Low-Temperature Specific Heat of C_{60}

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(Received 13 January 1992)

We have measured a large specific heat of polycrystalline C_{60} from $T=1.4$ to 20 K. The data were adequately fitted by a model containing Debye terms, Einstein oscillators, and a linear contribution. An analysis incorporating both vibrational and strongly coupled rotational degrees of freedom expected for the simple-cubic structure at low temperatures is proposed. We also discuss a possible interpretation based on a fairly narrow feature in the excitation spectrum. The large linear term may be a consequence of disorder resulting in a distribution of two-level tunneling centers.

PACS numbers: 65.40.−f, 61.50.−f, 63.20.Pw

Many unusual features of the new types of solids built of large structures such as C_{60}, called buckminsterfullerene, have been examined in recent years [1]. The arrangement of large structural units into a crystalline solid may lead to interesting electronic and lattice properties which are absent in conventional materials. The intramolecular vibrational features of C_{60} were examined both by optical [2] and neutron-scattering [3] experiments, and the experimental findings are in full agreement with the modes calculated for buckminsterfullerenes. In addition, various experiments also give clear indications for rotation of the C_{60} molecules at high temperatures [4,5].

In this paper, we describe specific-heat experiments on C_{60} molecules crystallized in a fcc lattice at room temperature. A large specific heat is observed at low temperatures, and this is analyzed in terms of a standard Debye model, together with a contribution from a low-lying mode (or modes) which dominates the low-temperature thermodynamic properties. A physically intuitive description based on the vibrational and strongly coupled rotational degrees of freedom of the low-temperature simple-cubic (sc) structure is discussed. Finally, a very significant linear term is seen in the data, and we propose that a uniform distribution of two-level tunneling centers of unknown origin may be responsible.

The procedures for making the C_{60} powder were the same as those already described [6]. After synthesizing, the powder was pressed into a cylindrical pellet approximately 3 mm in diameter and 1 mm high and characterized by x-ray diffraction. These measurements show that the sample has a fcc structure at room temperature with a lattice constant that is consistent with previously obtained results [7].

The specific heat was measured using a thermal-relaxation technique [8] that is well suited for small samples of ~10 mg. Data were collected from $T=1.4$ to 20 K with the sample attached to a thermometer/heater sapphire platform by a small amount of Wakefield grease, and τ_2 effects, which result from a significant thermal impedance between the sample and the thermometer/heater platform, were judged negligible at all measurement temperatures. After subtracting the addenda, determined by a separate measurement, the specific heat normalized per unit mass is plotted as C vs T in Fig. 1. For comparison, a measurement of graphite by De Sorbo and Nichols [9] is also plotted. Notice that the specific heat of C_{60} is approximately 1 order of magnitude larger than graphite over our whole range of measurement temperatures. For the remaining discussion, the specific-heat data are normalized per mole C_{60}.

Perhaps the most striking feature of the data is the pronounced curvature when graphed as C/T vs T in either Fig. 2(a) or 3(a). This implies the existence of excitations in addition to a Debye contribution arising from a

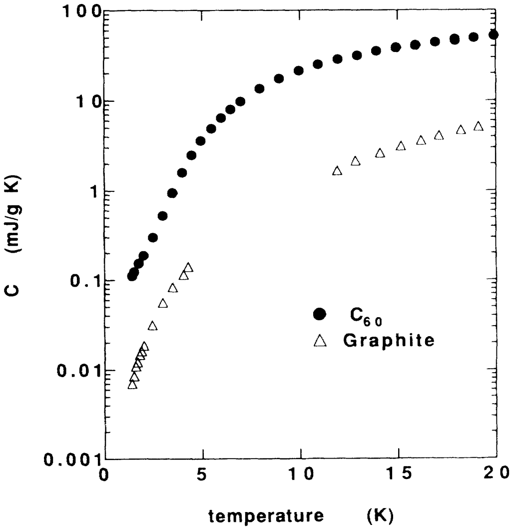

FIG. 1. Specific heat of polycrystalline C_{60} normalized per unit mass as a function of temperature. Also plotted for comparison is the specific heat of graphite reported in Ref. [9].

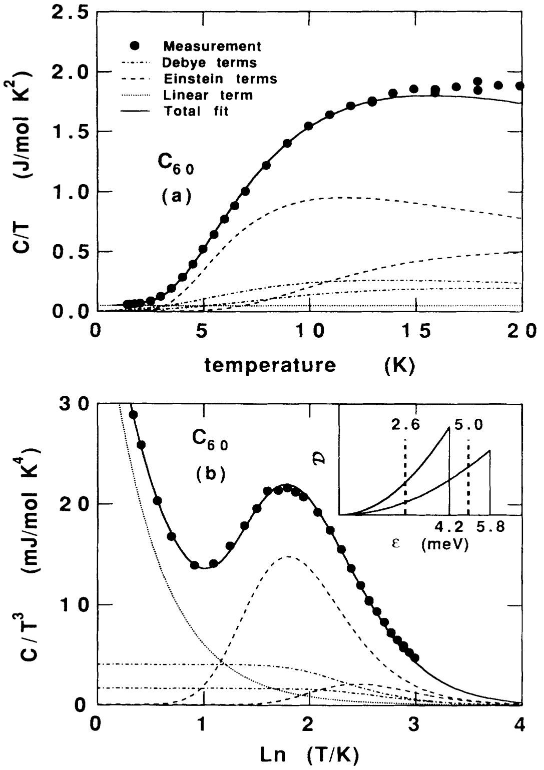

FIG. 2. The specific heat of polycrystalline C60. In (a) the data are plotted as C/T vs T while in (b) the specific heat is displayed as C/T^3 vs $\ln(T)$ so that the individual contributions are more easily recognized. In addition to a linear component, this model represents the vibrational and rotational degrees of freedom by a pair of Debye and Einstein terms. The inset, where the units of the ordinate are arbitrary, shows the density of states D as a function of energy ε used to represent the Debye and Einstein contributions.

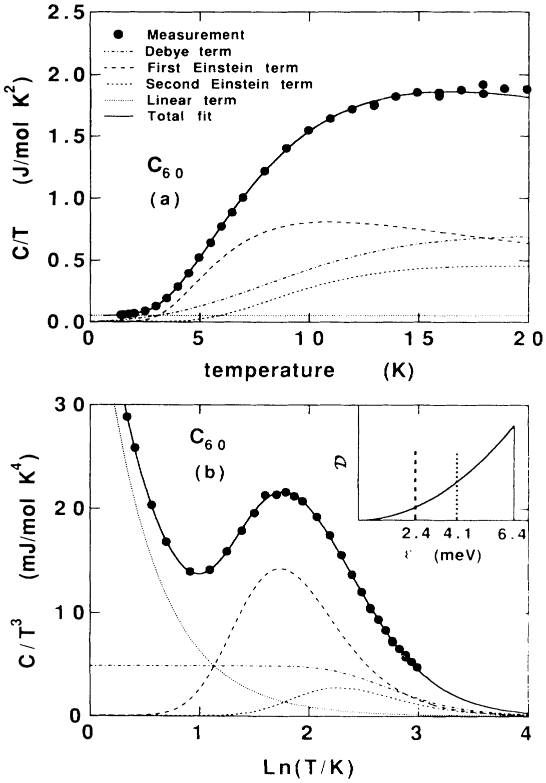

FIG. 3. The measured and modeled specific heat of polycrystalline C60, displayed in the same fashion as in Fig. 2. The model used in this fit contains a Debye term, two Einstein terms, and a contribution that is linear in temperature. The combined contributions for the best fit is the solid line. Each of the individual contributions in the model is also displayed.

simple acoustic mode. These contributions are even more evident when the data are plotted as C/T^3 vs $\ln(T)$. A graph of this type presents an approximate image of $D(\omega)/\omega^2$ vs $\ln(\hbar\omega/4.93k_BT)$ where $D(\omega)$ is the phonon spectrum [10]. Hence, a Debye dependence will appear constant up to the Debye temperature Θ_D, above which it drops to zero. Two additional features are quite evident: The large broad peak at $\ln(T)\sim 2$ indicates that some type of optical mode (i.e., a mode without much dispersion) is present, and a sharp low-temperature upturn signifying a significant linear-temperature component exists.

These general observations were quantified by fitting the measured specific heat to a model containing five contributions. This procedure for analyzing vibrational contributions to the specific heat is not new [11], and it was previously applied to the $A15$ [10] and the high-T_c [12] superconductors. For the vibrational-acoustic modes, the Debye term (the dash-dotted lines in Fig. 2)

$$C_{DV}=\frac{9n_{DV}R}{x_{DV}^3}\int_0^{x_{DV}}\frac{x^4e^x}{(e^x-1)^2}dx$$

was used where $R=8.314$ J/mol K is the gas constant. The only two variables in this term are $x_{DV}=\Theta_{DV}/T$ and the number of oscillators per formula unit n_{DV}. To adequately model the optical modes responsible for the broad peak around $\ln(T)\sim 2$, an Einstein oscillator term (the dashed lines in Fig. 2) of the form

$$C_{EV}=3n_{EV}R\frac{x_{EV}^2e^{x_{EV}}}{(e^{x_{EV}}-1)^2}$$

was necessary. In this expression, $x_{EV}=\Theta_{EV}/T$.

The high degree of sphericity of C60 allows each molecule to spin at its lattice site, and this was experimentally observed by nuclear-magnetic resonance [4] and x-ray diffraction [5]. Of course, rotational modes of the individual balls could play an important role in the specific heat. If we neglect the potential energy contribution, the specific heat of a free spherical rotator starts from zero, goes through a shallow maximum, and above the temperature $T_R\sim\hbar^2/2Ik_B$ saturates at the equipartition value of 12.5 J/mol K [13]. Because the C60 molecule has such a large moment of inertia I, $T_R\sim 5$ mK, and the complete rotational contribution would be observed at our lowest temperatures. We must therefore consider the potential energy term so that only rotational oscillations about an equilibrium position are allowed at low temperatures. These torsional waves are similar to harmonic-oscillator-type compressional waves, and the specific-heat contribution can be modeled with an additional set of Debye and Einstein terms, which are parametrized by n_{DR}, $x_{DR}=\Theta_{DR}/T$, n_{ER}, and $x_{ER}=\Theta_{ER}/T$, analogous to those used for phonons.

Finally, a fairly significant component that is linear in temperature (the dotted lines in Fig. 2) had to be added. Including the linear term $C_L=\gamma T$, the five contributions are characterized by a total of nine parameters; however, considerations of the crystal structure allow us to set the number of oscillators associated with each mode. Below $T\sim 250$ K, orientational ordering occurs, changing the structure from fcc to sc with a basis of four C_{60} molecules per primitive unit cell [5]. Thus, three of the branches are acoustic, while the other nine are optical. Assuming the different polarizations of each branch are identical, the number of oscillators per molecule in a given mode are constrained to $n_{DV}=0.25$, $n_{EV}=0.75$, $n_{DR}=0.25$, and $n_{ER}=0.75$. This leaves the four characteristic energies and γ as the only adjustable parameters. The best fit to the measured data was obtained with $\Theta_{D1}=49$ K, $\Theta_{E1}=30$ K, $\Theta_{D2}=67$ K, $\Theta_{E2}=58$ K, and $\gamma=45$ mJ/mol K^2. Each of the separate contributions along with the total fit and the measurement are plotted in Fig. 2. In the inset of Fig. 2(b) the density of states for the Debye and Einstein contributions incorporated in our model are displayed to show the relative energy scales associated with the various terms. On specifying the characteristic energies, any reference to either the vibrational or rotational nature of the modes (i.e., the subscripts V and R) was dropped because a determination of which set of modes are vibrational and which are rotational is not possible from our experiments. We note that in crystalline benzene the vibrational excitations are $\sim 25\%$ lower in energy than the rotational modes [14].

As expected in a material composed of heavy balls bound by weak van der Waals interactions, the Debye temperature is quite low, reflecting the softness of the lattice. Taking the lower-energy Debye mode as vibrational, the bulk modulus B can be estimated from the measured Debye temperature and compared to the value determined directly from measurements of the lattice constants as a function of hydrostatic pressure. For an isotropic solid, $B=\lambda+2\mu$ where λ and μ are the Lamé coefficients. These coefficients are related to the transverse and longitudinal velocities of sound by the expression $\lambda=\rho(c_l^2-2c_t^2)$ and $\mu=\rho c_t^2$; here $\rho=1.72$ g/cm^3 is the density. If we assume that Cauchy's criterion holds [15], which is approximately true for most isotropic materials, $\lambda=\mu$ and $c_l=\sqrt{3}c_t$. Within the Debye approximation, we can use

$$k_B\Theta_{D1}=\hbar\left[\frac{18\pi^2 n_{DV} n}{c_l^{-3}+2c_t^{-3}}\right]^{1/3}$$

along with the above assumptions to calculate $c_t=2.1\times 10^5$ cm/s and $c_l=3.6\times 10^5$ cm/s. The density of C_{60} molecules n was taken to be 1.44×10^{21} cm^{-3}. These estimates for the sound velocities yield a value of 13 GPa for the bulk modulus which compares very favorably, considering the crudeness of our calculations, to Fischer *et al.*'s [16] direct measurement of 14 GPa at room temperature.

The analysis above is based on a specific interpretation of the dynamics in crystalline C_{60}, and it is difficult to say if this most accurately represents the true excitational spectrum. A different approach is to adopt a single Debye term and two Einstein oscillators, and then optimize the fit to the data by adjusting the number of oscillators per formula unit for the Einstein terms and the characteristic energies. Neglecting any orientational ordering, there is one C_{60} molecule per primitive unit cell. Thus, $n_D\equiv 1$ while Θ_D, the Θ_E's, the n_E's, and γ were allowed to vary. Despite one less term in this model, we have an additional adjustable parameter. The best fit to the data is displayed in Fig. 3 using $\Theta_D=74$ K, $n_{E1}=0.60$, $\Theta_{E1}=28$ K, $n_{E2}=0.57$, $\Theta_{E2}=48$ K, and $\gamma=47$ mJ/mol K^2. Again the inset in Fig. 3(b) displays the density of states used to represent the Debye and Einstein contributions.

Dominating the response between $T\sim 3$ and ~ 19 K is a quasidispersionless excitation. Even though the fit to this model is slightly better than in the previous case, the fundamental physics behind this narrow feature remains unspecified. Both explanations rely on similar excitation spectrums with Debye contributions of comparable magnitude and some type of narrow frequency structure centered around 3.3 to 3.8 meV whose width (or separation?) is 1.7 to 2.4 meV. Van Hove singularities in the density of states, which are present even in very simple lattice structures, may also account for some features. Since the specific heat is an integral of the density of states $D(\varepsilon)$ over all energies, our models are insensitive to the fine details in $D(\varepsilon)$ and just characterize the real underlying structure with a few parameters. The first model, however, derives $D(\varepsilon)$ from a very specific interpretation, which includes both vibrational and rotational degrees of freedom, and it may actually be closer to reality. Inelastic-neutron-scattering experiments could better delineate $D(\varepsilon)$.

The γ's derived from the fits are 45 to 47 mJ/mol K^2 (62 to 65 μJ/g K^2), which are particularly large in comparison to uncorrelated materials. Since this system is an insulator without a Fermi-liquid ground state, the only commonly known mechanism responsible for a linear specific-heat contribution is disorder [17], though the magnitude of the effect is usually a few μJ/g K^2 [18]. It is possible that either crystallographic or some type of coupled orientational disorder simulates a uniform distribution of two-level systems up to a cutoff energy Δ_0. Provided the barrier height is such that phonon-assisted tunneling is favored over resonant tunneling and the system can attain thermal equilibrium during the duration of the measurement, then a linear specific heat is found for

$k_B T \ll \Delta_0$ of the form

$$C_L = (\pi^2/6) k_B R D_0 T ,$$

where the density of tunneling centers $D_0 = N/\Delta_0$. In this expression N is the number of two-level systems per C_{60} molecule. Using the measured γ, we find $D_0 \sim 39$ states/eV C_{60} molecule, which is 3 orders of magnitude larger than in fused silica. If we take $N=1$, then $\Delta_0 \sim 26$ meV (~ 300 K), which corresponds closely to the orientational-ordering transition reported at 249 K. In fused silica, ultrasonic attenuation measurements [19] find $\Delta_0 \sim 0.1$ eV, which is consistent with the 1700-K melting point, and this yields $N \sim 1/250$ tunneling center per SiO_2. Currently, we are unaware of any indications in other experiments, such as x-ray diffraction, that point to a large degree of disorder at low temperatures. One can envision x equilibrium positions separated by potential barriers associated with an x-fold rotation. Because the electrons on one ball have a different arrangement with respect to those on a neighboring ball for adjacent equilibrium orientations, the energies of these two positions may be different. Whether a uniform distribution of energy levels results from a single two-level system of the isolated pair of C_{60} molecules when they are surrounded by the rest of their nearest neighbors is still questionable. Another possibility is that the disorder is associated with a uniform distribution of Einstein modes. If this distribution has a smaller cutoff energy of 30 to 50 K, the density of defects centers is reduced by more than an order of magnitude.

Our specific-heat experiments suggest that low-lying modes are present in C_{60}. These modes are not due to intramolecular vibrations which have significantly higher energies; rather they are expected to arise from the motion of complete molecular units. A strong possibility may be rotational degrees of freedom of the coupled individual molecules, though the presence of some other exotic excitations not associated with the movement of molecules cannot be ruled out. More microscopic experiments and further theoretical work are needed to answer these questions and determine if these features are important for superconductivity in electronically doped C_{60}. The linear term of the specific heat cannot be due to electronic excitations of a degenerate Fermi gas, but most likely arises from disorder-induced localized states similar to those found in glasses and amorphous semiconductors.

Work at Los Alamos National Laboratory was performed under the auspices of the U.S. Department of Energy. We want to also acknowledge useful conversations with W. G. Clark, K. Holczer, and R. L. Whetten.

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