Melting transition of the S_1 phase of ethane adsorbed on graphite

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Heat-capacity measurements of ethane adsorbed on graphite at the melting transition of the low-density submonolayer solid phase S_1 show only a weak and broad anomaly which suggests that this transition is continuous. The results are compared with those for the melting of ethylene on graphite and it is proposed that the same melting mechanism might be at work for both systems.

In the field of physisorption the study of the melting transition of monolayer films is the area which has attracted the greatest deal of effort in experiments, computer simulations, and theoretical calculations[1] ever since it was first suggested by Kosterlitz and Thouless[2] that the melting transition could be continuous for two-dimensional systems, a behavior which is radically different from that which is observed in the melting of bulk matter. The two-dimensional melting theory was further developed by Halperin and Nelson[3] and by Young.[4]

It has been thought that the more likely experimental candidates for exhibiting Kosterlitz-Thouless-Halperin-Nelson-Young- (KTNHY) like behavior among physisorbed systems are those in which the two-dimensional solid phase is incommensurate with the underlying substrate since these systems are more truly two-dimensional. However, the picture which has emerged from the different systems studied shows that most of them exhibit other types of melting behavior.[1] The one notable exception in the submonolayer range is ethylene on graphite.[5] Up to the present, this is the only system for which heat-capacity measurements have shown only a weak, broad peak at the melting transition at submonolayer coverages, indicating that this is a continuous transition. In this paper we present results which indicate that the melting of submonolayer ethane on graphite is also continuous.

Monolayer ethane on graphite is a system that has been extensively studied with structural[6-15] and dynamical[16-18] probes. The currently proposed phase diagram for this system, which is presented in Fig. 1, is the result of neutron scattering,[6-8,15,17,18] low-energy electron diffraction (LEED),[9-13] and vapor-pressure isotherm measurements.[19] Three distinct solid phases have been identified in the first layer for this system. At the lowest coverages a solid called S_1 coexists with a two-dimensional (2D) vapor. The structure of S_1 is that of a $4 \times \sqrt{3}$ commensurate solid in which the C-C axes of the molecules are ordered forming a herringbone pattern.[7,8,15] At intermediate submonolayer coverages a higher-density solid S_2 exists. The structure of S_2 has been resolved only recently. It is a rectangular incommensurate mesh in which the C-C axes are, again, essentially parallel to the graphite plane.[12-14] At higher coverages, in the monolayer completion region, the ethane molecules stand on their methyl tripods with their C-C axes perpendicular to

the graphite plane and forming a $\sqrt{3} \times \sqrt{3}$ solid.[7,8,10,15] This phase is called S_3 and it is used to determine the coverage scale for the ethane system ($n = 1$ corresponds to one complete layer of S_3).

The melting transition from S_1, the lowest-density phase has been studied by neutron scattering[7,8,15,17,18] and by LEED.[8,9,11] S_1 melts to a highly ordered liquid phase (a "lattice liquid") named I_1.[9,11] Initially it was thought that I_1 was an intermediate phase between the solid S_1 and a true 2D liquid and the melting transition from S_1 was first identified as an orientational transition similar to the one present in submonolayer N_2 on graphite.[8] Near the transition temperature I_1 has a 2×2 structure commensurate with the substrate. Both I_1 and S_1 have the same areal density.[9,11] Quasielastic neutron-scattering (QENS) measurements have shown that I_1 is in fact a liquid.[17,18] More recent LEED studies have shown that there is only a gradual progression from I_1 to an isotropic liquid as the temperature is increased, with no phase boundary separating I_1 from the 2D liquid phase.[13] Early neutron scattering experiments[7,8,15] and more recent (LEED) (Ref. 11) measurements have identified the
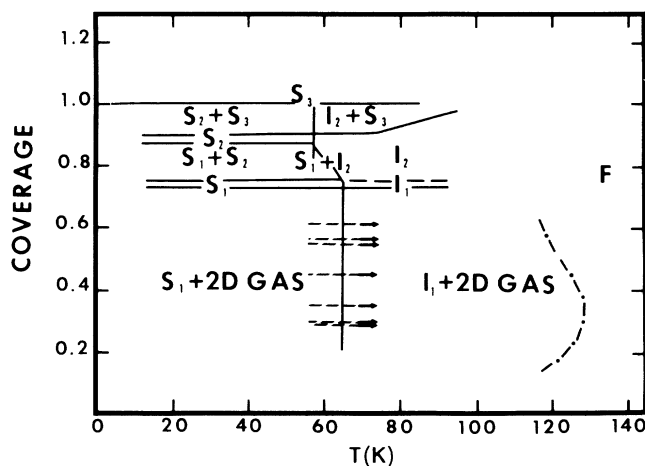

FIG. 1. Phase diagram for monolayer ethane adsorbed on graphite from Refs. 7–13, 15, and 19. The dashed lines with arrowheads indicate the region of the phase diagram studied in this work.

melting of S_1 as a first-order phase transition. This identification was based on hysteresis effects observed near the transition temperature and on the observation of a finite-temperature region of S_1-I_1 coexistence. It should be noted, however, that a finite-temperature region of S_1-I_1 coexistence is forbidden by the Gibbs phase rule. At these coverages and for all temperatures up to the 2D critical point there is a 2D vapor phase coexisting with either S_1 or I_1. All three phases can only coexist at one temperature. In the LEED study[11] the apparent S_1-I_1 coexistence region was explained by heterogeneities in the substrate pinning down the less stable phase in a temperature range in which it is forbidden. It was also suggested that this pinning probably occurred because at temperatures close to the transition the free energies of S_1 and I_1 are very similar.[11] Because the apparent S_1-I_1 coexistence is observed in a region where it is forbidden by the Gibbs phase rule its occurrence is not an indication of the first-order nature of the transition. Instead, this forbidden coexistence region suggests that the melting of S_1 is a weak process, i.e., either a continuous transition or a weakly first-order one.

We report here the results of a specific-heat study of the melting transition of the S_1 phase of ethane adsorbed on graphite foam. The technique employed in our measurements is ac calorimetry.[20] Details on our automated experimental apparatus are provided elsewhere.[21]

Seven coverages between $n = 0.29$ and $n = 0.61$ were studied. The coverage scale for this study was determined by performing a N_2 vapor-pressure adsorption isotherm at 77 K. This isotherm has a substep which corresponds to a two-phase coexistence region between a $\sqrt{3} \times \sqrt{3}$ solid and a fluid phase.[22] The top of the substep taken at this temperature is used to identify the $n = 1$ coverage.

In Fig. 2 we present heat-capacity results for a coverage of $n = 0.293$. The background contribution to the heat capacity due to the calorimeter has not been subtracted in this figure. The characteristic feature for this coverage is
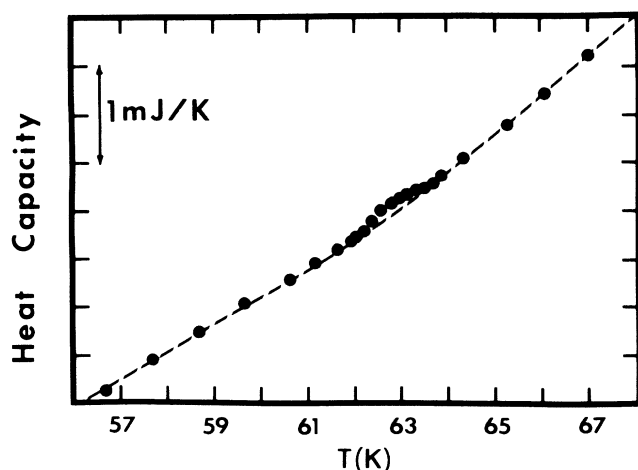
typical of what is observed throughout the coverage range studied: a broad and weak heat-capacity anomaly centered about 62.5 K.

In order to verify that our calorimeter was in fact operating properly after obtaining the first ethane results, we removed the ethane from the sample cell and placed in the calorimeter a coverage of $n = 0.55$ of N_2. We measured the heat-capacity signal at the melting transition for this N_2 coverage and obtained the characteristic sawtoothlike peaks, which have been reported previously for this system.[23] The width and height of the melting specific-heat signal also agreed very well with previously reported results for this system: The height of the specific-heat peak was ~ 60 C/Nk_B and the full width at half maximum ~ 1.5 K. This test indicates that our calorimeter is working properly. As a comparison, the signal due to the melting transition of N_2 is on the order of 20–25 times larger than that corresponding to the S_1 melting of ethane.

The melting transition temperature found in our study of ~ 62.5 K is in good agreement with that reported in previous structural measurements.[6–9,11,15] Some of our specific-heat data are shown in Fig. 3. Here the background contribution to the heat capacity due to the calorimeter has been subtracted. The results are independent of coverage in the range of S_1 coverages that we measured. The height of the specific-heat peaks are between 1.8 and 3 in units of C/Nk_B. The full width at half maximum of the peaks is on the order of ~ 2 K. There
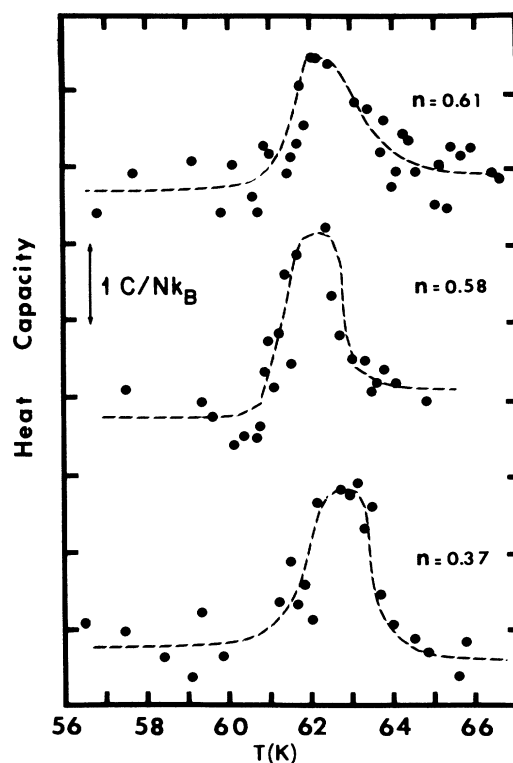

FIG. 2. Heat-capacity trace for a $n = 0.293$ ethane on graphite coverage. The background contribution from the calorimeter has not been subtracted. To emphasize the peak region a smooth curve (dashed line) has been drawn in to guide the eye. Data are presented in units of mJ/K.

FIG. 3. Heat-capacity traces for three ethane coverages: $n = 0.578$, $n = 0.614$, and $n = 0.367$ at the melting transition. The background contribution has been subtracted. Data are presented in units of C/Nk_B.

are no sharp peak features present in the data in any of the coverages that we studied. All of these characteristics of the specific-heat signatures suggest that the melting of S_1 is a continuous transition, not first order as was originally suggested in the structural studies. The height, width, and shape of the specific-heat peaks due to the S_1 melting transition of ethane on graphite are quite similar to those reported for the melting of ethylene on graphite.[5]

The entropy change corresponding to the melting transition from S_1 was obtained by integrating the heat-capacity data and was found to be $\sim 0.1 k_B$. For comparison the entropy change at the melting transition for methane (which has a very strong first-order triple-point melting transition) is $\sim 0.7 k_B$ (Ref. 24) and that for ethylene (which has a continuous melting transition) is on the order of $\sim 0.4 k_B$.[5] The smaller value of the entropy change for the S_1 melting transition is to be expected since close to the melting temperature the liquid phase I_1 is highly ordered.[9] The same degree of order is not present in the 2D liquid phases of either methane or ethylene.

Further support for the identification of the S_1 melting transition as being continuous comes from comparing the results reported of QENS measurements for ethane[17,18] on graphite with similar results for methane[25,26] and ethylene[26] on graphite. QENS measurements have been used to determine rotational and translational diffusion coefficients for these systems. A large nonzero translational diffusion coefficient indicates the presence of a liquid phase. For the case of methane, which has a very strong first-order melting transition, the value of the diffusion coefficient discontinuously jumps from approximately 2.5×10^{-5} cm^2/sec to below 1×10^{-6} cm^2/sec at the submonolayer melting temperature.[25,26] On the other hand, for ethylene, the translational diffusion coefficient near the melting transition decreases continuously with decreasing temperature in a much more gradual manner, with no indication of any discontinuity at the transition temperature.[26] QENS results for ethane on graphite[17,18] exhibit the same type of behavior as ethylene: For ethane, the magnitude of the diffusion coefficient decreases continuously as the temperature is lowered approaching the melting transition, with no sign of discontinuity. Unfortunately, a more quantitative comparison between the QENS data for ethylene and ethane is not possible because only five temperatures near the melting transition were studied for ethane.[18]

A very recent computer-simulation study of the melting of ethylene[27] and the ethylene QENS study[26] have suggested that the reason why the melting transition is continuous for ethylene lies in the fact that the ethylene molecules can create vacancies in the solid film by flipping up and standing with their C-C axes perpendicular to the graphite plane. In turn, this could produce a drop in the

barrier to translational diffusion and could result in a continuous melting transition. The important criterion determining whether or not such a flipping mechanism is possible for a given type of physisorbed system is the aspect ratio of the adsorbed molecule.

We believe that the melting behavior of the S_1 phase of ethane on graphite could present another example of this same type of mechanism at work. The size and shape of ethane and ethylene are similar. There is also some similarity in the first-layer phase diagram of these two systems, since both compounds form a phase in which the C-C axis of the respective molecules are perpendicular to the graphite plane at high-monolayer coverages. As stated above, the diffusion-coefficient data near the melting transition are similar for both systems. And, as we have shown, the specific-heat signatures at the melting transition are also similar. It is interesting to note that this similarity in the melting signature exists even though in one case (ethylene) the solid phase that is melting is incommensurate with the substrate while in the other (ethane) it is commensurate. This result underscores the importance that the molecular shape has in determining the melting behavior for nonspherical molecules.

It is still possible, however, that despite all of the above stated similarities between ethylene and ethane a different melting mechanism might be at work in each case. Computer simulations for the melting of ethane would be of great value for gaining a better understanding of this transition, as they have proven to be for ethylene.[27]

In summary, we have presented evidence from our heat-capacity measurements which strongly suggests that the melting transition from the S_1 phase of ethane is continuous. We have argued that the interpretation of our heat-capacity results in terms of a continuous melting transition is in good agreement with the QENS results on this same system. We have also compared the melting behavior of ethane with that of the only other submonolayer system which has a continuous specific-heat melting signal, ethylene on graphite, and we have suggested that the same melting mechanism might be operating in both cases.

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