PHYSICAL REVIEW B VOLUME 55, NUMBER 19 15 MAY 1997-I

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Surface silicon-deuterium bond energy from gas-phase equilibration''

Conyers Herring* and Chris G. Van de Walle
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304

(Received 22 February 1996)

In a recent paper [Phys. Rev. B **48**, 4492 (1993)] Wampler, Myers, and Follstaedt (WMF) have reported measurements of equilibrium adsorption of deuterium on cavity walls in crystalline silicon. Their procedure provides in principle a more reliable source of information regarding the Si-H bond energy than any previous work. Here we propose an analysis of the data that has some advantages over the analysis given by WMF and that yields a significantly higher binding energy. We first argue that the measure of binding most directly following from the observations is the free energy at 800° of a deuterium atom attached to an average surface silicon tetrahedrally bonded to three other silicons, relative to an 800° surface with a ''dangling bond'' at this site and a deuterium at rest far outside; this free energy is 3.29 ± 0.1 eV. We then discuss ways of extracting from this a value for the binding energy E_B at absolute zero, to compare with recent predictions from first-principles quantum-mechanical calculations. This step requires some assumptions about the effect of chemisorption on crystal vibrations; reasonable assumptions give about 3.15 eV, with a probable error modestly larger than that of the 800 °C free energy; the theoretical predictions range above and below this value by one or two tenths of an eV, depending on assumptions about reconstructions. [S0163-1829(97)00620-6]

It has been recognized for some time that a knowledge of the structure and energetics of the chemisorption bond between a hydrogen atom and a silicon surface is important for the understanding of many technologically interesting processes, such as surface passivation, etching, and growth. Naturally, therefore, numerous efforts have been made to determine the energy E_B of this bond, defined specifically as the amount by which the energy of hydrogen bound to a surface silicon atom with three other silicons as neighbors lies below that of a hydrogen atom at rest at infinity with a ''dangling bond'' left behind on the silicon. (This E_B may depend, but probably only slightly, on the arrangement of other silicon atoms on the surface.)

Most previous efforts to determine E_B have been based on studies of rates of thermal desorption of hydrogen.[1] Unfortunately, the interpretation of desorption data is beset by many uncertainties. For the conditions normally available, the desorbing species is H_2, and the interpretation of the rate depends on the model assumed for the breaking of SiH bonds and the formation of H_2. Not surprisingly, there seems to be a sizable activation barrier both for desorption and for the reverse process of adsorption into the chemisorbed state. The height of this activation barrier need have no simple relation to E_B, yet it is all important for the slopes of Arrhenius plots of desorption or adsorption rates.

Recognizing these sources of uncertainty, Myers *et al.*[2–4] have designed experiments measuring chemisorption under thermodynamic equilibrium conditions. Since rapid equilibration requires high temperature, where sizable adsorption requires high gas pressure, which interferes with measurements of adsorption, they opted to replace the usual study of adsorption on external surfaces with a study of adsorption on the walls of swarms of hollow cavities inside a silicon crystal. The cavities were generated by helium implantation followed by annealing to heal damage and expel the helium. Measurements of the amount of chemisorbed hydrogen could be made after quenching from the equilibration temperature and removal of the external hydrogen, since escape of hydrogen from the cavities via diffusion through the crystal was slow enough to be negligible during the quench. The amount chemisorbed could be inferred from measurements of infrared absorption bands or more accurately, since the chemisorbed hydrogen was greatly in excess of the hydrogen in other forms, from measurements of the yield of the transmutation reaction $D(^3He,p)\,^4He$. The earlier papers[2,3] focused on the kinetics of hydrogen loss from the chemisorbed layers on the cavity walls, which could be related to the previously known chemical potential and diffusion coefficient of hydrogen in interstitial solution at bulk sites of the crystal; this hydrogen remained essentially in equilibrium with the chemisorbed species during the anneals. In the most recent paper, by Wampler, Myers, and Follstaedt[4] (WMF) the chemisorption was studied at various known pressures of H_2 gas, and with the aid of auxiliary measurements that we shall not attempt to critique, the authors argued that all the important factors had finally been brought under control: equilibrium, thermodynamics of the H_2 phase, knowledge of surface area (from electron-microscopic study of the cavity distribution), stability of the chemisorption coverage under quenching, and its quantitative measurement.

Our primary goal in this communication is to point out that among the various possible descriptors of the strength of binding of a deuterium atom to a three-coordinated silicon surface atom, there is one, the mean free energy of binding to such surface atoms at 800 °C, that can be inferred from the experimental results of WMF without any reliance on other measurements on the silicon-hydrogen system or any assumptions about it, other than the assumption (made already by WMF) of independent binding to the dangling-bond sites. Our analysis thus provides an attractive alternative to that given by WMF, which deduced the energy of binding at 800 °C, rather than the free energy, by an argument making use of experimental results in the literature on the high-temperature solubility of hydrogen in bulk silicon, and incorporating some additional assumptions about the interpretation of these solubility results and about the similarity of the entropy changes associated with bulk and surface binding. The difference between our free energy and the energy inferred by WMF is larger than seems reasonable for the temperature-times-entropy term, and we believe that our number is the more reliable because it does not involve the ‘‘additional assumptions’’ just mentioned.

A second goal of the present work is to infer, from the 800 °C free energy of binding, as good an estimate as possible for the energy of binding at absolute zero, and to compare this with the predictions of recent first-principles theoretical calculations.[5,6] Such an estimate requires knowledge about the effect of hydrogen adsorption on the vibrational energy and entropy of the crystal surface, hence it requires the use of additional experimental and theoretical assumptions. Though further work needs to be done on these factors, we shall argue that a simple approximation using available data on hydrogen infrared modes is likely to provide a reasonable estimate, and one unaffected by uncertainties in the properties of bond-centered hydrogen at bulk sites.

In the experiment of WMF a silicon sample containing near-surface cavities was heated for a long time in a hydrogen atmosphere at each of several different pressures. This produced a state in which three subsystems were all in equilibrium with each other: the external H_2 gas, the cavity surfaces with adsorbed hydrogen, and the bulk of the crystalline silicon, with whatever fixed defects may have been present in it. In the heavily cavitated subsurface region, the amount of hydrogen bound on the cavity walls greatly exceeded the amount in bulk solution, on the external surface, or present as gas in the cavities. It could thus be measured after quenching, by a nuclear-transmutation technique.

Our analysis uses two inputs, the chemical potential of gaseous H_2 at the hydrogenation temperature and pressure (a well-known quantity, though not used in the analysis of WMF), and the measured concentration of adsorbed hydrogen on the cavity walls. The chemical potential of the latter hydrogen can be simply related (as was done by WMF) to the average free energy of binding of hydrogen to an adsorption site, if the interaction of adsorbates on different sites is neglected. Equating the two chemical potentials thus gives the free energy of binding. As was pointed out some years ago in a reinterpretation[7] of high-temperature solubility data,[8] such a free energy, obtainable from data at any single temperature, is likely to be more reliable than a binding energy obtained from the slope of an Arrhenius line, especially if data points for the latter are available only over a narrow temperature range.

We assume a fixed number N_s of cavity-wall chemisorption sites, each of which can bind a neutral H atom with a ground-state energy E_B relative to that of an isolated atom. We neglect interactions of chemisorbed atoms with each other, but allow each such atom to have an extra energy $E_{\rm vib}$ and entropy $S_{\rm vib}$ due to vibrational motion at the experimental temperature T. Then if the total energy of $N=\theta N_s$ adsorbed atoms is E_a and the total entropy S_a, the hydrogen chemical potential is

$$\mu_H=\left[\frac{\partial}{\partial N}(E_a-TS_a)\right]_{T,N_s}$$

$$=-E_B+E_{\rm vib}-TS_{\rm vib}-kT\ln\left(\frac{1-\theta}{\theta}\right), \qquad (1)$$

relative to the isolated-atom ground state. This μ_H must be the same as that of the gas phase

$$\mu_H=-\frac{E_D}{2}+\frac{H_g-TS_g}{2N_A}+\frac{kT}{2}\ln\frac{p}{1\,\text{atm}}\,, \qquad (2)$$

where the first term is half the dissociation energy E_D of the H_2 molecule, N_A is Avogadro’s number, H_g, S_g are, respectively, the enthalpy and entropy of hydrogen gas at the experimental temperature and one atmosphere pressure, and p is the experimental gas pressure. Equating Eq. (2) to Eq. (1) gives for the pressure dependence of the coverage θ,

$$\theta=\frac{c(p/1\ \text{atm})^{1/2}}{1+c(p/1\ \text{atm})^{1/2}}, \qquad (3)$$

where

$$c=\exp\left[\frac{E_B-E_{\rm vib}+TS_{\rm vib}-E_D/2+(H_g-TS_g)/2N_A}{kT}\right]. \qquad (4)$$

Figure 2 of WMF compares the observed $\theta(p)$ values with plots of Eq. (3) for three values of c. The central plot, which gives the best fit to the data, corresponds to $c=5.28$ at 800 °C, so that, with $E_D=-4.556$ eV, $(H_g-TS_g)/2N_A=-0.85$ eV for deuterium at this temperature,[9] one gets

$$E_B-E_{\rm vib}+TS_{\rm vib}=3.29\ \text{eV}. \qquad (5)$$

The result (5) is a fairly clean and unambiguous conclusion if one accepts the measurements of WMF and the approximate validity of a model with chemisorption on a single type of neutral noninteracting sites, a validity consistent with the fit of the theoretical and experimental $\theta(p)$ curves referred to above. To compare with the *ab initio* calculations of Refs. 5 and 6, we must make some guesses about adsorbate vibrations, which affect the ground-state energy E_B via their zero-point energy and also determine the last two terms on the left of Eq. (5). These contributions should properly be determined as differences of vibrational energy and entropy between states with and without the presence of chemisorbed hydrogen. The chemisorption adds three new modes per hydrogen, and it may also, by inertial loading and bond-bond

TABLE I. Comparison of estimates of the average binding energy of deuterium to a silicon surface dangling bond at $T=0$, obtained by starting from the experimental 800 °C measurements of Ref. 4, or from the first-principles calculations of Refs. 5 and 6.

Starting point	Major assumptions	Average binding energy, eV
Experiments	The last two terms on the left-hand side of Eq. (5) $\approx$ contribution of H modes $\approx$ 0.14 eV	3.15
First-principles theory	The surface is initially (111) 7×7, and	
	all changed to 1×1 by hydrogenation	3.35 (Refs. 5 and 11)
	all remains 7×7 after hydrogenation	3.08 (Ref. 6)

interaction, increase or decrease the frequencies of the remaining modes. For hydrogen attachment at a ''dangling bond'' site, however, it may well be that these effects on the silicon modes are rather smaller than the contributions of the new hydrogen modes, since the mass-loading effect is surely small, the hydrogen provides no other steric impediment to the motions of the silicons, and the effect of the new bond on the stiffness of the silicon-silicon bonds has been calculated, in some cases at least, to be fairly small. So pending the performance of more complete calculations, we shall make the crude assumption of equating E_{vib} and S_{vib} to the contributions of the hydrogen modes to these quantities.

Reference 2 reported a set of infrared absorption peaks associated with deuterium on cavity walls, with frequencies clustered about an average of about 1520 cm^{-1}, and presumably associated with stretching modes of Si-^{2}H bonds in several slightly different environments. If we evaluate the last two terms on the left of Eq. (5) for a stretching mode of this frequency plus two wagging modes of a third this frequency (as found by Cardona[10] for ^{1}H), we get $E_B \approx 3.15$ eV for the binding energy of deuterium to a surface monohydride site at $T=0$. The theoretical value predicted by the calculations of Ref. 5 was 3.60 eV, for a Si-H bond on a (111) 1×1 surface. This value included the effect of zero-point energy (0.21 eV) for ^{1}H; the corresponding zero-point energy for deuterium is 0.16 eV, leading to a theoretical binding energy of 3.65 eV.

The discussion just given has been carried out as if all the hydrogen bonding sites were like those on on a simple (111) 1×1 surface. This was what was assumed for the first-principles theoretical calculations in Ref. 5. For the experimental determinations of $\theta(p)$, this assumption may require a modest correction for two reasons: not all the cavity walls were of (111) orientation, since some (100) facets were observed, and higher-index orientations must also have been present; also, on the (111) facets, it is not certain whether all dangling bonds are equivalent, despite the disappearance of the 7×7 low-energy electron diffraction pattern at high temperature or hydrogenation. Without attempting to sort out these issues here, we wish merely to point out one fact. According to a recent estimate[11] the clean 7×7 surface has an energy lower than that of a hypothetical simple 1×1 surface by about 0.3 eV per surface atom. As noted in Ref. 5, the energy lowering, per surface atom, produced by first changing the 7×7 surface at $T=0$ to 1×1 and then adsorbing a ^{2}H atom on every surface site ($\theta=1$) would be $3.65-0.3=3.35$ eV. Now the same final state could be reached by progressively adsorbing small amounts of ^{2}H until $\theta=1$ is reached, with any appropriate modification of the reconstruction after each step, subject to ending up as 1×1. Therefore, the 3.35 eV could be regarded as the prediction of first-principles theory for the average, $\langle E_B\rangle$, of E_B over the successive steps, and over sites at each step.

For a non-(111) surface, or if the coverage with hydrogen does not completely convert the (111) 7×7 surface to a 1×1, some or all of the hydrogens will end up bonded to silicons with a substrate environment different from that of an atom on a 1×1 surface, and the theoretical average binding energy will be different. [The calculations of Ref. 6, for example, gave values ranging from 2.9 eV to 3.5 eV for attachment of a single ^{1}H atom to the different types of dangling bonds on a 7×7 surface. It is noteworthy, however, that earlier infrared measurements discussed in Ref. 4 indicated very similar binding energies for (111) surfaces and for monohydride coverage on (100).] A rather improbable extreme case would be adsorption on all the dangling bonds of an otherwise unaltered 7×7 surface. From Ref. 6, with the addition of about 0.05 eV to correct from ^{1}H to ^{2}H, this case gives $\langle E_B\rangle \approx 3.08$ eV.

Table I summarizes the reasoning we have used to get approximate comparisons of experimental and theoretical binding energies. The difference between the two theoretical entries is probably mostly due to the difference in assumptions described in the second column, rather than to the fact that Refs. 5 and 6 made independent calculations by somewhat different techniques, since for the one case calculated by both [saturation coverage of a (111) 1×1 surface] the two methods gave binding energies differing by only 0.1 eV. The agreement of the numbers in the last column is as good as could be expected in view of the uncertainties mentioned in the second column.

This is, we believe, the best that one can say at present regarding the relation of the experiments of WMF to first-principles theoretical calculations. A more accurate comparison will be possible if more information becomes available on the effects of chemisorption on the stiffness parameters of the silicon lattice. However, we do not believe that the crudity of our assumptions on this subject is a major cause of the contrast between our present conclusion and the apparent import of the words ''The bond strength of deuterium (D) to the surface of silicon was determined to be 2.67 ± 0.1 eV...'' in the first line of the abstract of WMF. The latter number was inferred by WMF as the enthalpy lowering, $-E_T$ per adsorbed atom, when deuterium is removed from D_2 gas at 800 °C and attached to dangling bonds at a silicon surface at this temperature, plus half the low-temperature dissociation energy of a molecule. It is thus not directly comparable with the 800 °C free energy of our Eq. (5) or with the $T=0$ energies of Table I. We may obtain a more convenient quantity for discussion if we add to $-E_T$ half the enthalpy gain (0.32 eV per molecule) when the gas is heated from the absolute zero to 800 °C. This gives the energy change per atom on converting ground-state molecules to chemisorbed atoms on an 800 °C surface. Combining with the half dissociation energy as before now gives the energy lowering ($E_B - E_{\mathrm{vib}}$, in the notation used above) on converting ground-state atoms to chemisorbed atoms on the 800 °C surface; with an additional 0.02 eV to correct the 4.60 eV room-temperature energy of WMF to the $T=0$ value 4.56 eV, one gets finally, at 800 °C,

$$(E_B - E_{\mathrm{vib}})_{\mathrm{WMF}} = 2.67 - 0.16 - 0.02 = 2.49 \pm 0.1 \text{ eV}. \quad (6)$$

The correct ($E_B - E_{\mathrm{vib}}$) at 800 °C should differ from Eq. (5) simply by the term TS_{vib}; however, a surprisingly large value, 0.8 eV, would be required for the latter quantity to make Eq. (6) and Eq. (5) agree. The rough model we have proposed above (neglect of the alteration of the ‘‘silicon modes’’ by chemisorption) predicts only about 0.30 eV for TS_{vib}. So we must conclude either that there is a marked softening of the ‘‘silicon modes’’ by the chemisorption, so that our model vastly underestimates S_{vib}, or else that the two physical assumptions used by WMF to infer the value (6) from the experimental data are not to be trusted. The first of these assumptions, explicitly stated in Ref. 4, was as follows:

(a) The changes in vibrational energy and entropy due to attaching a hydrogen atom to a surface dangling bond are nearly the same as those produced by inserting a hydrogen atom at a bond-center position deep in the silicon lattice.

The second assumption, not stated explicitly but implicit in the absence of any mention of charge states of dissolved hydrogen, was as follows:

(b) The dissolved hydrogen measured in existing solubility studies above ~1000 K (e.g., the early work of van Wieringen and Warmoltz[8] or the recent work of Binns *et al.*[12]) consists of nearly all the monatomic neutral species H^0.

Actually, this assumption can be relaxed somewhat, as Eq. (3) of WMF, the key equation used to extract the chemisorption energy, uses only one datum from the solubility experiments, namely, the prefactor C_0 in the Arrhenius expression for what is interpreted as the concentration of dissolved H^0. Thus (b) can be replaced by the less restrictive assumption

(b′) The intercept of the Arrhenius line for dissolved H^0 (at constant gas pressure) differs negligibly from that which has been reported for total dissolved hydrogen.

There are good reasons for mistrusting (a) and (b′). We shall start with a few general remarks about why (a) is qualitatively implausible, and then raise some quantitative issues about high-temperature solubility that probably imply that even if (b′) is not far wrong, (a) is a poor approximation. Our general distrust of (a) is due to the fact that bonding of hydrogen is very different in the chemisorption and solid-solution cases. For the former, the approximate description of the bond in molecular-orbital terms is that there is a double occupancy of a bonding orbital formed from a hydrogen 1*s* orbital and a tetrahedral silicon *s*-*p* orbital. For solid-solution hydrogen at a bond-center site, the corresponding approximation has single occupancy of an antibonding orbital formed from the tetrahedral orbitals of the two neighboring silicons. Unlike the hydrogen 1*s* orbital, this antibonding orbital has a node at the position of the hydrogen when the latter is at its mean (bond-center) position, though the Coulomb field makes it crowd more toward this node than the antibonding orbital between silicons would in the absence of the hydrogen. This picture is confirmed by the low hyperfine splitting found in electron spin resonance of dissolved hydrogen[13,14] or ‘‘anomalous’’ muonium.[15] Besides this difference in bonding, the chemisorbed and solid-solution cases differ greatly in their geometry, the former having a free attachment to one silicon, and the latter having hydrogen squeezed in between two silicon neighbors.

There are several as yet unresolved uncertainties regarding the proper interpretation of existing high-temperature solubility data, and it would be inappropriate to try to discuss these fully in the present paper. We shall merely mention a few facts and puzzles that bear on the reliability of (b′), and more importantly on the reliability of (a).

To begin with, studies published since Ref. 4 have established conclusively that near and below room temperature the H^0/H^+ donor level is high,[14] near the conduction-band edge, while the H^-/H^0 acceptor level is near midgap,[16] so that hydrogen is a strongly ‘‘negative-*U*’’ impurity. Assuming a qualitatively similar picture at 1000°–1300 °C, we must expect monatomic hydrogen in intrinsic silicon at these temperatures to be mostly H^+, not H^0. If the donor level were independent of temperature, the Arrhenius prefactors for H^0 and H^+ would only differ by a factor two (the spin degeneracy), an inconsequential amount. However, a larger difference could occur if the donor level varies with temperature (i.e., if the vibrational entropies of H^+ and H^0 are different). While a seriously large difference in prefactors would probably only occur if one of the species ‘‘rattles,’’ i.e., has access to a rather large volume around its minimum-energy position within which its adiabatic potential is no more than one or two kT above its minimum value, it happens that the likelihood of just such a rattling was explicitly pointed out a few years ago on the basis of first-principles energy calculations.[17]

Moreover, there is experimental evidence for ‘‘rattling’’ of the dominant species (presumably H^+). By reasoning closely paralleling that of Eqs. (1)–(5) above, one can relate the concentration of the latter in equilibrium at any temperature T to its binding energy E_B at $T=0$ and the change per dissolved atom in the vibrational free energy at temperature T. Thus the height and slope of the Arrhenius line on any small region of temperatures determine E_B and the hydrogen-induced change S_{vib} in vibrational entropy. It turns out that either of the Arrhenius lines for total dissolved hydrogen reported in Refs. 8 and 12, respectively, requires, if interpreted as dominated by H^+, that the value of S_{vib} for H^+ at around 1400 K be about (10–11)k, about twice the value that would be contributed by stretching and wagging modes of frequencies similar to those for surface-bound hydrogen.[2,10] But a ‘‘rattling’’ of the H^+ over a volume almost an order of magnitude larger than that accessible to an atom vibrating with typical hydrogen-mode frequencies might account for the large S_{vib}. Alternative explanations, which we would regard as less plausible, could be a marked softening of the silicon-silicon bonding by the presence of H^+, or a large contribution of some other species, e.g., H_2, to the measured total dissolved hydrogen.

It should now be clear that the simultaneous validity of assumptions (a) and (b′) is very unlikely. If among the alternatives mentioned at the end of the last paragraph the favored one—rattling of H^+—is correct, (b′) can be correct only if bond-centered H^0 rattles with similar parameters. But in such a case assumption (a) is surely wrong, since surface-bound H^0 surely does not rattle. The hypothesis of silicon-silicon bond softening by H^+ could allow the validity of both (a) and (b′) if there were a remarkable three-way coincidence of the amounts of bond softening by bond-centered H^0, bond-centered H^+, and surface-bound H^0. And if a species like H_2 were steering the Arrhenius line of the solubility, this line would have no relevance to the chemisorption of a single H^0.

So much for our preferring to focus attention on Eq. (5) and Table I rather than on the procedure used by WMF to estimate binding energy. Similar arguments, which we shall not describe in detail, suggest an upward revision of the estimates of E_B derived in Refs. 2 and 3 from the measured escape rate of hydrogen from the cavities through the bulk. This is because the analysis in the latter studies, though in principle correct, again made use of what we believe to be an inappropriate interpretation of the results of Ref. 8.

In conclusion we would like to stress the desirability of further experimental work, perhaps simply extensions of the work of WMF. It might be possible, for example, to refine the numerical data and explore their dependence on the mix of crystallographic planes involved. And, perhaps more importantly, if a wide enough temperature range could be covered to construct an Arrhenius line, the intercept of the latter could provide an experimental check on the estimation of the E_{vib} and S_{vib} occurring in Eq. (5).

We acknowledge useful discussions with D. Biegelsen and J. E. Northrup. We would also like to thank the authors of Ref. 4 for an illuminating correspondence.

---

[*] Permanent address: Department of Applied Physics, Stanford University, Stanford, California 94305.

[1] M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, Surf. Sci. **258**, 166 (1991), and references therein.

[2] S. M. Myers, D. M. Follstaedt, H. J. Stein, and W. R. Wampler, Phys. Rev. B **45**, 3914 (1992).

[3] S. M. Myers, D. M. Follstaedt, H. J. Stein, and W. R. Wampler, Phys. Rev. B **47** 13 380 (1993).

[4] W. R. Wampler, S. M. Myers, and D. M. Follstaedt, Phys. Rev. B **48**, 4492 (1993).

[5] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[6] H. Lim, K. Cho, I. Park, J. D. Joannopoulos, and E. Kaxiras, Phys. Rev. B **52**, 17 231 (1995).

[7] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986); C. Herring and N. M. Johnson, in *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic Press, Boston, 1991), Sec. III 2 b, Chap. 10.

[8] A. van Wieringen and N. Warmoltz, Physica **22**, 849 (1956).

[9] D. R. Stull and H. Prophet, in *JANAF Thermochemical Tables*, 2nd ed., Natl. Bur. Stand. (U.S.) No. NSRDS-NBS 37 (U.S. GPO, Washington, D.C., 1971).

[10] M. Cardona, Phys. Status Solidi B **118**, 463 (1983).

[11] I. Štich, M. C. Payne, R. D. King-Smith, J.-S. Lin, and L. J. Clarke, Phys. Rev. Lett. **68**, 1351 (1992).

[12] M. J. Binns, R. C. Newman, S. A. McQuaid, and E. C. Lightowlers, Mater. Sci. Forum **143-147**, 861 (1994).

[13] Yu. V. Gorelkinskii and N. N. Nevinnyi, Pis'ma Zh. Tekh. Fys. **13**, 105 (1987) [Sov. Tech. Phys. Lett. **13**, 45 (1987)]; Physica B **170**, 155 (1991).

[14] B. Bech Nielsen, K. Bonde Nielsen, and J. R. Byberg, Mater. Sci. Forum **143-147**, 909 (1994).

[15] R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988).

[16] N. M. Johnson, C. Herring, and C. G. Van de Walle, Phys. Rev. Lett. **73**, 130 (1994).

[17] C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988); C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).