). In that case the apparent loss of specular intensity must be attributed to cross section changes for specular

reflection from the exposed layers. This might even be conceivable in the X-ray study, since the experiment has been conducted at grazing incidence and the electronic density of states near the Fermi level changes throughout the phase transition. Another potential problem might arise from a different cross section for scattering from two monomers compared to that from one dimer. The grazing incidence X-ray data may be affected through one or both of these features, in contrast to the low energy electrons used in the present study.

The only remaining issue is that of the interpretation in terms of a three-level model [1] versus our one-level modeling. The authors of Ref. [1] admit that they need "unphysical" monomer densities in their upper level (and vacancies in the lowest level!) to explain the data in their Fig. 3. We claim that not only monomer densities of 50% and higher are unphysical but also much lower densities of roughly 30% are unphysical too. We also heavily challenge the obtained dimer formation energy of 0.33 eV [1], being clearly at variance with theoretical results too [17].

In short, we see no significant discrepancy between our data and those of Johnson et al. [1]. Our model thus provides a suitable framework to describe the latter as well. We do challenge Johnson et al.'s three-level model and find that it leads to unphysical results both in number density of vacancies/adatoms and in dimer formation energy.

In conclusion, the reversible (2×1)-(1×1)/Ge(0 0 1) phase transition occurs between 900 and 1100 K. It is unequivocally driven by a very substantial dimer breakup. The surface atoms continuously associate to form dimers and dissociate within the plane. The dimer formation energy amounts to 1.5 ± 0.2 eV. The equilibrium dimer concentration varies from "one" for $T < 900$ K to "zero" close to the melting temperature. In the latter situation dimers may be formed temporarily without preference for even or odd lattice sites. At higher dimer concentration the surrounding (2×1)-domains yield more strict constraints. The concentration of dimers during the phase transition is described in a quantitative model. The gain in vibration entropy for atoms in the first three layers is the most probable thermodynamic force driving the transition. Initially the (2×1) domains become smaller. Substantial step proliferation occurs during advanced stages. Above ~1130 K a "non-reversible" planar surface roughening occurs facilitated by translation entropy gain of an adatom compared to an embedded atom. Further simulations are needed to investigate the consequences of neglecting the dimer–dimer interactions underlying the applied lattice model.

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