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THERMODYNAMIC IMPLICATIONS OF BAND STRUCTURE
EFFECTS FOR RARE GASES ON GRAPHITE

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ABSTRACT

Recent analyses of atomic beam scattering data have suggested that an anisotropic He-C pair interaction is appropriate to the problem of He on graphite. This results in considerably more corrugated equipotential surfaces than previously assumed, and correspondingly manifest band structure effects. These have been observed for He/graphite in the specific heat for temperature $T > 3$ K. The implications for other gases and temperatures and for the effective adatom-adatom interaction are discussed.

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INTRODUCTION

Calculations of film properties often assume for simplicity the strictly two-dimensional (2D) approximation, thus neglecting the lateral variation of the potential energy $V(\vec{r})$ and adatom motion perpendicular to the substrate [1]. However, surface corrugation should cause even high temperature, low coverage He on graphite to exhibit marked deviation from 2D ideal gas behavior. We describe here the basis for this prediction [2] and its subsequent experimental confirmation [3].

Early work leading to the 2D model [4,5] started by choosing

$$V(\vec{r}) = \sum_i U(\vec{r} - \vec{R}_i) \quad , \quad (1)$$

and assuming the pair potential $U(\vec{x})$ to depend only on the magnitude $x = |\vec{r} - \vec{R}_i|$ of the adatom-substrate separation [6]. As described below, the results of He scattering experiments [7,8] have led us to conclude instead [9,10] that an anisotropic pair potential, varying with the orientation of $\vec{x}$, is appropriate to rare gases on graphite. The resulting potential is less uniform than was calculated previously, resulting in larger band structure effects and more favorable energies of epitaxial phases [11].

The predicted band structure governs the density of states for adsorbed atoms in the low coverage limit. The result is revealed in the heat capacity of ^3He and ^4He after a thermodynamic analysis which eliminates both the effects of substrate inhomogeneity and He-He interactions [3].

POTENTIAL AND BAND STRUCTURE

Atomic beam scattering is a remarkably direct way of investigating the gas-surface interaction. [12]. A bound state resonance (BSR), which occurs when the incident state is coupled by the periodic potential to a surface bound state shows up dramatically in the reflected beam intensity. The resonance condition is degeneracy of the two states: $E_{\text{inc}} = E_{\text{bound}}$. In the approximation of free propagation along the surface, this becomes

$$\hbar^2 (k_z^2 + \vec{k}_{\parallel}^2) / 2m \approx \epsilon_{nz} + \hbar^2 (\vec{K}_{\parallel} + \vec{G})^2 / 2m \quad , \quad (2)$$

where the wave vectors are those of the incident beam, $\vec{G}$ is a 2D reciprocal lattice vector, $\epsilon_{nz} < 0$ is a discrete eigenvalue of the laterally averaged potential $V_0(z)$. The latter is the

leading term in the Fourier expansion of the potential

$$V(\vec{r}) = V_0(z) + \sum_{\vec{G} \neq 0} V_{\vec{G}}(z) \exp(i\vec{G} \cdot \vec{r}) \quad (3)$$

Because graphite provides a relatively smooth potential (as compared with LiF, for example) the periodic part of $V(\vec{r})$ is relatively small in the spatial region sampled by the bound states (see Fig. 1). Consequently deviations from Eq. (2), i.e., band structure corrections, can be treated as a perturbation in analyzing the data [10,13]. The observed deviations then yield matrix elements of the perturbation between the unperturbed eigenfunctions $\phi_n(z)$:

$$V_{\vec{G}}^{mn} = \int dz \phi_m^*(z) V_{\vec{G}}(z) \phi_n(z) \quad (4)$$

Ref. [10] demonstrated how the 19 values of ϵ_{nz} and $V_{\vec{G}}^{mn}$ obtained by Boato et al. [7] and Derry et al. [8] could be used to assess hypothetical forms of $V(\vec{r})$. In particular, isotropic pair potentials $U(|\vec{r} - \vec{R}_i|)$ were found to yield corrugations (i.e., $V_{\vec{G}}^{mn}$ values) smaller than were observed experimentally. Consistency was obtained, however, with anisotropic potentials, e.g.,

$$U(\vec{x}) = 4\epsilon\{(\sigma/x)^{12}[1 + \gamma_R(1 - \frac{6}{5}\mu^2)] - (\sigma/x)^6[1 + \gamma_A(1 - \frac{3}{2}\mu^2)]\} \quad (5)$$

where μ is the cosine of the angle between $\vec{x} = \vec{r} - \vec{R}_i$ and the surface normal. The parameter $\gamma_A = 0.4$ was determined ab initio from the polarizability anisotropy of graphite. Its effect is to decrease the attraction when the He atom is above a C atom - a configuration for which the van der Waals interaction is small [10,14].

Fig. 1 shows the potential derived from Eq. (5) with parameters optimized to yield good agreement with the scattering data. It is less deep and less smooth than previous potentials [4]. For example, well depths above the C atom and hexagon center are 15.5 and 19.1 meV, respectively, compared to earlier values of 20.3 and 22 meV. The previous potentials, which were derived by rough estimation of isotropic potentials, are inconsistent with the present data [10].

A similar conclusion concerning the corrugation follows from an "empirical" band structure

calculation of Carlos and Cole [2]. Their technique employed the experimental values of ϵ_{nz} and V_G^{mn} in the Hamiltonian matrix; this obviated any assumptions, e.g., Eq. (1), about the form of $V(\vec{r})$. The computed band gaps are approximately twice as large as those derived previously, corresponding to considerably less free translation across the surface. The effective mass is enhanced by a factor 1.06 for ^4He and 1.03 for ^3He ; the latter isotope's lower mass increases its delocalization.

A further test of these calculations comes from a recent neutron scattering study. By measuring the adsorbate enhancement of the (002) Bragg reflection from the graphite, Passell and co-workers [15] have derived a preliminary value of the adatom-substrate separation in favorable agreement with $\langle z \rangle = 2.92 \text{ \AA}$ computed for the potential of Fig. 1.

In closing this Section, we remark that the derivation [9,10] of anisotropy in $U(\vec{r})$ applies to other rare gases on graphite, in fact, the value $\gamma_A = 0.4$ is the same for all.

BAND STRUCTURE EFFECTS IN THE HEAT CAPACITY

The isosteric heat capacity of the film, C_N , is a function of the single particle density of states $n(\epsilon)$. For a smooth substrate, strictly 2D motion leads to $n(\epsilon) = \text{constant}$ and thereby to the prediction $C_N/Nk_B = 1$ in the limit of low density. Since, however, the substrate is periodic, the relevant energies ϵ are those of the band states. One would thus expect C_N/Nk_B to deviate from its ideal value. Unfortunately, if the coverage N is not small, C_N also depends on the effects of He-He interactions and quantum degeneracy, while at very low N , C_N is difficult to measure, and in any case is dominated by the influence of unavoidable substrate inhomogeneities. These factors have in the past obscured the influence of band structure on C_N .

Elgin and Goodstein [16] have shown, however, how a knowledge of the distribution of inhomogeneities on the surface, together with sufficiently complete thermodynamic data, may be used to correct C_N to find the values it would have on an ideally homogeneous graphite surface. We have performed the necessary analysis for their ^3He and ^4He data to obtain values of $C_N^0(T)$ where C_N^0 is the $N \rightarrow 0$ limit of C_N on an ideal graphite substrate [3]. Values of C_N^0/Nk_B are obtained from the corrected data by extrapolating to $N=0$

plots of C_N/Nk_B versus ρ , the 2D density. This procedure is standard for analyzing a virial gas. One would expect the plots to yield straight lines intercepting at 1. Results for C_N^0/Nk_B are shown in Fig. 2 where they are compared to the band structure predictions of Carlos and Cole [2]. The effects of band structure are strikingly evident in the data, particularly in the case of ^3He , where more complete data are available.

The shape of the curves in Fig. 2 is a consequence of the gap of forbidden states introduced by the 2D periodicity of the substrate. As T rises, the heat capacity falls as the missing states in the gap are encountered, then rises again as the next band begins to be populated.

We wish to describe briefly our method of correcting the C_N data. The distribution of binding energies for helium on the Grafoil substrate used for the measurements has been shown [3] to be fitted by the form

$$\epsilon(N) = -E_b [1 + (1 + N/N_0)^{-3}] , \quad (6)$$

where N_0 , crudely the number of sites of binding energy substantially different from the ideal binding energy, E_b , corresponds to approximately 0.025 monolayers, and $E_b/k_B = 142$ K for ^4He [3], and 136 K for ^3He [6].

The procedure involves the division of the system into a large but finite number of subsystems with binding energies ϵ_i and number of sites N^i designed to reproduce closely Eq. (6). The equilibrium amount adsorbed on each subsystem, $N_i = \rho_i N^i$, where ρ_i is the equilibrium density, is determined by the condition that the chemical potential, μ , of the entire system be uniform. An activated site has an increased binding energy compensated by an increased density. The increase in density needed to compensate a given increase in binding energy is taken directly from the experimental data for the chemical potential as a function of density. The empirical chemical potential is modified slightly to prevent double occupancy of highly activated sites.

The picture, then, is of a large unactivated subsystem, whose density $\rho_0 = N_0/N^0$ is lower than average, in equilibrium with a known distribution of activated subsystems with higher densities. Each subsystem is assumed to have the thermodynamic properties that the entire film is

measured to have at the same temperature when the overall density is equal to the subsystem density.

For the system as a whole, the energy U may be written as $dU = TdS + \mu dN$; for the subsystems, one has $dU_i = TdS_i + \mu_i dN_i$. Expressing dU as

$$dU = \left(\frac{\partial U}{\partial T} \right)_{\{N_i\}} dT + \sum_i \left(\frac{\partial U}{\partial N_i} \right)_{T, \{N_{i-1}\}} dN_i$$

where in $\left(\frac{\partial U}{\partial N_i} \right)_{T, \{N_{i-1}\}}$ one N_i is changed while the others are kept fixed, leads to

$$C_N = \sum_i C_{N_i} - T \sum_i \left(\frac{\partial \mu_i}{\partial T} \right)_{N_i} \left(\frac{\partial N_i}{\partial T} \right)_N \quad (7)$$

where C_{N_i} is the heat capacity of each subsystem.

All quantities in Eq. (7) except C_{N_0} are known by the procedure outlined above. It is thus possible to deduce C_{N_0} at the correct coverage N_0 using Eq. (7).

We have found that the procedure breaks down for coverages below about 0.2 monolayers, because the corrections then become sensitive to the way in which second layer formation has been prevented and to the fact that we have used a discrete rather than continuous distribution of subsystems. Only data above 0.2 monolayers were therefore used in the analysis leading to Fig. 2.

CONCLUSION

The earliest scattering results for ^4He on graphite [7] were found to give a ground state energy in remarkable agreement with the thermodynamically determined binding energy of that system [16]. The ensuing interplay of scattering experiments [8], thermodynamic experiment [17] and theory [9,10,13] has led to a highly detailed understanding of the interactions of He with a graphite surface, culminating in the predictions [2] and confirmation [3] of band structure for 2D motion of He in the graphite basal plane.

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Fig. 1. Full curve represents the potential energy of a He atom as a function of distance z above symmetry points in the basal plane (hexagon center (S), C atom (A) and potential point (SP)), obtained from ref. [10]. Dashed curve is the probability density $P = \phi_0^2(z)$ for a ^4He atom in the laterally averaged potential $V_0(z)$.

Fig. 2. Specific heat of He isotopes in the limit of zero coverage. Full curve was calculated from density of states of ref. [2]. Data are from ref. [3]. The dashed curve represents the 2D result $C = Nk_B$. Note the axis labels.