Neutron-scattering study of C_{60}^{n-} ($n=3,6$) librations in alkali-metal fullerides

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We have measured the low-energy inelastic neutron scattering spectra of superconducting K_3C_{60} and insulating Rb_6C_{60}. Well-defined peaks are observed at room temperature at 3.59(4) meV [full width at half maximum (FWHM) =1.11(15) meV] and 5.49(38) meV [FWHM = 3.41(44) meV], respectively. They harden with decreasing temperature and the dependence of their intensities on the scattering vector shows that they are due to small-amplitude librational motion. No anomalous behavior of the librational peak was observed on cooling through the superconducting transition temperature, indicating that electron-librational coupling is weak. The energy barrier for reorientation is estimated to be at least twice as large in K_3C_{60} as in C_{60}. Substantial disorder persists for K_3C_{60} in the superconducting state.

Alkali-metal intercalation of solid C_{60} leads to superconducting compositions with stoichiometry A_3C_{60}.[1] The electrostatic guest-host interactions favor orientational ordering of the C_{60} molecular units and A_3C_{60} crystallizes in a face-centered-cubic structure with the C_{60}^{3-} ions randomly distributed between two orientations, related to each other by 90° rotations.[2] Saturation-doped insulating A_6C_{60} adopts a body-centered-cubic structure with the C_{60}^{6-} units orientationally frozen at room temperature.[3] At present, little is known about the details of the orientational potential in the fulleride phases. Superconductivity in the fullerides has been interpreted in terms of either electronic[4] or phonon-mediated pairing.[5] Inelastic neutron scattering (INS) experiments are consistent with the predictions of *intramolecular* phonon-mediated pairing models, and show that electron-phonon coupling strength is distributed among radial and tangential modes.[6] On the other hand, the postulated role of low-energy *intermolecular* modes[7] in superconductivity has not been experimentally investigated.

In this paper, we report inelastic neutron scattering measurements of low-energy excitations in superconducting K_3C_{60} [at 4.04(3) meV (12 K), decreasing to 3.59(4) meV (300 K)] and insulating Rb_6C_{60} [at 6.11(16) meV (150 K), decreasing to 5.55(28) meV (350 K)]. The momentum-transfer dependence of the intensity leads to their assignment as librational modes whose energies are substantially higher than those in the orientationally ordered phase of C_{60},[8] reflecting a stronger potential due to the ionic character of the fullerides. The librational am-

plitudes increase with increasing temperature and with increasing oxidation state of the carbon cage ($C_{60}^{6-} \rightarrow C_{60}^{3-} \rightarrow C_{60}$). No anomalous change in the position or width of these phonons is observed for K_3C_{60} as the sample is cooled below the superconducting transition temperature $T_c = 19.3$ K. Given the proximity of these modes to the superconducting energy gap ($2\Delta \sim 3.6$–8.8 meV),[9] this observation introduces severe constraints on the magnitude of the coupling of the librational modes with the electrons.

K_6C_{60} and Rb_6C_{60} powder samples were prepared by reaction of C_{60} with K and Rb metal in sealed, evacuated Pyrex tubes; K_3C_{60} was prepared[20] by reaction of K_6C_{60} with C_{60}. The ~700-mg samples were characterized by powder x-ray and neutron diffraction and ^{13}C NMR spectroscopy. Prompt gamma-ray neutron activation analysis[10] showed a hydrogen content of 0.0038±0.0006 atom per C atom for K_3C_{60} and an upper limit of 0.026 atom per C atom for Rb_6C_{60}.[11] The neutron scattering measurements were performed at the Neutron Beam Split-core Reactor (NBSR) at the National Institute of Standards and Technology using the BT4 triple-axis spectrometer with fixed incident neutron energies E_i of 28 meV for the K_3C_{60} and 35 meV for the Rb_6C_{60} experiments. The incident neutron beam was monochromated using the Cu (220) reflection and the scattered neutrons were analyzed using the pyrolytic graphite (004) reflection. The measured resolution at the elastic line for 60'-40'-40'-40' collimations was 1.0 meV full width at half maximum for $E_i = 28$ meV and 1.2 meV for $E_i = 35$ meV. The powder samples, loaded under helium in indium-

wire-sealed aluminum cylindrical cans, were placed inside a close-cycle He refrigerator. Background runs were subtracted and the spectra were symmetrized and corrected for variable spectrometer resolution. Fits to the data included a sum of a δ function and a Gaussian component at zero energy transfer and a Lorentzian centered at nonzero energy transfer, each convoluted with a Gaussian instrumental resolution function. Comparable fits, where a Lorentzian component at zero energy transfer was used, were found inferior at most temperatures and scattering vectors. The diffraction profile of K_3C_{60} was recorded at 12 K using the high-resolution powder diffractometer BT1 with a wavelength of 1.54 Å.

Figures 1(a)–1(c) present representative INS spectra for K_3C_{60} below and above T_c and at 300 K, at a scattering vector $Q=5.72$ Å^{-1}; Fig. 1(d) shows the corresponding Rb_6C_{60} spectrum at room temperature at $Q=5.93$ Å^{-1}. The solid circles are the corrected experimental data, the solid line is the fit described above, and the broken lines show its Gaussian and Lorentzian components. Well-defined peaks are observed at nonzero energy transfer at all temperatures studied, and are assigned to librational modes of the C_{60}^{n-} ions (vide infra). Inelastic peaks previously observed in low-temperature time-of-flight measurements, at 4.3(2) meV or K_3C_{60} (Ref. 6) and 6.4(2) meV for Rb_6C_{60},[6] should also be assigned as librations. Figures 2(a) and 2(b) show the temperature evolution of the librational energy and width, respectively. The C_{60} results[8] are included for comparison. The energy of the librational modes increases as the ionicity of the C_{60} unit is increased. This is due to an increase in the interaction strength in going from C_{60}, where the predominant forces are of van der Waals origin, to Rb_6C_{60}, where Coulomb forces between highly charged ions dominate. In all cases, the librations soften as the temperature increases; however, the softening is markedly smaller in K_3C_{60} (~11% of the low-temperature value between 12 and 300 K) and Rb_6C_{60} (~12% by extrapolation), compared to C_{60} [~35% (Refs. 8 and 12)]. The widths of the librational peaks [Fig. 2(b)] are not resolution limited. This observation, and the small amount of softening with temperature, indicate the presence of dispersion effects, including anisotropies in the rotational potential. The width changes less with temperature in K_3C_{60} than in C_{60}. The integrated intensity of the librational peaks increases smoothly with temperature, roughly following a harmonic behavior.

The experimental data of Fig. 1 clearly show the presence of additional scattering under the elastic line for both K_3C_{60} and Rb_6C_{60}. The intensity and width of the Gaussian line used to describe this scattering change very little with temperature. In contrast, the intensity of the purely elastic component changes appreciably with temperature, possibly because thermal expansion shifts the Bragg peaks slightly. For Rb_6C_{60} the Q dependence of the intensity is shown in Fig. 3(a). It is intriguing that this scattering is well described by the calculation for complete orientational disorder. At present, we are unable to explain the origin of this additional scattering; it appears to arise from some distribution of relaxation pro-

cesses which give rise to a Gaussian line shape. A Lorentzian line shape would have been more appropriate if it were associated with a single overdamped mode.

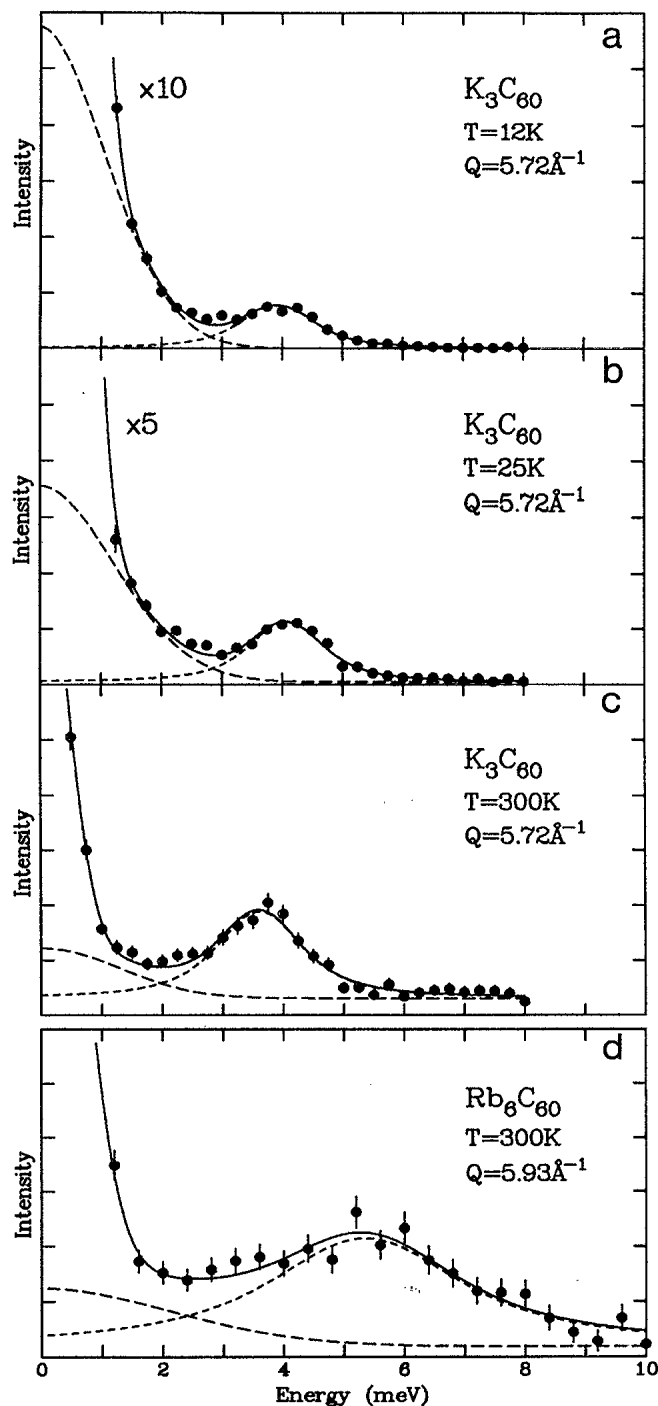Of particular interest is the behavior of the librational

FIG. 1. Representative INS spectra at constant Q. K_3C_{60}, $Q=5.72$ Å^{-1}, with (a) $T=12$ K, (b) $T=25$ K, and (c) $T=300$ K. (d) Rb_6C_{60}, $Q=5.93$ Å^{-1}, with $T=300$ K. The solid circles are experimental points and the solid lines are best fits, including a Lorentzian component at nonzero energy transfer (dashed line) and a Gaussian component, centered below the elastic line (dashed line), as discussed in the text. Note changes in the intensity scale for K_3C_{60}.
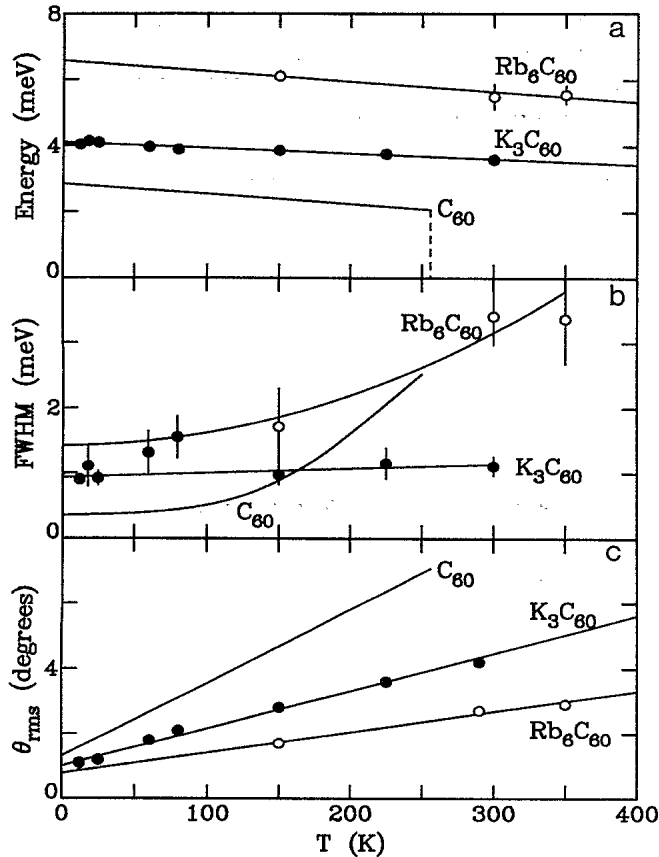
FIG. 2. Temperature evolution of (a) the librational energy, (b) the width of the librational peak, and (c) the root-mean-square amplitude of libration for C_{60} (Ref. 8), K_3C_{60}, and Rb_6C_{60}. Lines are guides to the eye. Points represent experimental measurements; points for C_{60} are omitted in the interest of clarity.

modes in K_3C_{60} as the sample is cooled below T_c. We performed measurements at 25 and 12 K and found that within the experimental resolution, neither the energy nor the width of the librational excitation is affected. The changes in energy and width estimated from the fits shown in Fig. 1 are $\Delta\omega(25\ K - 12\ K) = (0.06 \pm 0.05)$ meV and $\Delta\gamma(25\ K - 12\ K) = (0.02 \pm 0.13)$ meV, respectively. The superconducting energy gap $2\Delta(0)$ in K_3C_{60} has been measured by scanning tunneling microscopy (STM) point contact tunneling to be 8.8 meV, while infrared measurements give 8.0 ± 2.5 meV and ^{13}C NMR measurements give 3.6 meV.[9] For phonons with energies less than $2\Delta(T)$, the contribution to their lifetime due to the electron-phonon interaction disappears in the superconducting state, and sharpening of the order of γ_{ep} (Ref. 13) is expected. Here γ_{ep} is the contribution to the damping due to electron-phonon coupling, which can be estimated by $\gamma_{ep} = (1/g)\pi N(0)\lambda_{lib}\omega^2$, where g is the degeneracy of the mode, $N(0)$ is the density of states at the Fermi level, ω is the librational frequency, and λ_{lib} is the electron-librational coupling constant. Our results show that with $N(0) = 14$ states per eV per C_{60} per spin[14] and $\omega = 4.1$ meV, the observed linewidth changes are only consistent

with small values of λ_{lib}, ≤ 0.08. This is in sharp contrast to the predictions of some theories of phonon-mediated pairing interactions in the fullerides,[7] which necessitate a large value of $\lambda_{lib} \sim 1.9-2.7$ and predict $\gamma_{ep} \sim 0.5-0.7$ meV, requiring that roughly 60–80 % of the experimentally observed linewidth be due to electron-librational coupling. The experimental results clearly indicate that the coupling of electrons to librational modes does not substantially contribute to the formation of Cooper pairs.

The integrated intensity of the librational peaks of K_3C_{60} and Rb_6C_{60} at room temperature is shown as a function of Q in Fig. 3(a). Exact calculations for completely orientationally disordered molecules (dashed line), and Monte Carlo calculations for uncorrelated isotropic molecular librations with a root-mean-square amplitude $\theta_{rms} = 6.7°$ (solid line),[12] are also included. The calculations were arbitrarily scaled to the $Q \sim 5.75$ Å^{-1} peak.
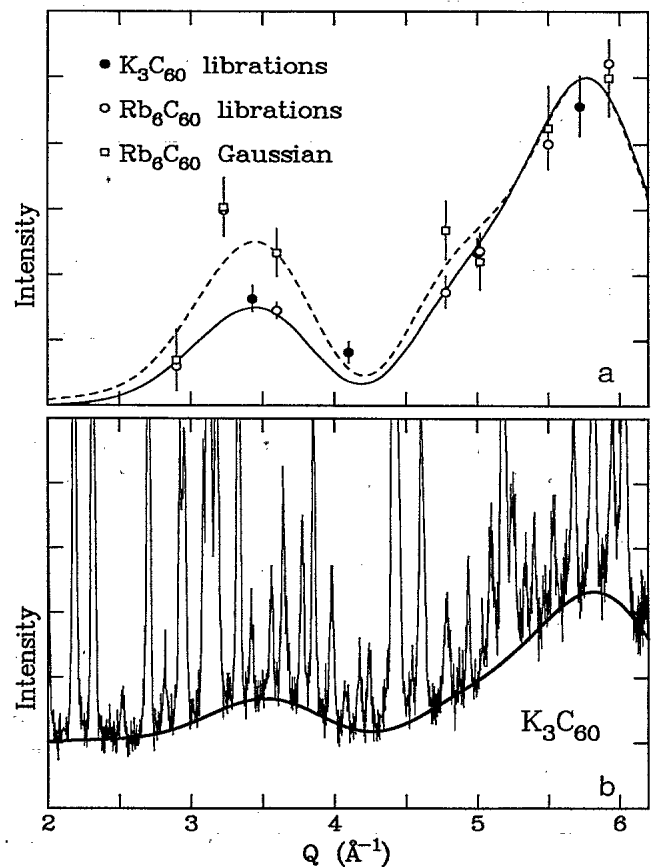

FIG. 3. Q dependence at 300 K of the intensity of the librational mode in K_3C_{60} (solid circles), the librational mode in Rb_6C_{60} (open circles), and the zero-energy-transfer centered Gaussian component in Rb_6C_{60} (open squares). The dashed line is the intensity variation calculated for complete orientational disorder while the solid line is for uncorrelated isotropic librations with a root-mean-square amplitude of 6.7°. Calculations are arbitrarily normalized to the $Q \sim 5.75$ Å^{-1} peak. (b) Diffraction profile of K_3C_{60} at 12 K with the diffuse scattering clearly present. Bragg lines arising from the aluminum sample holder are also present. The heavy solid line is the calculated intensity of the diffuse scattering, using a Monte Carlo method and assuming a two-state model (Ref. 2) with a rms librational amplitude of 1.1° for both equilibrium orientations.

There is satisfactory agreement between the experimental data and the librational model calculation, confirming our assignment of the inelastic scattering peak to molecular librations. We also show for comparison the diffraction profile of K_3C_{60} at 12 K [Fig.3 (b)]; the diffuse scattering present, even at this temperature, presumably arises through a superposition of both static and dynamic disorder, as the molecules perform small-amplitude librations about their equilibrium positions. Using a Monte Carlo method, the calculated diffuse scattering intensity within a two-state model,[2] including a rms amplitude of libration for the $C_{60}{}^{3-}$ ions of 1.1° [Fig. 3(b)], is in reasonable agreement with experiment.

We have estimated the temperature evolution of θ_{rms} within the harmonic approximation, using the expression $(\theta_{rms})^2 = (2\hbar/I\omega)\coth(\hbar\omega2kT)$, where $I \sim 1.0 \times 10^{-43}$ kg m^2 is the moment of inertia of the C_{60} units. The librational amplitudes in K_3C_{60} are found to vary from $\approx 1.1°$ below T_c to $\approx 4.2°$ at room temperature [Fig. 2(c)]. They are always larger than those in Rb_6C_{60} and smaller than those in C_{60}. The magnitude of the angular displacements again reflects the relative strength of the interactions in the fullerene solids. An estimate can also be made of the rotational barrier in K_3C_{60}, assuming that a simple sinusoidal hindrance potential of the form $V = V_0(1-\cos\theta)/2$ is sufficient to describe the rotational motion of the librating group.[15] Here V_0 is the potential barrier and $(2\pi/n)$ is the angle between neighboring potential minima. For small amplitudes of libration, $V_0 \propto (I\omega^2/n^2)$. For $n=5$, the potential barrier is found to be at least twice as large (~ 500 meV) as in the ordered phase of C_{60}. We note that barriers of ~ 420 meV are deduced from recent ^{13}C NMR measurements on K_3C_{60}.[16]

Densities of states for librational motions at room temperature have been calculated for K_3C_{60} and K_6C_{60} using molecular-dynamics simulations.[17] In K_3C_{60} the libra-

tions occur in a sharp band at ~ 3.60 meV with ~ 0.95 meV width; in K_6C_{60} they lead to a broad asymmetric band at ~ 5.80 meV with ~ 2.90 meV width. These results are in general agreement with the experimental data, implying that the model orientational potential which is dominated by strong Coulomb interactions is reasonable. This is in contrast to pristine C_{60} where subtle electrostatic contributions to the van der Waals intermolecular interactions have to be taken into account[6,18] in order to achieve satisfactory agreement between model calculations[19] and experiment.[8,12] Finally, the success of the molecular-dynamics simulations in predicting the librational linewidth of metallic K_3C_{60} is consistent with a small contribution to the electron-phonon coupling strength from librational modes.

In conclusion, we have measured the low-energy INS spectra of alkali-metal-doped fullerides as a function of scattering vector at various temperatures. The fullerene units are found to undergo small-amplitude librations about their equilibrium positions, giving rise to well-defined librational peaks near 4 and 6 meV for K_3C_{60} and Rb_6C_{60}, respectively. The librational energy is larger than in C_{60}, reflecting the stronger electrostatic interactions present in the fullerides. The librations soften and their amplitudes increase as the temperature increases. No anomalous stiffening or sharpening is observed below T_c, providing strong evidence against a large contribution to the total electron-phonon coupling strength from low-energy librational modes.

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