Depth-dependent ordering, two-length-scale phenomena, and crossover behavior in a crystal featuring a skin layer with defects

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Structural defects in a crystal are responsible for the "two-length-scale" behavior in which a sharp central peak is superimposed over a broad peak in critical diffuse x-ray scattering. We have previously measured the scaling behavior of the central peak by scattering from a near-surface region of a V_2H crystal, which has a first-order transition in the bulk. As the temperature is lowered toward the critical temperature, a crossover in critical behavior is seen, with the temperature range nearest to the critical point being characterized by mean-field exponents. Near the transition, a small two-phase coexistence region is observed. The values of transition and crossover temperatures decay with depth. An explanation of these experimental results is here proposed by means of a theory in which edge dislocations in the near-surface region occur in walls oriented in the two directions normal to the surface. The strain caused by the dislocation lines causes the ordering in the crystal to occur as growth of roughly cylindrically shaped regions. After the regions have reached a certain size, the crossover in the critical behavior occurs, and mean-field behavior prevails. At a still lower temperature, the rest of the material between the cylindrical regions orders via a weak first-order transition.

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I. INTRODUCTION

Since defects exist in any real system, the understanding of their influence on ordering and structural phase transitions is important. A signature of the presence of defects in a crystal near a phase transition is the so-called "two-length-scale" behavior, in which, in the critical diffuse scattering (CDS) of x rays or neutrons, a narrow "central peak" is found on top of a broad peak.[1,2] Previous theoretical studies of this behavior have established that one cause of this is the presence of dislocation lines.[1–3] These theories argue that the strain field associated with a dislocation line results in the growth of a roughly cylindrical ordered region near the dislocation line itself. Such regions order at a temperature higher than the defect-free crystal. Accordingly, while the order occurs in the cylindrical regions, the broad peak in the CDS is due to thermal fluctuations in regions of the material which are relatively unaffected by the strain field, while the narrow central peak is due to the fluctuations in regions where the enhanced ordering occurs.

Unaccounted for in these theories, however, is the fact that in many real systems defects do not exist uniformly throughout the crystal. Often defects are caused by surface treatments or surface reconstructions and in this case they accumulate near the surface and their density decays with depth. When this happens, the ordering properties and two-length-scale behavior depend on depth as well. Indeed, with high-resolution x-ray diffraction measurements, we have previously found that V_2H has two-length-scale and associated behavior that is depth dependent.[4,5] These measurements were performed in both reflection and transmission geometries, allowing us to compare the behavior of the crystal at different depths. In this paper, we propose a theoretical explanation of these experimental results that accounts for the depth dependence of the observed behavior.

Systematic studies of many materials in which two-length-scale behavior has been found,[6–16] including previous studies of V_2H,[4] have concluded that the narrow central peak of the CDS only occurs in the scattering from a defective "skin layer," that is a region of the material that starts a few hundred angstrom below the surface and extends several tens of micrometer below the surface. However, to the best of our knowledge, the two-length-scale behavior in V_2H is different from that which has been observed in any other material, because in V_2H the phase transition in the bulk is a first-order transition. In the skin layer, instead, the ordering is more complicated as found experimentally by a number of unusual phenomena including: (1) diffuse scattering which, as the temperature is lowered toward a critical value, consists of a broad peak that changes only slightly with temperature and a narrow central peak with an amplitude that diverges;[4] (2) an effective critical temperature $T_c(y)$ for the behavior of the central peak that changes with the depth y below the surface and extrapolates to a temperature T_c^∞ that always exceeds the bulk transition temperature T_0;[5] (3) a crossover in the universal critical behavior shown by the central peak from three-dimensional mean-field critical behavior to a different universality class as the temperature increases from $T_c(y)$;[4,5] (4) a narrow two-phase region and a weak first-order transition observed at temperatures $T_0(y)$ slightly below the critical value.[17]

In order to explain these experimental findings we present a theory which accounts for the distribution of defects ex-

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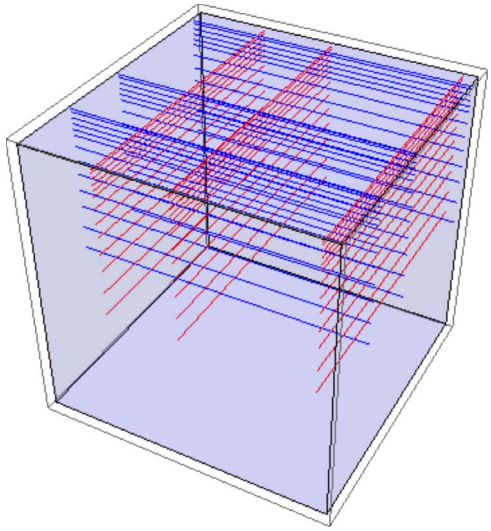

FIG. 1. (Color online) Schematic illustration of the arrangement of dislocation lines in V_2H. Edge dislocations are arranged in walls of parallel lines that extend in the directions normal to the surface, whose density decreases with depth. Two colors are used for clarity of presentation to distinguish the lines extending in the two directions but they do not correspond to any physical difference.

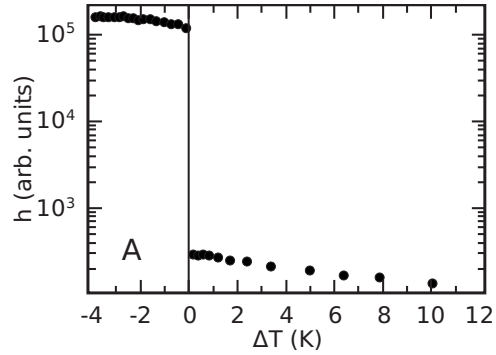

FIG. 2. Bulk measurements of the peak height h of the $(0\ 5/2\ \bar{5}/2)$ superstructure reflection vs $\Delta T = T - T_0$, where T_0 is the transition temperature for the bulk. The sudden jump of a few orders of magnitude in h is a clear indication that the transition is first order.

perimentally detected:[3] edge dislocations occur mostly in the skin layer, accumulating near the surface; they are arranged in arrays of parallel lines which we refer to as "walls;" each wall consists of lines that are oriented in either of the two directions *parallel* to the surface; the walls extend into the crystal and are thus oriented in either of the two directions *perpendicular* to the surface. In Fig. 1 we show a schematic of this arrangement of defects.

As with previous theories, the strain due to dislocation lines enhances the ordering in their vicinity. As the temperature is lowered toward the critical temperature, ordering in the skin layer first occurs in cylindrically shaped ordered regions (ORs) near the individual dislocation lines. However, in contrast to previous theories, which assumed the ORs grow freely, in our theory the interaction between lines constrains their collective growth. The ordering process responsible for the formation of the ORs is continuous and this explains the change in the order of the phase transition from first order in the bulk to continuous in the skin layer. Then, as the ORs grow and occupy more than a certain fraction of the material, the crossover in the universal critical behavior of the central peak occurs. Since the density of dislocation lines decreases with depth, the effective critical temperature also varies with depth. Finally, as the temperature is reduced further, below the effective critical temperature at any particular depth, the parts of the material in between the network of ORs undergo a weak first-order transition. Before presenting our theory, in the next section we recount in some detail the unusual experimental facts of the two-length-scale phenomena and associated behavior found in V_2H.

II. EXPERIMENTAL RESULTS

As in prior works,[3–5,17,18] we focus on the transition from the ordered monoclinic β_1 phase to the disordered body-centered tetragonal β_2 phase in which the c axis is along z (for the phase diagram see Ref. 19). In the β_1 phase, one half of the z-axis octahedral sites halfway between two V atoms, namely, the O_{z1} sites, are mostly occupied by hydrogen atoms, while in the β_2 phase both O_{z1} and O_{z2} sites are, on average, equally occupied.[20,21]

As first reported in Ref. 18, in transmission geometry there is clear evidence of a first-order transition in the bulk material (see Fig. 2). The diffuse scattering from the skin layer can be measured at various depths in reflection geometry by varying beam energy and reflection order. At temperatures above the bulk transition temperature, what we find is a broad peak corresponding to the bulk diffuse scattering, which increases slowly with decreasing temperature, coexisting with a central peak whose amplitude diverges at a temperature still higher than the bulk transition one.[4] The CDS of the central peak indicates that the transition is continuous in a skin layer that has a depth of several tens of micrometer. Remarkably, the temperature at which the CDS diverges depends on the depth probed. Thus, we find a depth-dependent critical temperature $T_c(y)$, where y is the effective scattering depth.[5] Furthermore, as shown in Ref. 4, there is a two-length-scale effect in the CDS from the skin layer. As the temperature is lowered toward $T_c(y)$, the height of the central peak, which is proportional to the susceptibility, shows a crossover in critical scaling behavior. In fact, for temperatures close to the critical temperature, the value of the critical exponent γ in the law $\chi \propto t^{-\gamma}$, describing the divergence of the susceptibility with the reduced temperature $t = T/T_c(y) - 1$, is always consistent with 1; similarly, the full width at half maximum of the central peak, which is proportional to the inverse correlation length κ, and which scales as t^{ν}, has its exponent always compatible with 0.5 (see two examples in Fig. 3). Also, we notice that, regardless of the depth, the value of γ is always compatible with 2ν. Note that these values of γ and ν, measured for small t, correspond to three-dimensional mean-field values.

We have considered the integrated intensities I of the superstructure reflections, which are proportional to $|t|^{2\beta}$. We find that the intensities exhibit power-law variations for temperatures below the critical value, but only if one neglects a

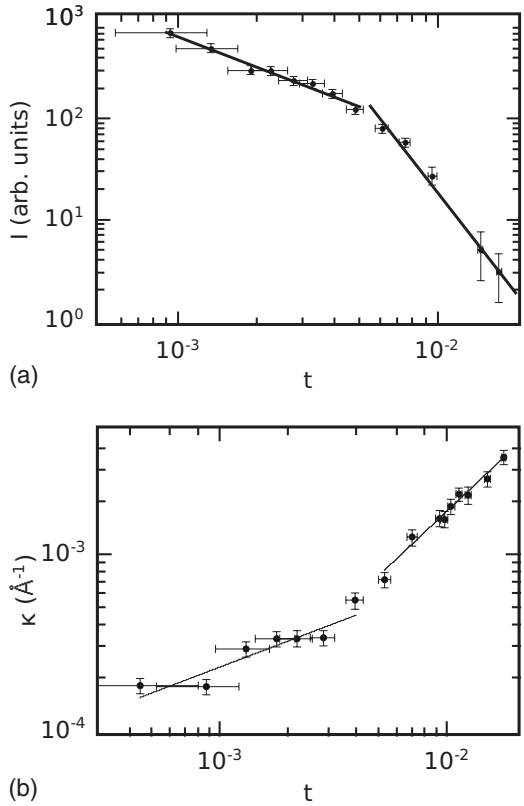

FIG. 3. (a) Peak height h of the $(0\ 5/2\ \bar{5}/2)$ superstructure reflection vs reduced temperature $t=\frac{T}{T_c(y)}-1$. The value of h is proportional to t^{γ} and thus shows the crossover of the critical exponent γ from a mean-field-compatible value of 0.93 ± 0.06 for small t to 3.3 ± 0.3 for higher t. The measurements were carried out at a depth y of 13.1 μm. (b) Inverse correlation length κ vs reduced temperature $t=\frac{T}{T_c(y)}-1$, showing the crossover of the critical exponent ν from a mean-field-compatible value of 0.49 ± 0.09 for small t to 1.22 ± 0.09 for higher t. The measurements were carried out at a depth y of 1.6 μm.

narrow temperature range of 0.6 K close to the critical point, which corresponds to a two-phase coexistence region (see Figs. 4 and 5). The existence of this region indicates that, even in the skin layer, there is an actual first-order transition, albeit with a weak character, as indicated by the power-law behavior outside the aforementioned small range of temperatures. The measured value of $\beta=0.174\pm0.003$, however, is not mean field but it is in agreement with an earlier measurement on a different crystal.[22]

Above the crossover, at larger t, different universal critical behavior is observed. Measurements indicating values of $\gamma=3.06\pm0.29$ and $\nu=0.69\pm0.09$ have previously been reported.[4] However, other data fits at these larger values of t give a range of values for γ and ν. For example, in Fig. 3 values of $\gamma=3.3\pm0.3$ and $\nu=1.22\pm0.09$ are found. Thus, unfortunately, the existing experimental data sets do not allow us to determine accurately the critical exponents for temperatures higher than the crossover. The available data show values for γ as low as about 1.8 and as high as 3 and values of ν from about 0.7 to 2.

Regarding the presence of defects in the material, dislocation walls are the only kind of defect that extends into the

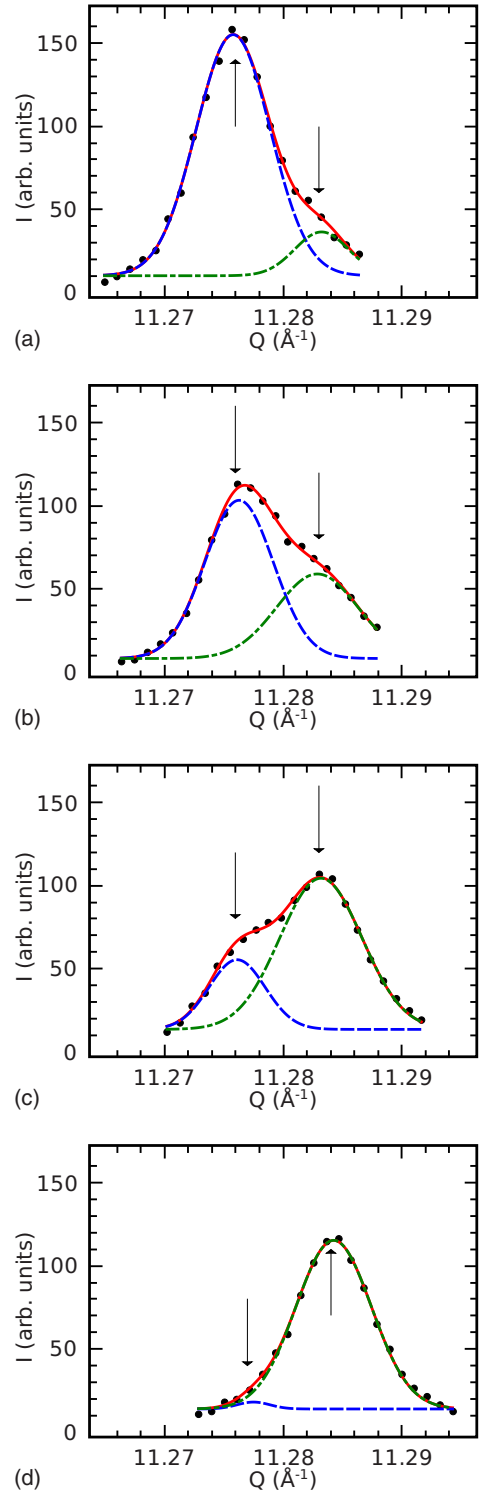

FIG. 4. (Color online) Intensities I of the $(0\ 4\ \bar{4})$ fundamental reflection in a range of temperatures of 0.6 K around the weak first-order transition temperature T_0' in the skin layer. From top to bottom, the measurements were taken at $T_0'-0.3$ K, $T_0'-0.1$ K, $T_0'+0.1$ K, and $T_0'+0.3$ K. The dashed blue and dashed-dotted green lines show individual Gaussian peak fits while the red lines are the convolutions of the single peaks. At all the temperatures we see peaks at $Q=11.276$ Å^{-1} and $Q=11.283$ Å^{-1} (indicated by arrows), corresponding to the β_1 and the β_2 phases, respectively. The measurements were carried out at a depth of 39 μm.

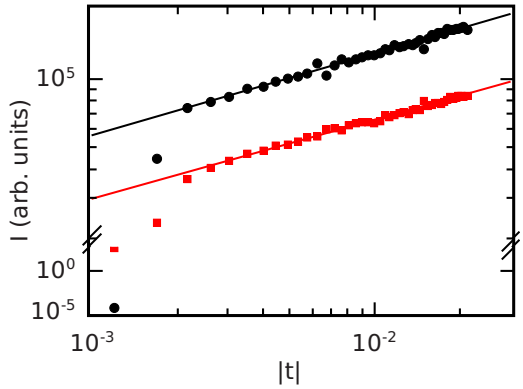

FIG. 5. (Color online) Integrated intensities I vs absolute value of reduced temperature $t=\frac{T}{T_c(y)}-1$. The integrated intensities, proportional to $|t|^{2\beta}$, allow us to estimate the long-range critical exponent β. The black circles correspond to the $(0\ 5/2\ \bar{5}/2)$ superstructure reflection, depth y of 25 μm; the red squares to the $(0\ 7/2\ \bar{7}/2)$ superstructure reflection, depth y of 34 μm. The like-colored lines show the results of fits which gave values for the critical exponent β of 0.180 ± 0.004 and 0.174 ± 0.003, respectively, obtained neglecting a narrow (0.6 K) region of two-phase coexistence.

crystal for several micrometer. Other kinds of defects are not found after the first 150 Å and the influence of this upper region on the scattering is negligible.[5] The arrangement of dislocation lines into walls, in the skin layer, is indicated by the mosaic spread. Walls occur inhomogeneously across the surface so that in planes parallel to the surface there is an inhomogeneous distribution of dislocation lines.[3]

III. THEORETICAL MODEL

In order to give a picture that describes the unusual experimental behavior of V_2H detailed above, let us consider a Ginzburg-Landau free energy density expansion for a crystal with an anisotropic distribution of dislocation lines. This free energy density is of the form

$$\mathcal{F}(r)=(\nabla\eta)^2+A_2\eta^2+A_4\eta^4+A_6\eta^6,$$

where $\eta(r)$ is the order parameter field, and A_2, A_4, and A_6 are coefficients that depend on position r, thermodynamic parameters, and, in some cases, the strain fields created by dislocations and structural ordering. In particular, the order parameter field is defined to be 0 for regions of the material which are in the disordered phase, 1 for points in the ordered phase with the hydrogen atoms in the O_{z1} sites, and -1 for the ordered phase with the hydrogen atoms in the O_{z2} sites. Also note that in the above equation the odd powers are missing as their presence is disallowed by the symmetry of the crystal structures.

Much of the unusual phenomenological behavior observed in V_2H can be explained through the behavior of the coefficients A_2 and A_4, which depends on the strain fields caused by the edge dislocations and on the structural ordering that occurs preferentially near them. In order to provide such explanation, we must not only understand the mechanism by which strain fields modify A_2 and A_4 in general, but also what specific modifications result from the particular morphological arrangement of dislocation lines that occurs in V_2H.

We will see that while the behavior of A_2 can explain the spatial variation in the critical temperature, the corrections to the fourth-order term justify instead the change in order of the transition. In particular, while a Ginzburg-Landau expansion yields critical behavior for vanishing odd-order terms, we can still describe a first-order transition by letting A_4 go negative.

In the remainder of this section, we will first discuss the effects of the defects on A_2, explaining the behavior of the critical temperature. Then, we will describe the shape of the ordered regions near the dislocation lines. Next, we will show how the ordering strains affect A_4, how this makes the transition in the skin-layer continuous, and how the crossover occurs. Finally, we will briefly discuss the effects of the depth-dependent crossover temperature on the size of the critical region and give an argument for the presence of a weak first-order transition in the skin layer.

A. Critical temperature

The compression-dilatation effect of an edge dislocation on a crystal is responsible for a change in critical temperature.[1] We can assume that the atoms of the crystal interact more strongly where they are pushed closer to each other, and vice versa that they interact more weakly in the opposite direction. As a first approximation we can assume that the correction to the critical temperature is proportional to the elastic strain in the crystal.

The elastic strain can be found following the general procedure described in Ref. 23. In the case of a single dislocation line this yields a trace of the stress tensor σ that in polar coordinates r and ϑ centered on the dislocation line is

$$\mathrm{Tr}\ \sigma=-\frac{\mu b}{\pi}\frac{1+\nu}{1-\nu}\frac{\sin\vartheta}{r}, \tag{1}$$

where μ is the shear modulus, ν is Poisson's ratio, and b is the magnitude of the Burgers vector. Making use of the relations between elastic constants,[24] we can rewrite Eq. (1) as

$$\mathrm{Tr}\ \sigma=-3\frac{Kb}{r}\frac{1}{2\pi}\frac{1-2\nu}{1-\nu}\sin\vartheta,$$

where K is the bulk modulus. The above equation, divided by $3K$, yields the strain, which, in our treatment, is proportional to the local relative critical temperature change τ_c,

$$\tau_c(r)\propto\frac{b}{r}\frac{1}{2\pi}\frac{1-2\nu}{1-\nu}\sin\vartheta, \tag{2}$$

where T_c' is the new critical temperature, and which is defined as

$$\tau_c=\frac{T_c'-T_c}{T_c} \tag{3}$$

with T_c the transition temperature for an undefected crystal. Notice that this result is in agreement with Ref. 1.

In the case of multiple dislocations, the effects of the single dislocation lines get superimposed. For walls of dislocations, this allows us to estimate the above quantities quite easily. Without loss of generality, we will consider a wall that extends in the y direction while the lines are parallel to z; we will indicate by $h(y)$ the local inverse linear density of defects, i.e., the local average distance between two lines. We rewrite then Eq. (2) in Cartesian coordinates as

$$\tau_c(r) \propto \frac{b}{2\pi}\frac{1-2\nu}{1-\nu}\frac{y}{x^2+y^2}, \tag{4}$$

where we used $\sin\vartheta = \frac{y}{\sqrt{x^2+y^2}}$ and $r=\sqrt{x^2+y^2}$. If $h(y)$ changes smoothly along the wall, we can then write

$$\tau_c(r) \propto \frac{b}{2\pi}\frac{1-2\nu}{1-\nu}\sum_{n=-\infty}^{n=+\infty}\frac{y+nh}{x^2+(y+nh)^2}, \tag{5}$$

where r is the radial distance outwards from the closest dislocation line and the dependence of h on y has been omitted for simplicity of writing. The sum of the series above is

$$\sum_{n=-\infty}^{n=+\infty}\frac{y+nh}{x^2+(y+nh)^2} = \frac{\pi}{l}\frac{\sin\left(\frac{2\pi y}{h}\right)}{\cosh\left(\frac{2\pi x}{h}\right)-\cos\left(\frac{2\pi y}{h}\right)}, \tag{6}$$

where l is the unit of length used. It should be noticed that the contribution decays exponentially with the normal distance x from the wall, in agreement with the experimental results in Ref. 3. Also, the rapid convergence of Eq. (6) suggests that h needs to vary slowly only over a short distance in order for the error made by considering it constant to be small. Substituting Eq. (6) in Eq. (5), we can then conclude that, in the case of dislocation walls, the local relative critical temperature change

$$\tau_c(r) \propto \frac{b}{2l}\frac{1-2\nu}{1-\nu}\frac{\sin\left(\frac{2\pi y}{h}\right)}{\cosh\left(\frac{2\pi x}{h}\right)-\cos\left(\frac{2\pi y}{h}\right)}. \tag{7}$$

Now, an expression can be found for the behavior of the critical temperature with depth. In first approximation,

$$T_c'(y+h) \approx T_c'(y) + \frac{\partial T_c'(r)}{\partial y}\delta y,$$

which can be rewritten as

$$T_c'(y+h) \approx T_c'(y) + \chi,$$

where

$$\chi \propto T_c h \frac{\partial \tau_c(r)}{\partial h}\frac{dh}{dy}.$$

Note that $\frac{dh}{dy}$ can be computed from experimental data, such as the ones reported in Fig. 5 of Ref. 3, while the other derivative can be computed from Eq. (7), yielding the following expression for χ,

$$\chi \propto T_c\frac{b}{2l}\frac{1-2\nu}{1-\nu}\frac{dh}{dy}\left(\frac{h\sin\left(\frac{2\pi y}{h}\right)\left[x\sinh\left(\frac{2\pi x}{h}\right)+y\sin\left(\frac{2\pi y}{h}\right)\right]}{\left\{x\left[\cosh\left(\frac{2\pi x}{h}\right)-\cos\left(\frac{2\pi y}{h}\right)\right]\right\}^2} - \frac{y\cos\left(\frac{2\pi y}{h}\right)}{h\left[\cosh\left(\frac{2\pi x}{h}\right)-\cosh\left(\frac{2\pi y}{h}\right)\right]}\right).$$

Notice that using typical values for the elastic constants, the proportionality factors in front of the functions in the above equations are of the order of unity.

As for A_2, the second-order coefficient in the free energy density expansion, we recall that without defects it is $A_2 = a(T-T_0)$ with a generic proportionality constant. From this expression and the definition of τ_c, we can write the new second-order coefficient of the expansion as

$$A_2'(r) = (1+\tau_c)A_2 - aT\tau_c.$$

The spatial dependence of the parameter is contained in the local relative critical temperature change, that we wrote here as τ_c for sake of simplicity, but which is actually $\tau_c(r)$. Thus, in contrast to A_2, A_2' varies in space.

Furthermore, summing the contributions coming from single dislocations or dislocation walls, one gets a field of relative critical temperature changes, which features in the free energy density expansion as follows:

$$\mathcal{F}(r) = (\nabla\eta)^2 + a\{T - T_0[\tau_c(r)+1]\}\eta^2 + A_4\eta^4 + A_6\eta^6.$$

In this treatment the strain field surrounding a dislocation line is spatially inhomogeneous and this leads to a spatial inhomogeneity of the ordering near a dislocation line. In fact, the strain field caused by a line is dipolelike. Because of this, at temperatures above the transition temperature of an undefected crystal, ordered regions exist below the dislocation lines, where the transition temperature is increased. On the other hand, the transition temperature on the other side of the line is symmetrically decreased. Thus, disordered regions exist within a dislocation wall even at a temperature T below the transition temperature of an ideal crystal. Then, at any depth, the correlation length along y cannot exceed a value

on the order of $h/2$; conversely, the local ordering temperature can only change when the density of defects changes, i.e., over a distance of at least a few h.

B. Shape of the ordered regions

To find the shape of the ordered regions, we first fix a value for the relative critical temperature change τ_c. Then, we solve Eq. (7) in order to find expressions relating x and y as functions of each other. These solutions correspond to the border of the ordered region for the chosen value of τ_c, and, up to a multiplicative factor that is on order of unity for typical values of the elastic constants, they are

$$y(x) = \frac{h}{\pi}\arctan\left\{\frac{\pi \pm \sqrt{\pi^2 + \tau_c^2\left[1 - \cosh^2\left(\frac{2\pi x}{h}\right)\right]}}{\tau_c\left[\cosh\left(\frac{2\pi x}{h}\right) + 1\right]}\right\}, \tag{8}$$

$$x(y) = \pm\frac{h}{2\pi}\operatorname{arccosh}\left\{\frac{2\pi\tan\left(\frac{\pi y}{h}\right) + \tau_c\left[1 - \tan^2\left(\frac{\pi y}{h}\right)\right]}{\tau_c\left[1 + \tan^2\left(\frac{\pi y}{h}\right)\right]}\right\}. \tag{9}$$

Note that the regions are symmetric with respect to the x and y directions.

From Eq. (8) it follows that the maximum extension of the regions along the y direction, D_y, happens at $x=0$, and its value is

$$D_y = \frac{h}{\pi}\arctan\left(\frac{\pi}{\tau_c}\right). \tag{10}$$

Notice that $D_y \to \frac{h}{2}$ when $\tau_c \to 0$, that is, the regions can never extend in y for a distance greater than $\frac{h}{2}$, as already stated in the previous section.

From Eq. (9), it follows that the maximum extension along the x direction, D_x, happens at $y=\frac{D_y}{2}$, and its value is

$$D_x = \frac{h}{\pi}\operatorname{arccosh}\left(\frac{2\pi\tan\left[\frac{1}{2}\arctan\left(\frac{\pi}{\tau_c}\right)\right] + \tau_c\left\{1 - \tan^2\left[\frac{1}{2}\arctan\left(\frac{\pi}{\tau_c}\right)\right]\right\}}{\tau_c\left\{1 + \tan^2\left[\frac{1}{2}\arctan\left(\frac{\pi}{\tau_c}\right)\right]\right\}}\right),$$

that can be rewritten as

$$D_x = \frac{h}{\pi}\operatorname{arcsech}\left(\frac{\tau_c}{\sqrt{\tau_c^2 + \pi^2}}\right). \tag{11}$$

Note that the center of the region is at $x=0$, $y=\frac{D_y}{2}$.

Now it is possible to show that the ordered regions grow from a rod-shaped nucleus with a circular cross section. With growth, their aspect ratio changes, making the cross section effectively elliptical. Finally, the constraint constituted by the order-inhibited zones above the dislocation lines introduces distortions in the shape. To show this, we prove that, for large values of τ_c, corresponding to the beginning of the growth of the regions, $\frac{x^2}{a^2}+\frac{y_C^2}{b^2}\approx 1$, where $a=\frac{D_x}{2}$, $b=\frac{D_y}{2}$ and $y_C=y-b$ is the y coordinate measured from the center of the region. In this regime, we can expand b as follows:

$$b \approx \frac{h}{2\tau_c} + O(\tau_c^{-3}).$$

Then, we use a similar treatment for a. First we expand the argument of the arcsech for large values of τ_c,

$$a \approx \frac{h}{2\pi}\operatorname{arcsech}\left[1 - \frac{\pi^2}{2\tau_c^2} + O(\tau_c^{-4})\right].$$

Then, we expand the arcsech for values of the argument close to 1, getting

$$a \approx \frac{h}{2\tau_c} + O(\tau_c^{-3}).$$

Expanding the argument of the arctan in Eq. (8) for large τ_c we get

$$y \approx \frac{h}{\pi}\arctan\left[\frac{\pi}{\tau_c}\frac{1}{\cosh\left(\frac{2\pi x}{h}\right) + 1} + O(\tau_c^{-2})\right],$$

where we have imposed the condition that the argument be real. Note that a big τ_c implies a small x. Then, it is

$$y \approx \frac{h}{2\tau_c} + O(\tau_c^{-3}). \tag{12}$$

Also note that in the beginning of the growth $a=b$. This means that the regions nucleate in the shape of narrow cylindrical rods along the dislocation lines. Figure 6 shows the shape of the cross section of the ordered regions for different values of τ_c.

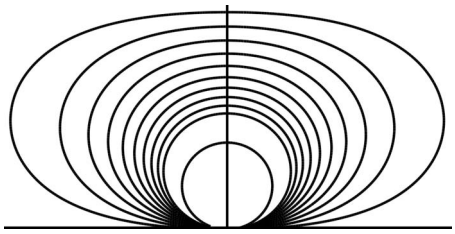

FIG. 6. Shape of the cross section of the ordered regions for different values of τ_c. From the outermost line inwards, the lines correspond to values of τ_c that range from 0.1 to 1, in steps of 0.1, except for the innermost line that corresponds to $\tau_c=1.5$.

Substituting Eq. (12) into Eq. (9), and expanding for high values of τ_c we find,

$$x \approx \pm \frac{h}{2\tau_c} O(\tau_c^{-3}).$$

Finally, we have

$$\lim_{\tau_c \to \infty} \frac{x^2}{a^2} + \frac{y_C^2}{b^2} = \frac{h^2}{4\tau_c^2}\frac{4\tau_c^2}{h^2} + \left(\frac{h}{2\tau_c} - \frac{h}{2\tau_c}\right)^2 \frac{4\tau_c^2}{h^2} = 1,$$

that is, for small sizes, the regions are effectively elliptical, and a and b can be identified with the major and minor semiaxes, respectively.

To understand the relative shape and size of the ordered regions in a wall at a particular fixed temperature, first notice that from the definition of τ_c [Eq. (3)] it follows that any given temperature T is critical for points in the crystal that satisfy the equation

$$T = T_c(\tau_c + 1),$$

that is to say, for points in which $\tau_c = \frac{T-T_c}{T_c}$. Then, from Eqs. (10) and (11), for a fixed value of τ_c the major and minor semiaxes of the ordered regions grow linearly with h. Consequently, for a fixed temperature, the density of defects decreasing with depth makes the size of the ordered regions grow with depth. Their aspect ratio, in contrast, remains the same. Of course, this argument is valid as long as the approximation employed to obtain Eq. (7) using Eq. (6) holds. Deep in the skin layer, where the density of defects almost vanishes, the strain field associated with any ordered region is restricted to that if a single dislocation line. Therefore, at great depths, the expression for τ_c tends to the form given in Eq. (4). Solving Eq. (4) yields

$$y(x) = \frac{1 \pm \sqrt{1 - 16\pi^2 x^2 \tau_c^2}}{4\pi\tau_c},$$

$$x(y) = \pm \sqrt{\frac{y(1 - 2\pi y \tau_c)}{2\pi\tau_c}}.$$

We can then calculate D_y and D_x as above,

$$D_y = y(0) = \frac{1}{2\pi\tau_c},$$

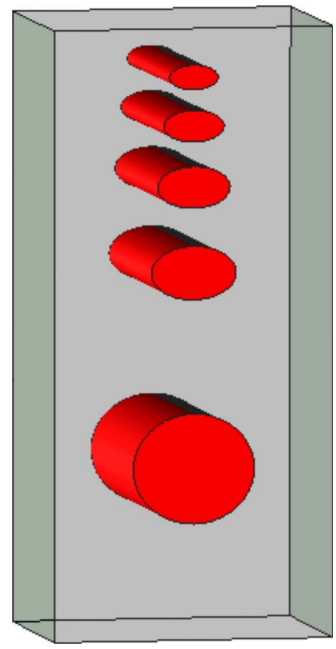

FIG. 7. (Color online) Schematic illustration of the shape and size of the ordered regions in a wall at a fixed temperature. The surface of the crystal is at the top of the image. The crystal extends beyond what pictured, that is just a region in the vicinity of a single wall. While in the skin layer the regions have an elliptical cross section whose aspect ratio is constant, at greater depths their shape becomes increasingly circular. Also, while the size of the regions increases with depth, their number density decreases.

$$D_x = 2x\left(\frac{D_y}{2}\right) = \frac{1}{2\pi\tau_c}.$$

Thus, as the depth increases, the shape of the cross section of the regions becomes increasingly circular (see Fig. 7).

C. Critical behavior

To determine how the defects affect the fourth-order term in the free energy density expansion, we start with finding the displacement field due to a point source of expansion by means of the tensor Green's function for the equilibrium equation. The displacement, which is purely radial, is

$$v_r = \frac{W}{4\pi(\lambda + 2\mu)}\frac{1}{r^2}, \tag{13}$$

where W is the work associated with this expansion, λ is Lamé's constant, and μ is the shear modulus.[23]

Then, consider the particular case of a local expansion due to the difference of structure between two points. Given our order-parameter field η, this expansion, purely hydrostatical since it is applied to an infinitesimal volume, can be thought of as due to an equivalent pressure

$$p = K\frac{\delta V}{V}[\eta(\vec{r}) - \eta(\vec{r}')] = K\frac{\delta V}{V}\eta(\vec{r}),$$

where K is the bulk modulus. Since we are associating a change in volume with a point, what we want to consider is

the smallest volume for which it makes sense to think about a change in structure, that is, the volume of a unit cell. So, calling v_O the volume of a unit cell in the ordered phase and v_D the one in the disordered phase, we have $\delta V = v_O - v_D$, hence

$$p = K\left(\frac{v_O}{v_D} - 1\right)\eta(\vec{r}). \tag{14}$$

The work done to achieve this deformation is

$$W = p\,\delta V = K\frac{(v_O - v_D)^2}{v_D}\eta(\vec{r}),$$

and we can use this expression in Eq. (13) to find the contribution to the displacement at the point $\vec{r}$ due to a point at $\vec{r}'$, which is

$$v_r = \frac{K}{4\pi(\lambda + 2\mu)}\frac{[v_O - v_D(\vec{r}')]^2}{v_D(\vec{r}')}\frac{\eta(\vec{r})}{r^2}.$$

Notice that we have made the dependence of v_D on the point explicit. For any particular $\vec{r}$, $v_O - v_D(\vec{r})$ vanishes in the limit of $T \to T_c(\vec{r})$. Then, knowing the field in every point, the total displacement at $\vec{r}$ is

$$\vec{u}(\vec{r}) = \frac{K}{4\pi(\lambda + 2\mu)}\eta(\vec{r})\int \mathrm{d}V'\frac{[v_O - v_D(\vec{r}')]^2}{v_D(\vec{r}')}\frac{\vec{r}'}{r'^3}, \tag{15}$$

where the integral is extended over all the points in the disordered phase.

Strictly speaking, Eq. (14) is valid when the transition is from the disordered to the ordered phase. For the inverse transition, δV has the opposite sign and the term in parentheses in Eq. (14) is $\frac{v_D}{v_O} - 1$. Yet, since $v_D \approx v_O$, the error committed in using the same formula is very small; in fact, in the subsequent equations the volume difference ends up squared, so that the error is actually of second order and is neglected in this linear treatment. Notice also that, after integration, the displacement is not necessarily purely hydrostatic.

From the displacement vector we can find the components of the strain tensor in Cartesian coordinates as

$$u_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \tag{16}$$

Then, from the generalized Hooke's law, we can find the correction to the free energy density due to the deformation induced by the phase transition, B, as

$$B = \mu\left(u_{ij} - \frac{1}{3}\delta_{ij}u_{kk}\right)^2 + \frac{1}{2}Ku_{kk}^2. \tag{17}$$

It is to be stressed that this quadratic form is always positive since K and μ are always positive. In fact, since the body is in equilibrium, in the absence of forces the energy must have a minimum at $u_{ij}=0$, that is, the quadratic form must be positive. Since this has to happen in any case, it also has to happen when the stress is a pure shear or a pure hydrostatic compression, that is, when only one of the two addenda is nonzero. This is the reason why both K and μ must always be positive.[24] Moreover the squares make this correction actually proportional to η^2. Then, when it is applied to the second-order coefficient in the free energy density expansion, where it belongs since its functional form is that of a strain, it yields a positive effective correction to the fourth-order term.

This correction, which corresponds exactly to the elastic free energy, does not depend on the actual structure of defects that causes it, but merely on the order-parameter field and, of course, on the elastic constants of the material. This means that, regardless if it is coming from a single dislocation, a wall of dislocations, or a more complicated framework of defects, once the elements of the strain tensor are known, they can be used to correct directly the free energy density expansion as discussed and as follows:

$$\mathcal{F}(r) = (\nabla\eta)^2 + a\{T - T_0[\tau_c(r) + 1]\}\eta^2 + \left[A_4 + \frac{B}{\eta^2}\right]\eta^4 + A_6\eta^6,$$

where τ_c is the local relative critical temperature change resulting from the superposition of the contributions of single dislocation lines [Eq. (2)] and dislocation walls [Eq. (7)]. While no quantitative solution of the above equations is offered here, notice that an explicit calculation would be very difficult. In fact, even in simpler cases of lattices in only two dimensions featuring regularly arranged point defects with short-range interactions, the results can be highly nontrivial.[25]

We know, however, that, from a purely phenomenological point of view, the change in order in a phase transition can be associated with the change in the sign of A_4, which determines whether the transition is continuous or discontinuous. The fact that the correction to this coefficient is always positive, shows how an originally negative A_4 can turn positive, thus resulting in a first-order transition becoming continuous in the presence of defects, as observed in V_2H.

Note that a correction to A_4 due to the ordering process exists also in an undefected material. However, at least in the beginning of the nucleation of the new phase in the disordered material, this correction is not greater than the one in the skin layer discussed above.[26] In fact, when the ordered phase starts to nucleate in a perfect crystal, the shape of the nucleus is that of an infinitely thin platelet.[27] The strain energy density contribution of the infinitesimal platelet is

$$\mathcal{F}_p = \frac{1}{2}C(\hat{n}_0), \tag{18}$$

where C is a linear function of the strains and $\hat{n}_0$ is the unitary vector minimizing C.[27] As before, the strains being proportional to η^2, the equation above yields an effective correction on the fourth-order term.

On the other hand, we have seen that the shape of the nucleus in the skin layer is that of an infinitesimal cylindrical rod. Then, Eq. (18) becomes

$$\mathcal{F}_s = \frac{1}{2}\langle C(\hat{n})\rangle,$$

where the brackets indicate the angular average of C. Since the average of a quantity is never smaller than its minimum,

the correction in the skin layer due to an infinitesimal nucleus cannot be smaller than the one in the bulk.

D. Tricritical behavior

Recalling Eq. (15), we notice that the more the order spreads, the more the domain over which the integral is carried out is reduced. Moreover, the contributions in the integral are weighted with the square of the distance to the point to which they apply.

Thus, with growing regions, the magnitude of the displacement vector will steadily decrease. Also, the displacement vector field will become spatially increasingly homogeneous, especially in points not too close to the borders. Therefore, the components of the strain tensor will decrease as well, since we know from Eq. (16) that they depend on the derivatives of the total displacement vector components, which are changing smoothly.

The fact that the correction to A_4 is proportional to the square of a linear combination of strain tensor components [Eq. (17)] guarantees that its value will be small and positive throughout the new transition. If this is added to a small negative "original" fourth-order coefficient, as it is the case in V_2H, whose bulk transition is first order, it will make A_4 effectively vanish, thereby making the transition behavior tricritical, and, because the upper critical dimension of this tricritical theory is 3, causing the mean-field values of the exponents that are observed experimentally.

Note that below a certain temperature where the wall lines have ordered independently, the walls consist of domains with order parameter of opposite signs. In the case of a complex framework of dislocation walls which intersect and interact with each other, on further lowering the temperature, one of the two signs will eventually spread throughout the network until the order parameter has the same sign everywhere (see also Fig. 8).

E. Effects on the critical region

The mechanism for tricriticality also provides an explanation for the depth dependence of the crossover temperature. In fact, the density of defects decreases with depth. Thus, in order for the domain of the integral in Eq. (15) to be sufficiently reduced, the temperature needs to be decreased more at greater depths. Consequently, the correlation length ξ has to increase more at greater depths than it has to in layers closer to the surface in order to reach the critical point. In other words, for the same change in reduced temperature, the change in correlation length is higher for shallower depths. The corresponding scaling law should then be modified so that the coefficient depend on depth,

$$\xi(d) = a(d)t^{-\nu}.$$

In particular, it is reasonable to expect $a(d)$ to be proportional to the density of defects, as it is in fact observed experimentally.[5] This mechanism provides an explanation as to why experimental measurements of ξ at different depths yield different values even if taken at corresponding reduced temperatures, once the depth dependence of the critical temperature has been accounted for, and even though the critical exponent remains the same. A treatment to collapse the data onto a single curve, including corrections for the experimental method used, has been proposed and verified in Ref. 5.

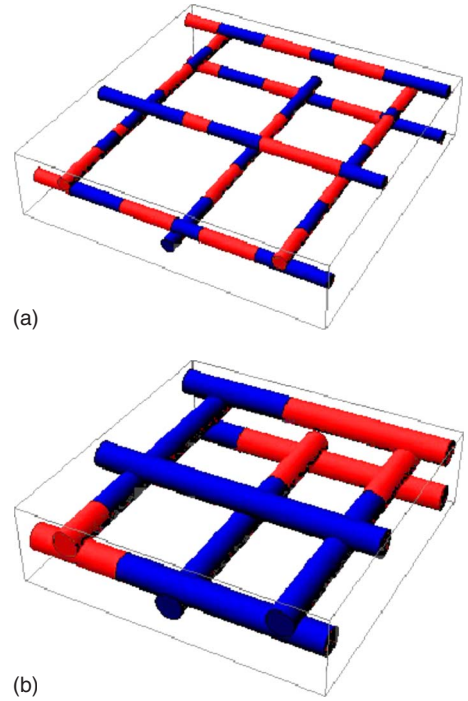

FIG. 8. (Color online) Schematic illustration of the ordering process near dislocation lines at an arbitrary depth. Red and light blue regions of the ordered regions distinguish different ordering domains, corresponding to the two different signs of the order parameter. At higher temperatures, shown in (a), the regions do not touch each other, the correlation length (average length of an ordered domain) is smaller than the distance between dislocation walls, and there is little or no correlation in the ordering in different regions. At lower temperatures, shown in (b), the ordered regions are thicker and now touch, the correlation length is longer than the average distance between dislocation walls, and the order is spreading throughout the network of regions.

F. Weak first-order transition

As the temperature is lowered below the critical point, the remaining material between the walls orders and a second, distinct, phase transition occurs. However, considering Eq. (15) again, we notice that the correction only applies to the material inside the "skeleton" of ORs. Therefore, for the material that is still between the ORs, the fourth-order coefficient is still negative. In such regions the transition is still first order but it is weaker than it is in an undefected crystal.

Because this transition is only weakly first order, a critical exponent β associated with it can still be measured as shown in Fig. 5. The measured values are 0.180 ± 0.004 and 0.174 ± 0.003. Such values confirm that the transition regime is not tricritical since in that case one would expect a mean-field exponent $\beta = 0.25$.[28]

IV. CONCLUSIONS

In conclusion, we have proposed a theoretical model which explains the two-length-scale phenomena and related

behavior observed experimentally in many materials, including the unusual ordering behavior observed in V_2H. In particular, the depth dependence of the critical temperature in the skin layer, reported recently,[5] is shown to be caused by the strain field induced by the presence of walls of dislocations. The ordering process itself crosses over between two regimes, causing the experimentally observed crossover in the values of the critical exponents. The additional strains induced by the formation of the ordered regions are responsible for increasing the effective value of the fourth-order coefficient in a Ginzburg-Landau free energy density expansion, thereby allowing the transition to become continuous in the skin layer even if it is first order in the bulk as we find in V_2H. Furthermore, the strength of this correction weakens during the spreading of the order through the network, driving the value of the fourth-order coefficient to zero, thus producing tricritical behavior and mean-field values of the critical exponents. Thus, when the temperature is lowered, first a continuous transition happens along the dislocations as described. Then, at a still lower temperature, the material between the cylindrical regions orders. However, it undergoes a transition that is first order, similar to the one that takes place in the bulk but weaker. The model also explains why, in the mean-field regime, the critical region has a depth-dependent size.

Although in this paper we have specifically considered the case of V_2H, the theoretical framework that we have developed should be broadly applicable for understanding ordering behavior in defective materials, particularly those that have an anisotropic distribution of defects. We considered a situation in which the bulk, and the material in between the interconnected network of cylindrical regions in the skin layer, orders through first-order transitions. However, the model we have developed is easily adaptable to a situation where the transition in between the cylindrical regions is continuous, and to a situation where both transitions are continuous. In the latter case, though, we would not expect to see a crossover in the scaling behavior of the central peak of the skin-layer CDS.

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