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LOW-TEMPERATURE HEAT CAPACITY OF TMS MONOLAYERS ADSORBED ON GRAPHITE AND MgO[*]

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Abstract

The heat capacity obtained below 30 K for the tetramethylsilane monolayers, which are adsorbed either on graphite or on the (100) surface of MgO, is analyzed to investigate the vibrational properties. The 2-D Debye temperatures are approximately 60% of the Debye temperature of the bulk solid (γ-phase), reflecting the dimensionality of lattice vibrations. The contributions from the vibrations perpendicular to the surface as well as the librational motions are determined by fitting the experimental heat capacities. All the results are consistent with those obtained from the incoherent inelastic neutron scattering and the molecular dynamics simulation.

Keywords: graphite, heat capacity, MgO, monolayer, tetramethylsilane

Introduction

According to our recent calorimetric investigation [1], the tetramethylsilane (TMS) monolayer adsorbed on graphite forms a 2-D solid and it undergoes an order-disorder phase transition at 107 K at the coverage $\theta<1$ and at 138 K at $1<\theta<2$ accompanied by a large entropy change, ranging from $R\ \ln 8$ to $R\ \ln 3$, depending on the coverage. We also reported that the molecules form a 2-D solid on the (100) surface of MgO and the monolayer undergoes the similar transition as on graphite [2]. In this paper, we concentrate on the low-temperature heat capacity obtained between 4 and 30 K for these monolayers to investigate the vibrational properties. We performed some neutron scattering experiment, which can give direct information on the vibrational density of states. A molecular dynamics (MD) simulation was also carried out to obtain the spectrum of vibrational motions perpendicular to the surface.

Experimental

Substrates

The graphite substrate used was a partially-oriented exfoliated graphite, Papyex (Le Carbone Lorraine). Since the specific surface area varied with different batches

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from the supplier, it was determined for each specimen by adsorption isotherm measurements at 77.4 K using nitrogen. Two specimens (15.6 and 8.81 m^2 g^{-1}) were subjected to the present study. It was degassed under vacuum at 400°C before use. The MgO substrate was prepared by us according to the procedure reported before [3]. Briefly, Mg ribbons (min. assay 99.9%, The Nilaco Corporation) were burned in an atmosphere of a mixture of argon (80%) and oxygen (20%) (Sumitomo Seika Chemicals). Floating particles in the smoke were collected and immediately degassed under vacuum at 950°C. The characterization by SEM demonstrated that the cube-like particles with (100) surfaces were typical with a side of approximately 0.2 μm. The specific surface area was determined for two samples (10.7 and 11.7 m^2 g^{-1}) from different batches. The powder was shaped into pellets to have better thermal contact in the calorimeter vessel and degassed again immediately before use.

Calorimetry

NMR standard grade of TMS (min. assay 99.5%, Wako Pure Chemical Industries) was dried over Molecular Sieve 4A and purified further by fractional distillation-condensation cycles. Known quantities of the adsorbates were added from the vapor through the needle valve equipped with the calorimeter vessel. No helium gas was introduced. The actual amounts of TMS introduced were 0.454 mmol for 10.57 g of Papyex (15.6 m^2 g^{-1}) and 0.826 mmol for 11.43 g of Papyex (8.81 m^2 g^{-1}), where the coverages are 0.61 and 1.81 respectively. Here, we assume a commensurate $\sqrt{7}\times\sqrt{7}R19°$ structure for the monolayer. This structure is actually realized in the monolayer of tetramethylgermane adsorbed on graphite [4]. For TMS/MgO, the amount of TMS was 0.504 mmol for 14.87 g of MgO (11.4 m^2 g^{-1}, a weighted average of two samples). The coverage is 0.66, assuming that the TMS molecule occupies the same area on MgO as on graphite.

The apparatus of adiabatic calorimetry was essentially the same as described before [5]. A platinum resistance thermometer (MINCO Products, Inc.) was used above 14 K. Below 15 K, a germanium resistance thermometer was used, either the one supplied by Scientific Instr., Inc. (for TMS/graphite) or the one by Lake Shore Cryotronics, Inc. (for TMS/MgO). The temperature scale is based on ITS-90 [6]. The heat capacity of the adsorbed layer was determined from the difference between that of calorimeter, adsorbent, and adsorbate, and that of the calorimeter and adsorbent only. Heat capacity measurements were made for the temperature range between 4 and 260 K for TMS/graphite and between 4 and 200 K for TMS/MgO.

Neutron scattering

Inelastic neutron scattering spectroscopy was carried out with an inverted-geometry time-of-flight spectrometer LAM-D installed at KEK, Tsukuba [7]. The instrument receives thermal neutrons to cover a wide range of energy (up to 300 meV) with a resolution of 0.4 meV at the elastic position or better than 6% at higher energies. Four bunks of the analyzer mirrors of pyrolytic graphite (PG) provide spectra at an average momentum transfer Q around 10 and 20 nm^{-1}. We used a cylindrical can made of aluminum with a needle valve. Although the use of the oriented graphite sample (with a mosaic spread in the orientation of the basal planes of about 30°) made it possible to obtain spectra of the *Q* vector parallel to the surface, the polarization was not perfect because of the instrumental geometry: the analyzer mirrors collect some of the scattered neutrons with the *Q* vector perpendicular to the surface. The measurement was made at 15 K at a single coverage (θ=1.02) for TMS/graphite.

Simulations

An MD simulation of a monolayer of TMS molecules supported on a graphite substrate was carried out to investigate the dynamics of the molecules. We used a software MASPHYC-SP (Fujitsu Ltd.) to generate the constant-*NVT* ensemble, where the constant-*T* was achieved by the method proposed by Nosé [8]. We applied a Gear fifth-order algorithm [9] with a time step of 0.5 fs. The simulation box had a dimension of 10.1×10.2 nm^2 and a 2-D periodic boundary condition was applied in the *X–Y* plane. The system contained 203 TMS molecules and three layers of graphite sheets underneath (3936 carbons for each sheet). None of the atoms were united for the TMS molecules and all the bond lengths and angles were allowed to vary. The graphite substrate, on the other hand, was fixed in the position to save the computing time. Initially the TMS molecules were placed in a hexagonal arrangement with a lattice constant of 0.7 nm which is significantly larger than that of the $\sqrt{7}\times\sqrt{7}R19°$ structure (0.651 nm). The total coverage was 0.72. DREIDING force field [10] was used with a cut-off distance of 1.3 nm. The system was equilibrated at 40 K for 200 ps before collecting data over another 200 ps.

Results and discussion

Low-temperature heat capacity

In our calorimetry, the contribution of the monolayer to the total heat capacity was extremely small. At θ=0.61 for TMS/graphite, for example, it was 2% below 15 K and decreased with the temperature (0.8% at 30 K). The resulting accuracy of the measurements is estimated to be 6%. The molar heat capacities obtained for TMS/graphite (θ=0.61 and 1.81) and for TMS/MgO (θ=0.66) are illustrated in Fig. 1, where the results obtained for the γ-phase of bulk solid [11] are also plotted for comparison. It is evident that the molar heat capacity of the monolayers is substantially larger than that of the bulk solid. As discussed below, the temperature dependence is also different between them, reflecting the dimensionality.

Apparent Debye characteristic temperature

The measured heat capacities are converted to the apparent characteristic temperatures in the framework of the 2-D Debye model, which is illustrated in Fig. 2. Here, we assume 2*N* degrees of freedom for the system. Also plotted in the figure are the

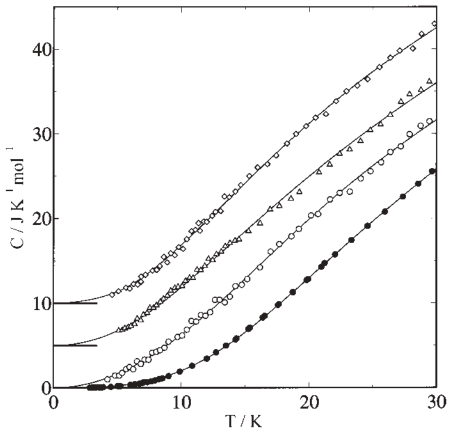

Fig. 1 Molar heat capacities obtained for TMS/graphite at θ=0.61 (open circles) and at θ=1.81 (triangles) and for TMS/MgO at θ=0.66 (squares). Those reported for the bulk γ-phase [11] are also plotted (filled circles) for comparison. Note that the vertical scale for each monolayer is shifted from the next by 5 J K^{-1} mol^{-1}

3-D Debye temperatures calculated from the experimental heat capacities of the bulk solid [11], where we assume $3N$ degrees of freedom. It should be noted here that the ratio Θ_D(2-D)/Θ_D(3-D) is approximately 0.6 at low-temperatures. This can simply be understood from the dimensionality. According to the Debye theory [12], the cut-off frequency ω_D is represented by $\omega_D^3(3\text{-D})=6\pi^2 v^3 n(3\text{-D})$, where v is the sound velocity and n(3-D) is the volume density. Likewise, with the 2-D Debye model for the same media we obtain the relation $\omega_D^3(2\text{-D})=2\pi v^2 n(2\text{-D})$. Here, the sound velocity is always constant without any polarization and the densities obtained from the n(2-D) and n(3-D) are the same. The ratio $\Theta_D(2\text{-D})/\Theta_D(3\text{-D})=\omega_D(2\text{-D})/\omega_D(3\text{-D})$ would therefore be $(2\pi)^{1/2}/(6\pi^2)^{1/3}$, which is 0.64. The fact that it works pretty well with the present system suggests that this monolayer is an ideal 2-D molecular solid in a sense that the medium is isotropic. The values of Θ_D(2-D) obtained below 7 K for three different monolayers are summarized in Table 1. As discussed below, other contributions become significant at higher temperatures and the apparent Debye temperatures fall rapidly as illustrated in Fig. 2.

Breakdown of the heat capacity

There are two other modes that start to be excited before the contribution from the intramolecular vibrations become significant above 25 K; vibrations of the whole molecule perpendicular to the surface and rotational vibrations (librations). All the intramolecular vibrational modes are already assigned from a normal coordinate analysis as well as spectroscopic investigations [13]. Having subtracted this contribution with Einstein functions as well as the lattice contribution mentioned above, we fitted the rest of the heat capacities (below 30 K) with two functions, one being an Einstein function with $\Theta_E(N)$ to describe the vibrations perpendicular to the surface

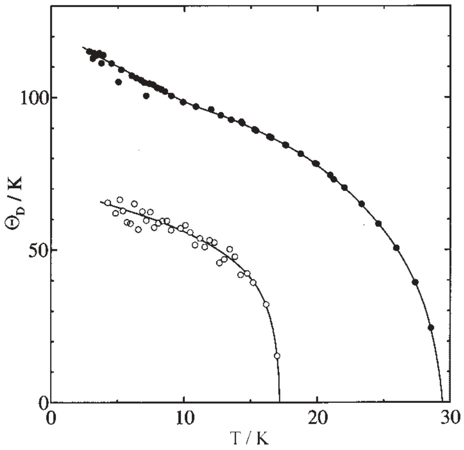

Fig. 2 Apparent Debye temperatures obtained from the experimental heat capacities for the TMS monolayer on graphite at θ=0.61 (open circles) and for the bulk solid (filled circles). Here, the 2-D and 3-D Debye models are applied respectively to obtain the characteristic temperatures

and another Einstein function with $\Theta_E(3N)$ to describe the librations. The former has N degrees of freedom and the latter $3N$. Here, we ignore any possible anisotropic nature of the rotational vibrations. The fitted results are summarized in Table 1 and a typical result is illustrated in Fig. 3. It should be pointed out that the values of Θ_E obtained for the librational mode (96 K at θ=0.61 and 105 K at θ=1.81 for TMS/graphite and 96 K for TMS/MgO) are similar to that obtained for the bulk γ-phase, 105 K.

Table 1 Characteristic temperatures obtained from the low-temperature heat capacity of the monolayers for TMS/graphite and TMS/MgO. Those obtained for the bulk solid [11] are also listed for comparison. The $\Theta_D^{\text{lattice}}$ stands for the characteristic Debye temperature for lattice vibrations. The Θ_E^{perp} and Θ_E^{lib} stand for the Einstein temperatures for vibrations perpendicular to the surface and librations, respectively

System	$\Theta_D^{\text{lattice}}$/K	Θ_E^{perp}/K	Θ_E^{lib}/K
TMS/graphite (θ=0.61)	61	71	96
TMS/graphite (θ=1.81)	59	58	105
TMS/MgO (θ=0.66)	68	45	96
Bulk TMS (γ-phase) [11]	~100	–	105

Vibrational mode perpendicular to the surface

One may ask how successfully the vibrations perpendicular to the surface can be described by an Einstein function. Here, we show an evidence obtained from the MD simulation. The velocity autocorrelation function was calculated from time evolution of the velocity of the center-of-mass. In this paper, we are only interested in the com-

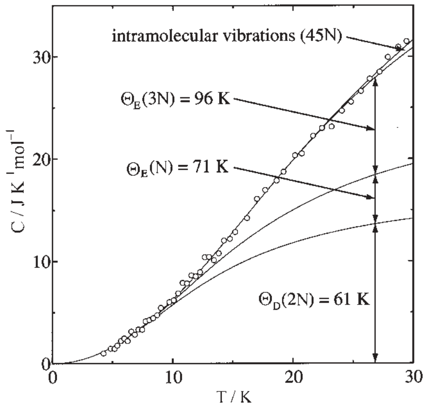

Fig. 3 Breakdown of the experimental heat capacities obtained for the TMS monolayer on graphite. See the details in the text

ponent perpendicular to the surface. The time-domain data were converted to the frequency-domain data by using Wiener–Khinchin relation. Figure 4 displays the spectrum, indicating that the vertical vibrations of the TMS molecules show only a weak dispersion and this mode can be described by an Einstein function. The peak value (8 meV or 93 K), however, is slightly larger than that obtained from the analysis of the low-temperature heat capacity.

Vibrational density of states

Figure 5 illustrates the vibrational density of states obtained from the incoherent neutron scattering for TMS/graphite at θ=1.02. The upper scale in Fig. 5a shows the corresponding temperature. It should be noted here that we investigate the system

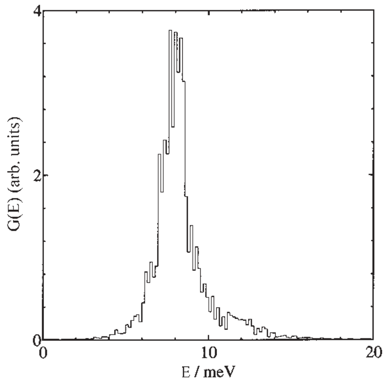

Fig. 4 Vibrational spectrum of the TMS molecules obtained by an MD simulation for TMS/graphite. The vibrational motions along the axis perpendicular to the graphite surface are selectively collected

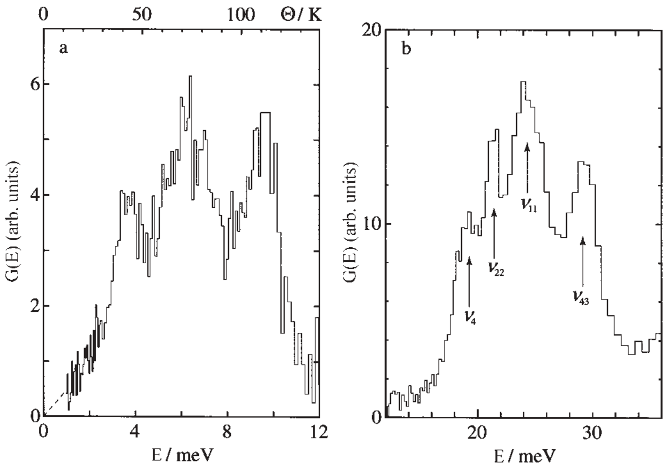

Fig. 5 Vibrational density of states obtained by neutron scattering for TMS/graphite at the coverage θ=1.02. a – Lattice vibrational modes appeared in the low-energy region. The corresponding temperature is given in the upper scale; b – Some of the intramolecular vibrations appeared in the higher energy region. The ν_4 and ν_{22} are the torsional modes, whereas the modes ν_{11} and ν_{43} are due to the C–Si–C deformation vibrations [13]

through the protons because proton has an enormous cross section in the incoherent neutron scattering. Therefore, it is not straightforward to obtain the intrinsic density of states directly related to the heat capacity. Moreover, the polarization was not complete in the measurement neither the orientation of the sample. Different modes may contribute to the density of states with different weights. Nevertheless, the result clearly indicates the presence of two-dimensional lattice vibrations (below 5 meV), vibrations perpendicular to the surface (at 6 mV), and librations (at 9.5 meV). Some of the intramolecular vibrations, the torsional modes (ν_4 and ν_{44}) and the C–Si–C deformation vibrational modes (ν_{11} and ν_{43}), are also obtained at higher energies as illustrated in Fig. 5b.

Summary

The vibrational properties of the TMS monolayers adsorbed both on the graphite surface and on the (100) surface of MgO are deduced from the low-temperature heat capacity. The 2-D character of the lattice vibrations are successfully described by the Debye model. The librational motions of the monolayers are similar to those of the bulk solid. An MD simulation gives a dispersionless mode for the vibrational motion of the whole molecule perpendicular to the surface. The neutron scattering spectroscopy gives a whole picture of the vibrational density of state including some of the intramolecular vibrational modes. Those evidences are consistent with the results obtained from the low-temperature heat capacity. Although we previously had some evidence that the TMS molecules are less mobile on MgO than on the graphite surface in the orientationally-disordered phase at higher temperatures [2], no prominent difference is found in their vibrational properties.

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