

## Critical Behavior of Hydrogen in Nb/Ta Superlattices

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We present an *in situ* x-ray scattering study showing the existence of the lattice-gas–lattice-liquid phase transition for H dissolved in Nb/Ta superlattices where it is found that critical fluctuations with wavelengths shorter than the superlattice periodicity are suppressed. Since fluctuations of only long wavelengths develop, phase separation into gas and liquid phases cannot occur. These results demonstrate that the coherent phase transition is sensitive to the microscopic properties of the H-H interaction.

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The gas-liquid phase transition is among the simplest and perhaps the most fundamental example of critical phenomena. Real gases, the lattice gas, and Ising ferromagnetism belong to the same universality class of critical phenomena since these are comprised of an ensemble of interacting two-state systems.<sup>1</sup> Within this class, atomic hydrogen dissolved on an interstitial host metal lattice acts as a lattice gas and differs from real gases and magnetic systems in that the elastically mediated two-body (H-H) interaction is long ranged, allowing mean-field theory to be applicable. In fact, the observed critical exponents for H-in-metal systems obey mean-field theory better than those for real gases and magnetic systems.<sup>2,3</sup>

Critical fluctuations are essential to facilitate the transition from an initially homogeneous density to the final, two-phase state (gas-liquid). However, the formation of these fluctuations is strongly coupled to the details of the two-body interaction which drives the phase transition. For example, since long-range interactions suppress short-wavelength fluctuations, the long-wavelength fluctuations develop over a range of temperatures before the two-phase state is achieved. Such behavior is referred to as a “coherent” phase transition<sup>4–8</sup> as opposed to an “incoherent” transition where the change from the homogeneous to the two-phase state occurs at a well-defined phase boundary. It has been shown that H-metal systems possess sufficiently long-range interactions that the coherent phase transition displays macroscopic density modes which are sensitive to the boundary conditions on the sample.<sup>4,5,9</sup> For H in a superlattice, we expect that a coherent phase transition can be observed on a much smaller, microscopic, length scale. Such a system would allow one to study the properties of a lattice gas in the presence of modulated interactions, as well as provide insight as to the role of the spatial dependence of the two-body interactions in critical phenomena.

In this Letter, we demonstrate that H dissolved in Nb/Ta superlattices exhibits a coherent lattice-gas-liquid phase transition. It is found that critical fluctuations develop for wavelengths only longer than a superlattice period, while shorter wavelengths are strongly suppressed as a result of the superlattice periodicity. Be-

cause of the absence of short-wavelength fluctuations, separation into gas and liquid phases cannot occur; thus, these results are novel as compared to bulk metal-H systems or any other gas-liquid phase transition.

Recently, we have found that the hydrogen induces a temperature-dependent strain modulation in the superlattice.<sup>10,11</sup> This modulation must be distinguished from critical fluctuations since the modulation constitutes a minimum in the free energy, driven by the spatial variation of the H-metal binding energy, while critical fluctuations result from a thermodynamic instability and signature a phase transformation. By measuring the temperature dependence of the strain modulation *above* the lattice-gas–liquid transition, information on the H-H and H-metal interaction energies can be obtained. We shall show that such experiments provide independent supporting evidence that short-wavelength critical fluctuations are suppressed in the superlattice.

While the scattering of x rays from hydrogen is negligible, the induced lattice expansion<sup>12</sup> can easily be observed through x-ray scattering techniques.<sup>8,10,11</sup> These experiments were performed *in situ* where the structural and thermodynamic properties could be monitored as a function of temperature. A Si(111) monochromator crystal was used to provide high resolution with Mo  $K\alpha_1$  radiation in a standard double-axis configuration. The Nb/Ta superlattices were grown by molecular-beam epitaxy (MBE) along the [110] direction on sapphire [11 $\bar{2}$ 0] substrates.

Although Nb and Ta have many similar physical properties, an important difference is that H in Nb exhibits the lattice-gas–liquid phase transition while no such behavior is observed in Ta.<sup>13,14</sup> Consequently, a superlattice containing a small fraction of Nb should not exhibit the gas-liquid phase transition, while a superlattice having a large fraction of Nb could display critical behavior.

Figure 1 shows x-ray scans of the  $s = \pm 1$  satellites about the (110) fundamental reflection for a 85-Å superlattice containing hydrogen and having a Ta fraction of 0.57. The two extreme temperatures (773 and 25 K) shown demonstrate that there is no phase transition occurring over this temperature range since a broadening

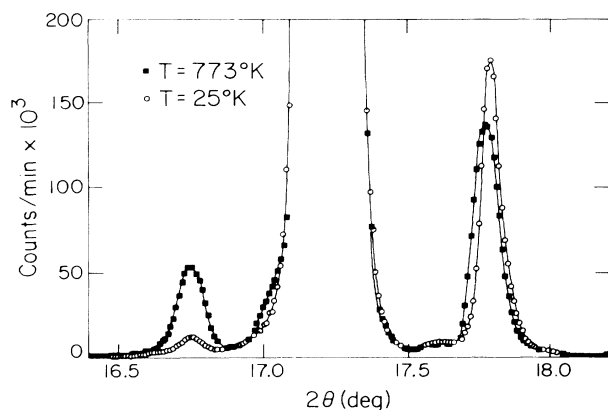


FIG. 1. X-ray scans of the  $\pm 1$  satellites for an 85-Å superlattice (Ta fraction=0.57) containing H. No critical behavior is observed from 773 to 25 K. The relative superlattice intensities change with temperature due to the H-induced strain modulation.

or splitting of these peaks is not observed.

Another 85-Å superlattice with hydrogen, having a Ta fraction of 0.17, is shown in Figs. 2(a) and 2(b), where a dramatic change in the peak shapes occurs upon lowering the temperature from 300 to 200°C. While the peak intensities have decreased, the transverse peak width was found to increase so that the integrated intensities of the (110) are the same at both temperatures. The peak profile in Fig. 2 at 200°C does not change as the temperature is lowered to room temperature; therefore these scans represent the state of the system before and after the phase transition. This critical behavior is reversible, since subsequently raising the temperature to 300°C gave the same scattering profile which was observed before the phase transition was originally encountered. Both samples contained the same H concentration. As determined from the lattice expansion of  $\Delta d/d \approx 0.01$ , we estimate 0.06 H/metal for both samples.

The data for the (110) reflection at 200°C has been fitted by three Gaussian curves [inset of Fig. 2(a)] and it is evident that there are two distinct contributions to the line shape: a narrow peak (single Gaussian) which is only slightly broadened as compared to the (110) at 300°C and a much broader peak (two Gaussians) exhibiting a slight asymmetry towards lower angles. This asymmetry, coupled with the experimental observation that the (110) peak shifted by more than what thermal expansion would allow between 300 and 200°C, suggests a relationship to the lattice-gas-liquid phase transition where the onset of a solubility gap would cause the (110) reflection to separate into two peaks.<sup>15</sup> Since the experimental resolution is much narrower ( $< 0.04^\circ$  in  $2\theta$ ) than the peak widths and the peak profiles do not change below 200°C, we conclude that the phase transition is coherent and does not exhibit phase separation.

An important feature of Fig. 2(b) is that at 200°C there is a large diffuse scattering between the fundamen-

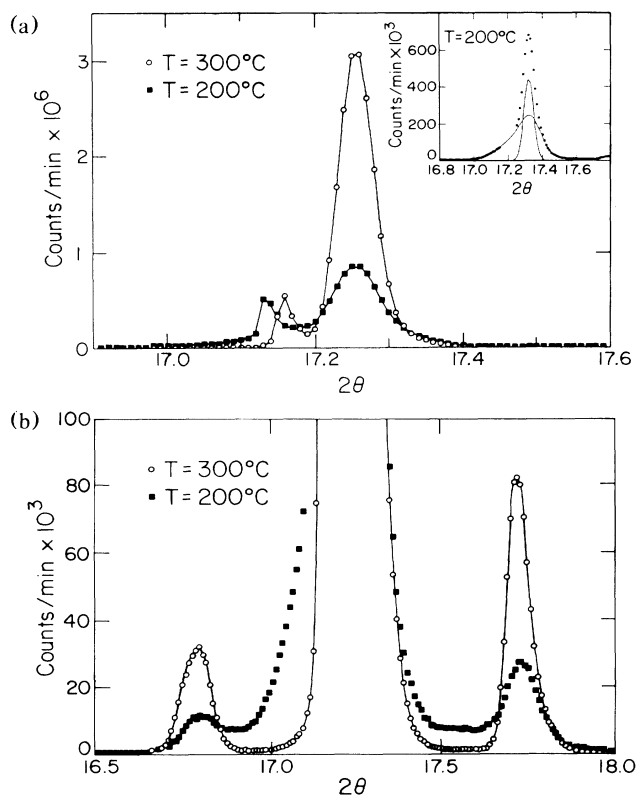


FIG. 2. (a) Fundamental reflection (110) for an 85-Å superlattice (Ta fraction=0.17) containing H. A dramatic change in the peak width, indicative of critical behavior, is observed at 200°C. There is no further change below this temperature. The small peak to the left is due to the substrate. Inset: A fit of the 200°C scan by three Gaussian line shapes. (b) Same scan as (a) except the vertical scale is changed to show the  $\pm 1$  satellites. At and below 200°C there is a large diffuse scattering which exists only between the first satellites. This suggests that strain fluctuations have wavelengths longer than the superlattice periodicity.

tal and the first satellite reflections. However, the diffuse scattering does not extend beyond these satellites, and thus, suggests the existence of hydrogen density fluctuations having wavelengths only longer than the superlattice periodicity, while fluctuations for wavelengths shorter than a superlattice period are suppressed. Therefore, for sufficiently large Nb fractions, the lattice-gas-liquid phase transition does occur in the superlattice, but with a novel modification: Distinct gas and liquid phases do not form because the high-frequency Fourier components necessary to construct a domain boundary are not present; thus, critical behavior consists of a transition to only long-wavelength density fluctuations.

These experimental observations must be examined within the framework of a coherent phase transition where the bulk metal-H behavior is modified by the artificially imposed periodicity. The details of the two-body interaction enter critical behavior through the spi-

nodal temperature,  $T_q$ , which determines the growth of mean square fluctuations<sup>8,16</sup>:

$$\langle(\delta c_q)^2\rangle = T/(T - T_q), \quad (1)$$

where  $T_q$  is proportional to the Fourier transform of the H-H interaction energy. Thus, the temperature at which a fluctuation diverges depends on its wavelength. Since the diffuse scattering in Fig. 2(b) ceases for wavelengths shorter than the superlattice period, Eq. (1) predicts that  $T_q$  diminishes for  $q$  near the first superlattice satellite.

Independent experimental evidence supporting this conclusion can be found from the temperature dependence of the strain modulation above the transition temperature, shown in Fig. 3. A strain modulation will modify the relative satellite intensities belonging to the same superlattice harmonic; thus, Fig. 3 was obtained directly from x-ray scattering experiments. It has been demonstrated that a strain modulation,  $\epsilon_q$ , of wave vector  $q$  is driven by the spatial variation of the H-metal binding energy and follows a Curie-Weiss law<sup>8,10,11,17</sup>:

$$\epsilon_q = -(\Delta d/d)U_q/(T - T_q), \quad (2)$$

where  $U_q$  is the Fourier transform of the H-metal binding energy and  $T_q$  is a spinodal temperature as in Eq. (1). Because the average lattice expansion ( $\Delta d/d$ ) is simply determined from the angular shift of the diffraction pattern due to the average H concentration, Eq. (2) allows a direct interpretation of these fundamental interaction energies from the experimental results of Fig. 3. These show that the spinodal temperature,  $T_q$ , for the two superlattice harmonics is negative, thus, implying that fluctuations at superlattice wavelengths are not favored at any temperature.

A schematic of how the superlattice modifies the

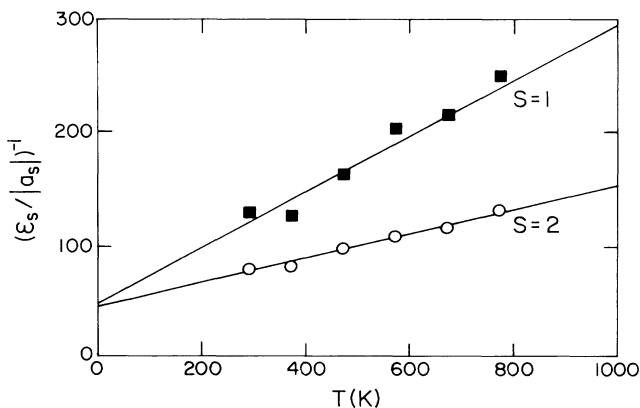


FIG. 3. Curie-Weiss temperature dependence of the strain modulation, obtained from x-ray diffraction, for the superlattice in Fig. 2, shown for two superlattice harmonics.  $\epsilon_S$  and  $a_S$  are the Fourier transforms of the strain and metallic-composition modulations, respectively. These data are taken above the phase transition and a fit (lines) to Eq. (2) provides information on the interaction energies.

Fourier transform of the H-H interaction is shown in Fig. 4, where the spinodal temperature is plotted versus  $|q|$ . The observed diffuse scattering [Fig. 2(b)] is represented by the series of circles for wave vectors between zero and the first superlattice harmonic. The squares represent the results of the strain versus temperature experiments (Fig. 3) performed at temperatures above the phase transition. Clearly, the curve must connect between the diffuse scattering and the first harmonic. This provides the essential feature that, as compared to the monotonic behavior of a bulk metal, there is a sharp drop in  $T_q$  as the first satellite wave vector is approached and the change is the H-H interaction introduced by the superlattice suppresses critical fluctuations for  $q$  larger than the first superlattice harmonic. These results are substantially different than for H in a homogeneous metal where the macroscopic density modes would appear near  $q=0$  and would be unresolved on the scale of Fig. 4. In the superlattice, the periodic insertion of Ta causes a repulsive contribution to the H-H interaction appearing at the superlattice reciprocal-lattice positions, since the Fourier transform accentuates the difference between the Nb and Ta counterparts at these wavelengths.

In an effort to explore further the interplay of the superlattice with the critical behavior of the hydrogen density, several samples were studied—three of which exhibited critical behavior. These results provide additional support for the above conclusions. In particular, it is confirmed that the width of the broad contribution to the peak [inset to Fig. 2(a)] scales with the superlattice period, as would be anticipated from Fig. 4. The detailed results, as well as a discussion of the H-H interaction, are presented elsewhere.<sup>8,17</sup>

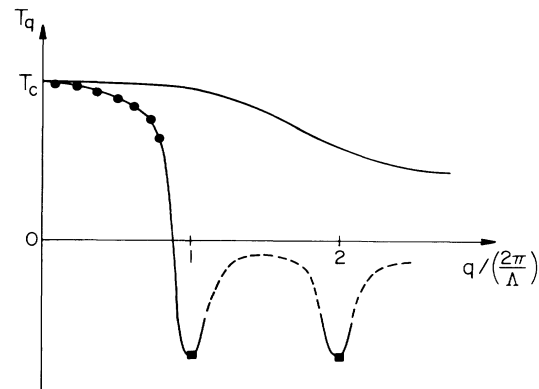


FIG. 4. Variation (schematic) of the spinodal temperature with wave vector in units of the superlattice periodicity. The filled circles represent the observed diffuse scattering between the fundamental and first satellites. The squares are obtained from the temperature dependence of the strain modulation in Fig. 3, where it is found that  $T_q$  is negative; thus, the curves must connect (dashed line is obviously speculation). The upper curve represents the unmodified spinodal temperature for a homogeneous metal.

In summary, the lattice-gas-liquid phase transition in a superlattice is observed. However, the H-H interaction is modified by the superlattice periodicity and suppresses critical fluctuations for wavelengths shorter than a superlattice period. This system provides a novel example of a coherent gas-liquid phase transition which is described by only long-wavelength fluctuations and, consequently, the formation of distinct gas and liquid phases is not observed. Most importantly, these experiments clearly demonstrate the sensitive role which the spatial distribution of the two-body interaction plays in determining critical behavior within the Ising universality class.

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