fects of salts on the transition.

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Observation of a Two-Step Melting in the Submonolayer Region of Tetramethyltin $Sn(CH_3)_4$ Adsorbed on (0001) Graphite, by Mössbauer Spectroscopy

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Mössbauer cross section isotherms of $Sn(CH_3)_4$ adsorbed on graphite show a two-step melting process which suggest the formation of two-dimensional moving islands in the intermediate phase. Above 0.65 of a monolayer and $T \lesssim 85$ K, the cross section increases sharply which we tentatively interpret as a coalescence of the islands into a large, still "continent." At $\simeq 100$ K, the islands melt into an isotropic fluid.

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During the last few years, there has been an increasing interest in the problems of melting of two-dimensional (2D) matter. Many experimental methods were used to investigate the phenomenon such as heat capacity,[1] neutrons,[2,3] Mössbauer effect,[4,5] etc. The results do not indicate any conclusive behavior. In some cases, the 2D melting transition appears to be first order,[6] where in some other cases higher-order transitions (continuous) were observed.[7]

A detailed 2D-melting theory was suggested recently by Halperin and Nelson (NH).[8] With use of the Kosterlitz-Thouless model which describes a dislocation mediated melting, they show that the transition from a 2D solid to a 2D liquid can occur, when on smooth substrate, in two *second*-order transitions. Frenkel and McTague (FM) pointed out[9] that an experimental verification of the NH theory can be complicated because of subtle changes in the physical quantities at the transition. They applied molecular-dynamics (md) calculation for supporting the NH theory. Abraham's thermodynamical computer experiments,[10] however, suggest that only one first-order melting transition can be expected in those systems. His view is supported by Toxvaerd[11]; using md calculations, he showed that the behavior of 2D Lennard-Jones systems is quite similar to the corresponding 3D case, with liquid-gas critical point, and *first*-order phase transition. In Toxvaerd's calculations, however, no evidence is found for the NH two-stage process in the melting of such a 2D system. It is evidently interesting to see if it is possible for a 2D system on a "smooth" substrate to transform into mobile phase in more than one stage, in practical systems. Motivated by these arguments, we looked for a system that will come as close as possible to the "smooth" substrate condition.

In this report, we present some experimental evidence of a premelting and melting process in a monolayer of large tetramethyltin (TMT), $Sn(CH_3)_4$ molecules adsorbed on graphite. Furthermore, our results suggest the possibility that the intermediate phase is 2D moving patches. The conclusions are based on Mössbauer spectroscopy.

The TMT is a large molecule (~7 Å diameter) with a vapor pressure of ~90 Torr ($T_{\rm room}$). It melts at T_m(3D) = 218 K. The adsorption vapor pressure isotherms follow a "type-I" pattern,[12] toward a completion of a single layer below the saturation pressure. The Mössbauer $Sn(CH_3)_4$ film samples were adsorbed on a 16-g stack (25 × 25 × 25 mm^3) of exfoliated graphite (Grafoil) sheets in a transmission cell. The completion of a monolayer was determined by its "point B" at 273 K.

A ^{119}Ba^m SnO$_3$ Mössbauer source was used, with $E_\gamma = 23.8$ keV and $\Gamma = 0.377$ mm/s. The radiation was filtered for x rays (25.3 keV) by a 50-μm-thick Pd foil which reduces 95% of the x rays and ~50% of the γ rays. Typical number of counts per channel: 3×10^6. Because of the preferential alignment of the Grafoil, it was possible to study the Mössbauer on resonance cross section σ in the direction perpendicular ($\sigma^\perp$)—and parallel ($\sigma^\parallel$) to the plane of the Grafoil sheets.[3] The definition and calculation of σ are described in Ref. 3. In its simplest form, however,

$$\sigma = \sigma_0 \exp[-2W_a(1+2\hbar k_\gamma{}^2 D/\Gamma \sin^2\theta)^{-1/2}],$$

where W_a is the Debye-Waller-like factor for the absorber, D is the diffusion coefficient, and θ is the angle between $\vec{k}_\gamma$ and the normal to the surface.

The TMT displays a relatively narrow simple single line with an average width 0.91 ± 0.07 mm/s which was analyzed by a least-squares fit to a Lorentzian. Generally the linewidth is known within 5%–10% (10% for last temperatures close to T_m, where $\sigma^\parallel$ is small) and σ could be determined to the accuracy of ~5%–10%. Within this framework, for $D \sim 10^{-5}$ cm^2/s (liquid) the broadening $\Delta\epsilon = 2\hbar k_\gamma{}^2 D/\Gamma$ will reach ~10^6; an ~10% inaccuracy in the linewidth determination corresponds to $D \sim 10^{-12}$ cm^2/s which practically describes a solid. With these limitations in accuracy, various temperatures and coverages were studied.

Our results show that while $\sigma_x{}^\perp(T)$ reveals no particular irregularity for any selected coverage $x \lesssim 1$ (as seen in Fig. 1), $\sigma^\parallel$ have some extraordinary apparent features: Figure 2 shows $\sigma_x{}^\parallel(T)$ and $\sigma_T{}^\parallel(x)$.

In $\sigma_x{}^\parallel(T)$, two irregular intensity crashes are observed, at ~85 and 95 K. We believe that these steps are caused by a sudden change in the mobility state of the adsorbed molecules, with a mechanism described in details elsewhere.[3] The first drop can be caused by a (slow) diffusion characterized by $D \simeq 10^{-8}$ cm^2/s. This value was confirmed in a different experiment[13] using the angular dependence of the Mössbauer cross section. Above 95 K, no quantitative evaluation could be made, but $D > 10^{-8}$ cm^2/s.

The other striking feature of this data is the behavior of $\sigma_T{}^\parallel(x)$, Fig. 2: Normally $\sigma_T{}^\parallel(x)$ is expected to change monotonically in a single- (2D) phase region. Being an extensive (dynamical) property of the system, $\sigma^\parallel$ should change linearly in a two-phase coexistence region. We observe, however, an abnormal step at $0.61 < x < 0.70$. This

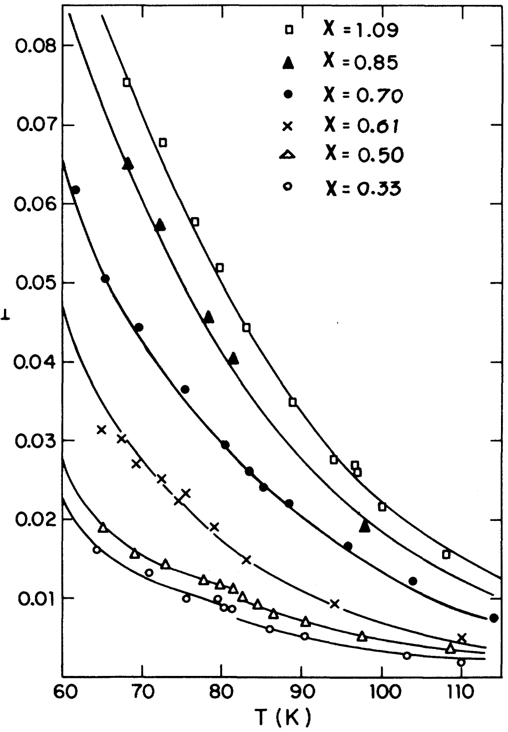

FIG. 1. The on-resonance Mössbauer cross section $\sigma_x{}^\perp(T)$ (with k_γ perpendicular to the plane of the Grafoil sheets). The technical details are described in Ref. 3. "On resonance" includes the Lorentzian least-squared best-fit area to the single line within the experimental velocity range (~12 linewidths).

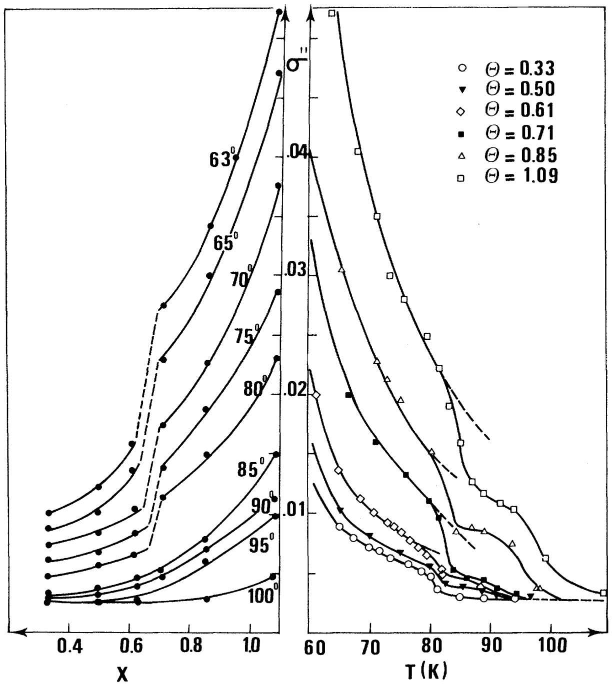

FIG. 2. The on-resonance Mössbauer cross section for $\vec{k}_\gamma$ parallel to the plane of the Grafoil sheets. Here, $\sigma_x^{\parallel}(T)$ is the experimental yield. $\sigma_T^{\parallel}(x)$, the "Mössbauer isotherms" are illustrated to the left of the figure. Two "melting" stages are noticed in $\sigma_x^{\parallel}(T)$ ($T_{m1} \sim 85$ K, $T_{m2} \sim 95$ K) and the rise of $\sigma_T^{\parallel}(x)$ at $0.61 < x < 0.70$. The limiting value $\sigma_x^{\parallel}(T)$ (right) in the "melted" state is due to the ill-oriented graphite crystallites resulting in some perpendicular contribution.

step vanishes towards higher temperatures, and for $T > 85$ K, $\sigma_T^{\parallel}(x)$ rises smoothly with x. We find that the slope of $\ln\sigma^{\parallel}$ vs $T(< 85$ K) appears to be the same below the step ($x < 0.61$), and above the step ($x > 0.70$), within the experimental error. This result suggests that the step at $x \sim 0.65$ is not a result of any significant change of the intrinsic dynamical (elastic) properties of the 2D solid phase represented by the Mössbauer line, but is rather due to a change in the motional state of the surface.

The large TMT molecules on graphite display therefore at least two independent melting temperatures, $T_{m1} \sim 85$ K, $T_{m2} \sim 95$ K. Even though we do not know at the moment the nature of the phase between T_{m1} and T_{m2} it is interesting to notice the occurrence of a two-step melting process which was theoretically suggested by NH.

As the width of the observed line is unchanged through the transition whereas the line width of moving molecules is much beyond the experimental energy range, we believe that the transitions are first order and are smeared across ΔT due to size effects,[14] in contradiction with the starting hypothesis of NH. Preliminary x-ray measurements at $x = 0.7$ and 0.9 suggest that at least part of the 2D matter is in the form of a close-packed 2D solid up to ~100 K with a d spacing of ~6.8 Å which corresponds to an incommensurate solid. It is therefore unlikely that T_{m1} and T_{m2} describe the two predicted NH transitions. Since the intermediate phase shows long-range order, a possible explanation of the data is the formation of 2D patches animated by a kind of Brownian motion analogous to that of 3D crystallites deposited on crystalline substrates when the epitaxy is not realized.[15] At low average surface densities, small isolated patches may grow at surface defects, surrounded by a 2D gas (fluid).[12] With increasing x the patches grow into larger islands. Some of the islands may be in a certain motional state about their anchored positions at the defects. Being large molecules, the TMT forms a "floating" 2D incommensurate solid.[8] With further increase of x, *some* of the islands may coalesce to form a 2D "continent" at a critical coverage $x_c \simeq 0.65$. At x_c, the motion stops and $\sigma(T < 85$ K) increases. For $x > 0.65$ and above T_{m1}, the 2D continent might be broken partly into 2D moving patches produced through the formation of a dislocation network. T_{m2} is probably the melting of the 2D matter into an isotropic 2D fluid, since $T_{m2}/T_m(3\text{D}) \simeq 0.45$ which is a common feature of physisorbed systems.[1]

We would like to point out that it is the first time that such an apparently two-step first-order melting transition is observed experimentally. It is also worth noticing that the sharp decrease in $\sigma_T(x)$ occurs at a critical coverage $x_c \simeq 0.65$ in good agreement with that predicted by 2D percolation theory.[16] Although the agreement may be fortuitous, the onset of percolation could explain the disappearance of island mobility due to the formation of a still continent at x_c. 2D superfluidity in helium films was also recently predicted to occur through a percolation process[17] but no experimental evidence so far exists.

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Structural Stability of Transition-Metal Binary Compounds

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It is shown that the coordinates ΔN and $\bar{N}$, where N is the periodic-table group number, effect a much better crystal-structure separation than do the coordinates of Zunger for 91 transition-metal–transition-metal compounds. It is concluded that there is no evidence from structure maps to support the assumption that s-p electrons control the crystal structure dependent part of the energy of this class of compounds nor is there evidence to deny that ***d*** electrons effectuate this control.

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There has been great interest recently in crystal-structure maps. Originally, the coordinates chosen for such maps had an empirical basis,[1,2] but with the work of St. John and Bloch,[3] who based their coordinates on an l-dependent, nonlocal pseudopotential,[4] coordinates based on "first principles" have been used in further developments of crystal-structure maps.[5-11]

The present paper is concerned with structure maps for 91 AB equiatomic binary compounds composed solely of transition elements. The reason for this interest in these particular compounds is the implication in the recent work of Zunger[9] that the s-p electrons are responsible for the crystal structures chosen by transition-metal–transition-metal (TM-TM) compounds. This implication is contrary to the results based on tight binding theory,[12] which lead to the conclusion that the directionality of the d orbitals dictates transition-metal crystal structures. This conflict of viewpoints led us to a review of the data upon which Zunger based his statement: "The success of the present dual coordinates in separating the crystal structures of many TM-TM... compounds... suggests that the structural part of the cohesive energies of compounds may be determined by s-p coordinates... ."

Zunger also stated: "I am unable to separate the closely related NiAs($B8_1$)-MnP($B31$) and the CsCl($B2$)-CuAu($L1_0$) pairs.... Also I find that the seventeen $B20$ (FeSi) compounds [omitted from Fig. 1(b) for clarity] overlap precisely with the $B8_1$, $B2$, and $B33$ domains, respectively. ... A better resolution of the TM-TM compounds may require a specialized scale involving d electrons more directly." It is not possible from the data presented in Zunger's paper to obtain a measure of how well or how poorly, in fact, the Zun-