PHYSICAL REVIEW B VOLUME 57, NUMBER 15 15 APRIL 1998-I

Effects of impurity on two-dimensional melting transitions

Jian Ma,* Eleanor D. Carter, and Hillary B. Kleinberg
Department of Physics, Amherst College, Amherst, Massachusetts 01002

(Received 20 August 1997)

We report a heat-capacity study of the melting of Ar-CH_4 and Ar-Xe mixture films on graphite. We find that in diluting a submonolayer Ar film with CH_4 impurities, the sharp melting peak of Ar diminishes rapidly and becomes *undetectable* when the CH_4 concentration exceeds 7%. No feature of the sharp melting peak is detected for Ar-Xe mixtures on graphite, for Xe concentration as low as 1.5%. These findings raise some intriguing possibilities. [S0163-1829(98)07615-2]

The nature of the melting transition in two dimensions remains an unresolved issue. It was proposed that the transformation from a two-dimensional (2D) solid to an isotropic 2D fluid can be a *continuous* process that occurs in two steps: the 2D solid first melts at a temperature T_c into a so-called hexatic fluid possessing short-range positional order but quasi-long-range bond orientational order; this hexatic phase then undergoes a second transition at a temperature higher than T_c to an isotropic fluid. The first transition occurs via unbinding of dislocation pairs, and the second via unbinding of disclination pairs. This two-step process is known as the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) process.[1] One key prediction of the KTHNY theory is that the specific heat should display an *undetectable* essential singularity at T_c which is followed by a broad anomaly at higher temperatures. Competing theories predict however that the KTHNY process is likely to be preempted by other mechanisms, resulting in a single first-order transition as observed in three-dimensional (3D) systems.[2]

A possible realization of the 2D melting transition is provided by physisorbed monolayers that are incommensurate with the underlying substrate. Extensive experimental studies of physisorbed films on graphite surfaces, however, have found a rich variety of melting behaviors and for the most part, first-order transitions.[3] Among these 2D systems, the melting behavior of Ar on graphite is perhaps the most intriguing. A low-energy electron-diffraction study observed that the symmetry axis of solid Ar overlayer is rotated with respect to the graphite substrate by an angle that decreases with increasing interatomic spacing.[4] Results from scattering studies show that Ar melts *continuously* from a rotated incommensurate solid to a rotated liquid in the submonolayer region, and the temperature evolution of the correlation length appears to be consistent with predictions of the KTHNY theory.[5] A high-precision heat-capacity study of submonolayer Ar, however, revealed at the melting temperature a small but *sharp* heat-capacity peak situated on the low temperature side of a broad anomaly.[6] The size of the peak is consistent with a density change of about 0.2% over a temperature range of 0.3 K. The broad heat-capacity anomaly appears to occur in the temperature range where the scattering studies see continuous decay in correlation length. The simplest interpretation of this finding appears to be that the sharp peak is the signature of a *weakly* first-order transition from the solid to a correlated fluid; and the broad anomaly is due to the gradual loss of the residual orientational order in the fluid.[6] A re-examination of earlier x-ray results also found a small and narrow peak in the temperature derivative of the inverse correlation length near melting.[7] In contrast to the melting behavior of Ar, the melting of CH_4 (or Xe) on graphite is *strongly* first order in the submonolayer region, as demonstrated by the δ-function-like heat-capacity peaks at the 2D triple point.[8,9]

It appeared to us that how melting takes place in Ar-CH_4 mixture films on graphite would be an interesting subject to investigate. Such a study may, among other things, lend additional insights into the melting processes in two dimensions. Thus we carried out a heat-capacity study of the melting of Ar-CH_4 mixtures on graphite. Since the ''sizes'' of Ar and CH_4 and the well depths of Ar-Ar and CH_4-CH_4 interactions are not very different, and the 2D melting temperatures of pure Ar and CH_4 on graphite are close ($\sim$49 and $\sim$57 K, respectively), we expect that Ar and CH_4 would form a miscible film on graphite, at least near the melting transition. This is supported by computer simulations.[10]

The ac calorimetry technique is used in this study.[11] The calorimeter consists of grafoil sheets compressed inside a coin-shaped brass container about 2 cm in diameter and 0.3 cm in height. The container is made from two thin (0.038 mm) overlapping brass cups soldered along the rims, with a heater and a thermometer attached to each of its flat surfaces. Also attached to the container is a 1.587-mm outer-diameter stainless-steel capillary, through which gas enters. A N_2 isotherm at 77 K shows that the total surface area of grafoil inside the cell is 12 m^2.

The Ar-CH_4 mixture films are prepared by first allowing a known amount of Ar gas into the sample cell, and taking a heat-capacity scan between 42 and 63 K. The cell is then cooled to 42 K and an appropriate amount of CH_4 impurity is introduced. With the valve to the cell closed, the cell is warmed to, and maintained at, 78 K for several hours to insure thorough mixing. The cell is then allowed to cool down slowly at a rate of 3 K per hour to 42 K. After measurements are made in the same temperature range, the cell is again cooled to 42 K, and an additional amount of CH_4 is introduced to the cell. The annealing process is then repeated to form a mixture film of higher CH_4 concentration. All data taken are found to be reproducible upon warming and cooling.

Figure 1 displays heat-capacity vs temperature scans for a pure Ar film and for several mixture films with low CH_4 con-

0163-1829/98/57(15)/9270(4)/$15.00

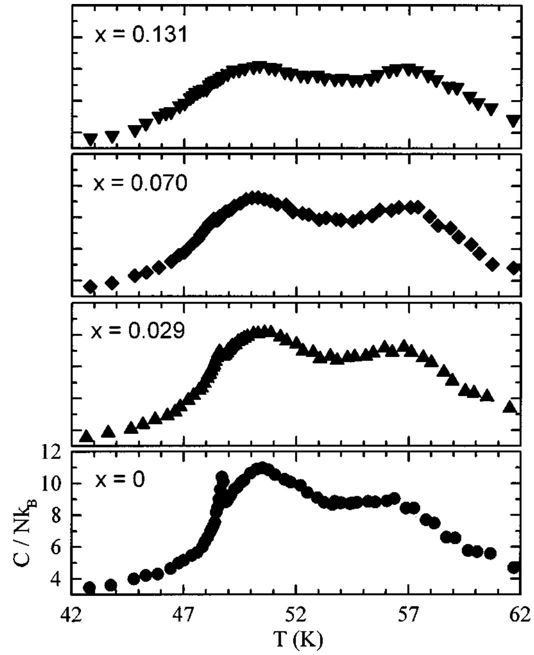

FIG. 1. Heat capacity temperature scans for several Ar-CH_4 mixture films on graphite, starting with an initial Ar coverage of $n=0.40$. x is the molar concentration of CH_4, i.e., $N_{CH_4}/(N_{Ar}+N_{CH_4})$. The total coverages for these films are, from bottom to top, $n=0.40$, 0.41, 0.43, and 0.46. All four panels in this figure have identical scales.

centrations (the contribution from the empty calorimeter has been subtracted here and below). The pure Ar film has a coverage of $n=0.40$ (where $n=1$ corresponds to a film coverage of one Ar atom for every three carbon hexagons). The heat-capacity scan for the pure Ar film shows a small but sharp peak at 48.7 K, followed by a broad anomaly centered around 50 K, and then another anomaly near 56 K (both the temperature and height of the sharp peak are essentially coverage independent, in the coverage range between $n=0.40$ and 0.88, consistent with the observations of Ref. 6). The first two features are attributed to the melting transition, and the third to the liquid-vapor transition. In diluting the Ar film with CH_4 impurities, both the sharp peak and broad anomaly decrease in magnitude with increasing CH_4 concentration, while the liquid-vapor signature remains essentially unchanged. Figure 2 is a ''blow-up'' picture of the sharp peak region in Fig. 1. It is striking that with increasing CH_4 concentration the sharp peak shifts to lower temperatures with rapidly diminishing height and becomes indiscernible when CH_4 concentration exceeds 7% [molar concentration, i.e., the $N_{CH_4}/(N_{Ar}+N_{CH_4})=0.07$]. The smooth evolution of the heat capacity peaks suggests that Ar and CH_4 are fully mixed for the CH_4 concentration up to, at least, 13.1%. We have also made measurements on two additional series of Ar-CH_4 mixture films, one starting with $n=0.25$ and another with $n=0.76$ layer of pure Ar, and observed essentially the same *evolution* of heat-capacity features with CH_4 concentration as displayed in Fig. 1.

Since the melting of CH_4 on graphite is *unambiguously* first order, and has often been used in the past to illustrate the difference between first-order and continuous transitions, we thought it would be informative to see how the presence of Ar impurities affect the melting behavior of CH_4 in the submonolayer region. Figure 3 shows heat-capacity scans for a pure CH_4 film and for the mixture films with low Ar concentrations. The pure CH_4 film also has a coverage of $n=0.40$, and the mixture films are prepared by following the same procedure as that for the Ar-rich films. For the pure CH_4 film, a triple-point-like heat-capacity peak is observed at 56.97 K, marking the triple-point melting transition (the

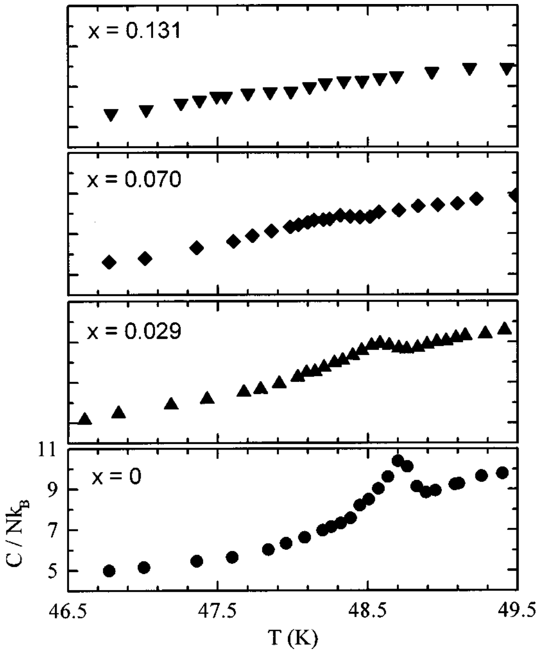

FIG. 2. The sharp peak region in Fig. 1 on a magnified scale.

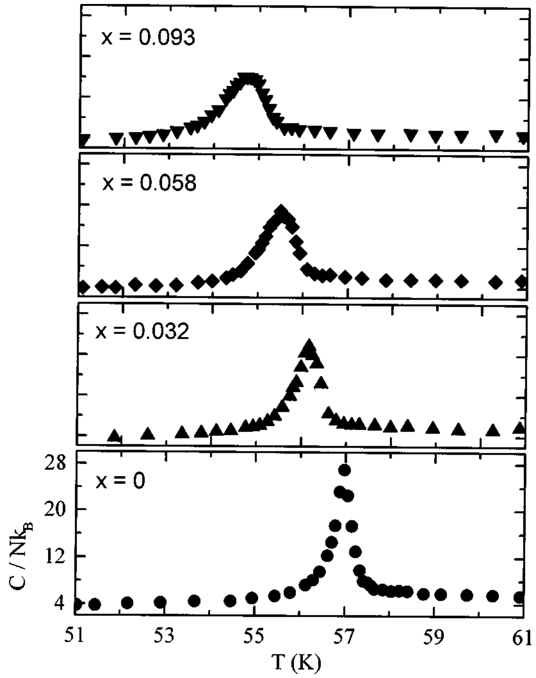

FIG. 3. Heat-capacity scans for several CH_4-rich films on graphite, starting with an initial CH_4 coverage of $n=0.40$. x is the molar concentration of Ar, $N_{Ar}/(N_{Ar}+N_{CH_4})$. The total coverages for these films are, from bottom to top, $n=0.40$, 0.41, 0.43, and 0.44. All four panels in this figure have identical scales.

triple-point peak is observed to be essentially coverage independent in the range between $n=0.3$ and 0.6, consistent with the findings of Ref. 8). As the CH_4 film is successively diluted with Ar impurities, we see that the melting peak moves progressively to lower temperatures, and that there is a corresponding broadening in the width and reduction in the height of the peak. The area under the peak remains undiminished, however. Further increases in Ar concentration beyond 10% seem to result in a structural change (possibly the formation of a commensurate phase) in the mixture films at low temperatures, which we shall discuss in more detail in another publication.

The fact that the sharp heat-capacity peak of Ar appears to evolve with impurity concentration in a qualitatively same manner as the CH_4 melting peak may be interpreted as additional support for the first-order nature of the Ar melting transition on graphite. The disappearance of the sharp melting peak of Ar when the CH_4 concentration exceeds 7%, however, raises a number of intriguing questions. In an attempt to gain further understanding of this phenomenon, we decided to examine the effects of a different kind of impurity, Xe, on the melting of Ar.[12] In contrast to CH_4, Xe differs considerably from Ar in size and well depth, and it melts on graphite at a much higher temperature (~ 100 K).

The Ar-Xe mixture films are prepared by first introducing a known number of Xe atoms into the sample cell at about 98 K and thereafter annealing the Xe film at 123 K for an hour. The cell is then cooled below 50 K, and an appropriate amount of Ar is introduced. The cell is then warmed up to and maintained at 110 K for several hours to insure thorough mixing, followed by a slow cooling (~ 3 K per hour) to 42 K. After heat-capacity measurements are made in the same temperature range as that for the Ar-CH_4 mixtures, the cell is again cooled below 50 K, and an additional amount of Ar introduced to the cell. The annealing process is then repeated to form a mixture film of lower Xe concentration. As in the case of Ar-CH_4 mixtures, all data taken are found to be reproducible upon warming and cooling.

We have made heat-capacity measurements on several Ar-Xe mixture films with varying Xe concentrations. In Figs. 4 and 5 are the heat-capacity vs temperature scans for the two most dilute mixture films, where Xe concentrations are 1.5% and 2.9%, respectively. The heat-capacity scan for the $n=0.40$ pure Ar film is also shown for comparison. We see that the overall features of the mixture heat-capacity scans resemble that of the pure Ar film; however, the sharp melting peak is absent, even when the Xe concentration is as low as 1.5%.

It appears to us that the simplest interpretation of the disappearance of the sharp melting peak of Ar might be that the melting has become *continuous*. Given that the lattice constants of incommensurate solid Xe and incommensurate solid CH_4 on graphite are about 15% and 10% larger than that of incommensurate solid Ar, respectively, it is conceivable that the mixing of certain concentration of Xe, or CH_4, impurities to an Ar submonolayer may increase the effective lattice constant of the solid phase of the mixture overlayer in such a way that the density ''jump'' between the 2D solid and liquid phases near melting is diminished.

There has been an investigation of a mechanical model of 2D hard-sphere binary mixtures.[13] It is found that for a mixture with a dilute array of large spheres embedded in a medium of smaller ones the translational and orientational order exhibit the characteristics of those in the hexatic phase, due to the tendency of the large sphere ''impurities'' to trap dislocations in the small sphere medium. This finding is also consistent with a later study of 2D solid films with quenched random impurities.[14] In light of these findings, the mixture systems we have studied, particularly the Ar-Xe mixtures, may be regarded as analogs of the above 2D binary mixture model in physisorbed systems. Thus, it is possible that the low temperature phases in our Ar-Xe mixture films, and likely also in the Ar-CH_4 mixture films with CH_4 concentration greater than 7%, are already hexaticlike, as a result of the dislocations induced by Xe, or CH_4, impurities in the Ar medium. In this scenario, the broad heat-capacity anomalies observed in these mixture films can be related to the *gradual* loss of the orientational order in the hexatic phase.

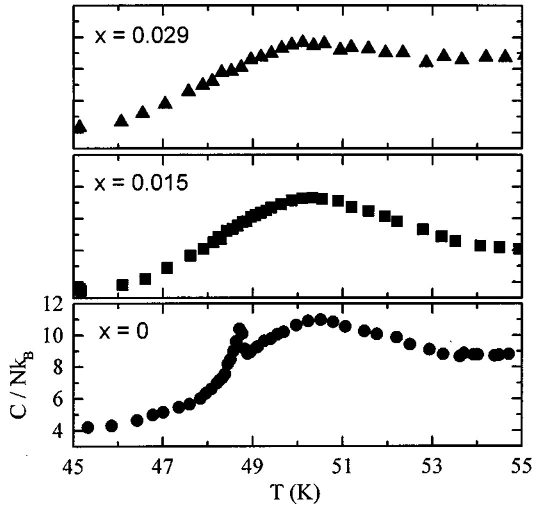

FIG. 4. Heat-capacity vs temperature scans for an $n=0.4$ pure Ar film and two Ar-Xe mixture films on graphite. x is the molar concentration of Xe, $N_{Xe}/(N_{Ar}+N_{Xe})$. The total coverages for these films are, from bottom to top, $n=0.40$, 0.77, and 0.42. All four panels in this figure have identical scales.

In summary, we have carried out a heat-capacity study of

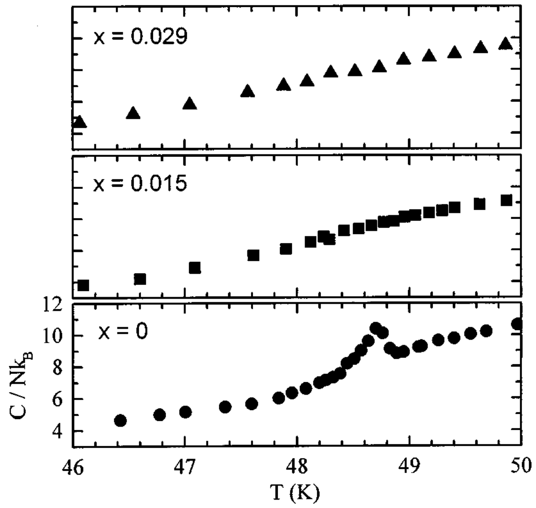

FIG. 5. The sharp peak region in Fig. 4 on a magnified scale.

the melting transitions of submonolayer Ar-CH_4 and Ar-Xe mixture films on graphite. These two mixture systems are found to be miscible, at least when the ''impurity'' concentration is low. We observe that in diluting a submonolayer Ar film with CH_4 impurities, the sharp melting peak of Ar diminishes dramatically and becomes undetectable when the CH_4 concentration exceeds 7%, whereas there are no remnants of the sharp melting peak observed in Ar-Xe mixtures (at least when the Xe concentration is as low as 1.5%). We interpret the disappearance of the sharp melting peak as an indication that the melting has become continuous. Moreover, the low-temperature phases in the mixture films which exhibit no sharp melting signature are likely to be hexatic-like. We hope that this work will stimulate high-resolution scattering studies and large-scale computer simulations to be performed on these mixture systems, to help identify various phases and shed more light on the underlying mechanisms involved.

We are grateful to Moses Chan, Aldo Migone, Jon Machta, David Nelson, and Daniele Finotello for valuable discussions. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research. One of us (J.M.) would like to acknowledge financial support from Amherst College that supported her sabbatical leave.

---

*Electronic address: JMA@AMHERST.EDU

[1] M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979); A. P. Young *ibid.* **19**, 1855 (1979).

[2] S. T. Chui, Phys. Rev. Lett. **48**, 933 (1982); Phys. Rev. B **28**, 178 (1983).

[3] Katherine J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988), and references therein; M. H. W. Chan, in *Phase Transitions in Surface Films*, Vol. 267 of *NATO Advanced Study Institute, Series B: Physics*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum, New York, 1991), and references therein.

[4] C. G. Shaw, S. C. Fain, Jr., and M. D. Chinn, Phys. Rev. Lett. **41**, 955 (1978).

[5] J. P. McTague, J. Als-Nielsen, J. Bohr, and M. Nielsen, Phys. Rev. B **25**, 7765 (1982); M. Nielsen, J. Als-Nielsen, J. Bohr, J. P. McTague, D. E. Moncton, and P. W. Stephens, *ibid.* **35**, 1419 (1987); K. L. D. Amico, J. Bohr, D. E. Moncton, and G. Gibbs, *ibid.* **41**, 4368 (1990).

[6] A. D. Migone, Z. R. Li, and M. H. W. Chan, Phys. Rev. Lett. **53**, 810 (1984).

[7] Q. M. Zhang and J. Z. Larese, Phys. Rev. B **43**, 938 (1991).

[8] H. K. Kim, Q. M. Zhang, and M. H. W. Chan, Phys. Rev. B **34**, 4699 (1986).

[9] J. A. Litzinger and G. A. Stewart, in *Ordering in Two-Dimensions*, edited by S. Sinha (North-Holland, New York, 1980), p. 267.

[10] Hye-young Kim and W. A. Steele (private communications).

[11] P. F. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968); M. H. W. Chan, A. D. Migone, K. D. Miner, and Z. R. Li, Phys. Rev. B **30**, 2681 (1984).

[12] Bohr and co-workers performed a synchrotron x-ray study of several mixtures, including Ar-Xe mixture, on graphite [see J. Bohr, M. Nielsen, J. Als-Nielsen, and K. Kjaer, Surf. Sci. **125**, 181 (1983); J. Bohr, Ph.D. thesis, Technical University of Denmark, 1984]. However, no specific information about the melting properties of Ar-Xe mixtures was discussed in their publications.

[13] D. R. Nelson, M. Rubenstein, and F. Spaepen, Philos. Mag. A **46**, 105 (1982).

[14] D. R. Nelson, Phys. Rev. B **27**, 2902 (1983).