Rotational Dynamics of C_{60} in Na_2RbC_{60}.

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Abstract. – We have measured the low-energy neutron inelastic-scattering (NIS) spectra of superconducting Na_2RbC_{60} in the temperature range 50–350 K. Well-defined librational peaks are observed at 50 K at 2.83(17) meV (FWHM = 1.7(5) meV). They soften and broaden with increasing temperature. Their behaviour mimics that found in solid C_{60} and differs markedly from K_3C_{60}. The rotational barrier for C_{60} reorientations in Na_2RbC_{60} is somewhat higher than in pristine C_{60} and approximately half as large as in K_3C_{60}. An order-disorder transition is anticipated at a temperature higher than that found in C_{60}.

Introduction. – The superconducting alkali-metal fullerides A_3C_{60} (A = K, Rb) crystallise in a face-centred-cubic (f.c.c.) structure with the C_{60}^{3-} ions randomly distributed between two orientations, related by 90° rotations (space group $Fm\bar{3}m$) [1]. The guest-host interactions, dominated by the repulsive part of the A^+-C interactions, favour orientational ordering of the C_{60} molecular units and these compounds remain orientationally ordered close to the decomposition temperature [2, 3]. The orientational potential is considerably harder than in pristine C_{60} where an orientational order-disorder transition is encountered at 260 K [4, 5]. On the other hand, the sodium [6] fullerides Na_2CsC_{60} [7] and Na_2RbC_{60} [8] are isostructural with C_{60}, adopting an orientationally ordered simple cubic (s.c.) structure (space group $Pa\bar{3}$), at low temperature. This reduces the coordination number of the alkali-metal ion on the tetrahedral site, A, from 24 in K_3C_{60} and Rb_3C_{60} to 12 in Na_2CsC_{60} and Na_2RbC_{60} [7]. The C_{60}-C_{60} intermolecular interactions now compete effectively with the alkali-C_{60} interactions. Na_2CsC_{60} also shows a transition to a f.c.c. orientational «liquid» phase (space group $Fm\bar{3}m$) on heating [7], in striking similarity to pristine C_{60}. Orientational ordering of C_{60} and the adoption of a different structure by these fullerides provide an additional dimension [7] to the well-established behaviour of f.c.c. merohedrally disordered fullerides [9]. Both ingredients of phonon-mediated pairing models (namely the density of states at the Fermi level [10] and the intramolecular [11] and intermolecular [2] electron-phonon coupling strength) should be sensitive to the structural changes and the modified intermolecular potential.

In this paper, we report neutron inelastic-scattering (NIS) measurements of the low-energy rotational excitations in superconducting Na_2RbC_{60} between 50 and 350 K. This provides information on how the intermolecular potential in fullerides is modified by intercalation of small alkali ions. The librational energies are substantially lower than those in the orientationally ordered phase of K_3C_{60} [2], reflecting a drastic change in the orientational potential between the two fullerides. Softening and broadening of the librational peaks are observed on heating, and the high-temperature data suggest that the system is close to an orientational order-disorder transition.

Experimental. – The Na_2RbC_{60} sample was prepared by reaction of stoichiometric quantities of C_{60}, Na and Rb, contained in a tantalum cell inside a sealed glass tube filled with helium to 600 Torr, at 200 °C for 12 hours and at 430 °C for three weeks with intermittent shaking. Phase purity was confirmed by X-ray and neutron diffraction and ^{13}C NMR measurements. Prompt gamma-ray neutron activation analysis [12] showed a hydrogen content of 0.0056(11) atom per C atom. The sample was superconducting [13] with a T_c of 3.5 K and a superconducting volume fraction > 10%. 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 energy, E_i, of 28 meV. The incident neutron beam was monochromated using the Cu(220) reflection and the scattered neutrons were analysed using the pyrolytic-graphite (004) reflection. The measured resolution at the elastic line for 60'-40'-40'-40' collimations was 1.047 meV full width at half maximum for $E_i = 28$ meV. The 500 mg powder sample, loaded under helium in indium-wire–sealed aluminium cylindrical can, was placed inside a closed-cycle helium refrigerator. Background runs were subtracted and the spectra were corrected for variable spectrometer resolution and symmetrised. Fits to the data included a sum of a δ-function and a Gaussian component at zero energy transfer and a Lorentzian centred at non-zero energy transfer, each convoluted with a Gaussian instrumental resolution function [14].

Results and discussion. – Figure 1 shows representative NIS spectra for Na_2RbC_{60} at temperatures between 100 and 350 K with $Q = 5.5$ Å^{-1}. The solid triangles are the corrected experimental data and the solid lines are the fits described above. The well-defined peaks present at all temperatures at non-zero energy transfer may be assigned to librational modes of the C_{60}^{3-} ions from their integrated intensity dependence on the scattering vector Q. This is shown in fig. 2 for the room temperature data together with exact calculations for completely orientationally disordered molecules (dashed line), and Monte Carlo calculations for uncorrelated isotropic molecular librations with a root-mean-square amplitude $\theta_{r.m.s.} = 8.6°$ (solid line). The calculations were arbitrarily scaled to the $Q \sim 5.5$ Å^{-1} point.

Figure 3a) presents the temperature dependence of the energy of the librational modes, as extracted from the fits. The C_{60} [15] and K_3C_{60} [2] results are also included for comparison. At low temperatures, the librational energy in Na_2RbC_{60} (2.83(17) meV at 50 K) is essentially the same as in C_{60} (2.77(6) meV at 20 K) but substantially lower than in K_3C_{60} (4.04(3) meV at 12 K). In fig. 4, we plot measured low-temperature librational energies as a function of the radius of the tetrahedral alkali ions. The dashed line at 1.12 Å corresponds to the size of the tetrahedral interstice in pristine C_{60}. When the radius of the tetrahedral ion (r_A) is less than 1.12 Å, the librational energy is roughly constant at ~ 2.8 meV, while when $r_A > 1.12$ Å it increases with the size of the ion. Thus for f.c.c. merohedrally disordered fullerides, the repulsive A^+-C interactions dominate the orientational potential, and are minimised by maximising the A-C distances as the C_{60} ions present hexagonal faces to the tetrahedral sites. This strong repulsive interaction results in a harder intermolecular potential [2] than in pristine C_{60} in which the weaker C-C interactions favour «nesting» of the bonds which fuse

hexagons opposite pentagonal (or hexagonal) faces of adjacent molecules [4]. In Na_2RbC_{60} (and presumably in Na_2CsC_{60}), due to the smaller size of the Na^+ ion, the repulsive A^+-C interaction is substantially diminished and no longer confines the C_{60} units in the two orientations found in K_3C_{60} and Rb_3C_{60}. The Coulomb part of the interaction then gains in relative importance [17], leading to the $Pa\bar{3}$ structure and an optimal Na^+-C_{60} coordination, in which each C_{60}^{3-} ion presents two hexagonal faces and six hexagon-hexagon fusions to its
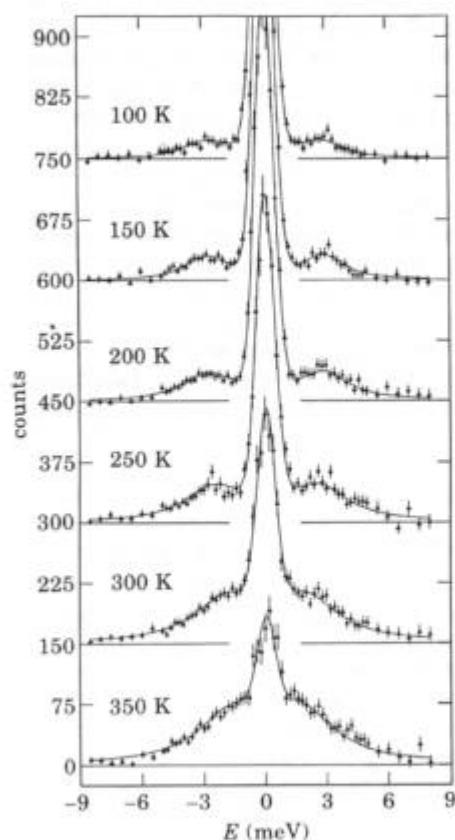

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 1. – Representative NIS spectra of Na_2RbC_{60} in the temperature range 100–350 K at constant $Q = 5.5\,\text{Å}^{-1}$. The solid triangles are experimental points and the solid lines are best fits, including a Lorentzian component at non-zero energy transfer.
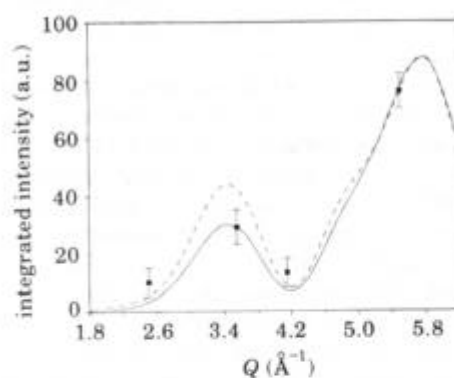
Fig. 2. – Q-dependence at 300 K of the intensity of the librational mode in Na_2RbC_{60} (solid squares). The dashed line is the intensity variation calculated for complete orientational disorder while the solid line is for uncorrelated isotropic librations with a root-mean-square amplitude of 8.6°. Calculations are arbitrarily normalised to the $Q = 5.5\,\text{Å}^{-1}$ datum.
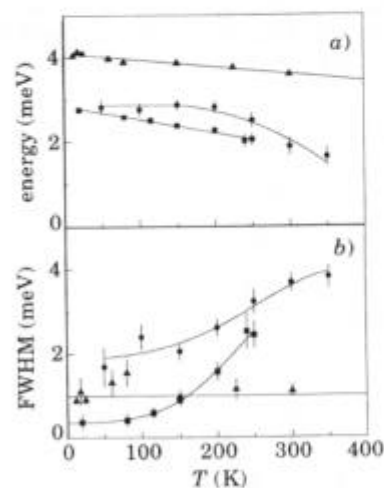
Fig. 3. – Temperature evolution of a) the librational energy and b) the width of the librational peak for Na_2RbC_{60} (circles), C_{60} (squares) [15], and K_3C_{60} (triangles) [2]. Lines are guides to the eye.

eight neighbouring Na$^+$ ions, reducing the coordination number of the Na$^+$ ion from 24 to 12 [7]. At the same time, the C_{60}-C_{60} interactions are also optimal but perhaps somewhat softer than in pristine C_{60} as the «nesting» hexagon-hexagon fusions expand and the pentagonal faces of adjacent molecules contract on reduction [7]. The net result is an intermolecular potential, and therefore librational energy, that is comparable with that of pristine C_{60}. There is also a substantial decrease in the librational mode energy in Na_2RbC_{60} with increasing temperature (fig. 3a)), reflecting considerable softening of the orientational potential, as the optimal interactions become disrupted with increasing amplitudes of libration. This effect is again comparable with that in pristine C_{60}, but markedly larger than in K_3C_{60}.

An estimate of the rotational barrier in Na_2RbC_{60} (and presumably Na_2CsC_{60}) can be made assuming that a simple sinusoidal hindrance potential is sufficient to describe the rotational motion of the librating group [2, 14, 18]. For small amplitudes of libration, $E_a = (E_{lib}^2/B)(\theta/2\pi)^2$, where E_a is the potential barrier, θ is the hopping angle between neighbouring potential minima, $B = 0.364 \cdot 10^{-3}$ meV is the rotational constant for C_{60} and E_{lib} the librational energy. Given the similarities between C_{60} and Na_2CsC_{60}, it is reasonable to take for Na_2RbC_{60} the same hopping angle of $\sim 42°$ [14, 18]. We then find that E_a is ~ 300 meV. We recall that the activation barrier in K_3C_{60} is ~ 500 meV [2, 19].

The full widths of the librations in pristine C_{60} increase by a factor of six [15] on approaching the phase transition where they collapse into a single quasi-elastic line. In somewhat similar fashion, the librations in Na_2RbC_{60} broaden by almost a factor of two between 50 and 350 K (fig. 3b)). This is in contrast to K_3C_{60} where the full widths show little change with temperature. These results taken together with the fact that the isostructural compound Na_2CsC_{60} undergoes a phase transition [7] to an f.c.c. structure between room temperature and 425 K, in which the C_{60}^{3-} ions are best described as spherically disordered, suggest that Na_2RbC_{60} undergoes a similar phase transition in the same temperature range. This

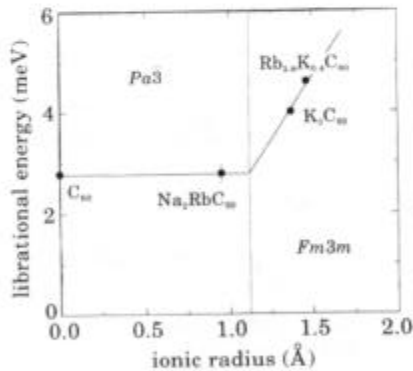Fig. 4.   Fig. 5.

Fig. 4. – Schematic diagram showing the dependence of the librational energy at low temperature on the ionic radius of the alkali ions occupying the tetrahedral interstices in A_3C_{60} fullerides. The dashed line at 1.12 Å corresponds to the size of the tetrahedral hole in pristine C_{60} and separates simple cubic ($Pa\bar{3}$) from f.c.c. ($Fm\bar{3}m$) solids. Results for C_{60} [15], K_3C_{60} [2], and $Rb_{2.6}K_{0.4}C_{60}$ [16] are taken from the literature.
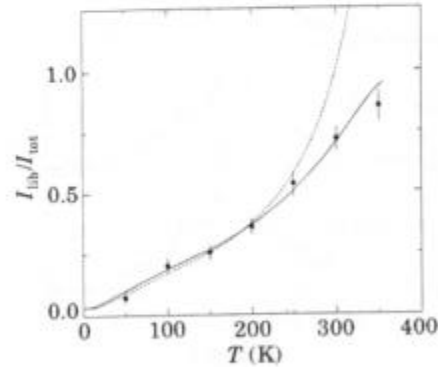
Fig. 5. – Temperature dependence of the ratio of the integrated intensity of the librational mode to the measured total intensity at $Q = 5.5$ Å^{-1} for Na_2RbC_{60} (solid circles). The dashed and solid lines show calculations in which the librational mode is associated with one-phonon and all inelastic scattering, respectively (see text).

is consistent with high-resolution X-ray diffraction data at room temperature [8] which show decreased intensity for the simple cubic reflections, compared to the low-temperature data.

In fig. 5 we show the temperature dependence of the reduced integrated intensity of the librational mode, I_{lib}/I_{tot}, at $Q = 5.5 \text{ Å}^{-1}$ (solid circles). For one-phonon scattering in the harmonic approximation, this ratio is given by the expression: $(C/E_{lib}) \operatorname{ctg}(E_{lib}/2kT)$. The dashed line in fig. 5 represents such a calculation with $C = 0.16 \text{ meV}$. Clearly this expression is unsatisfactory for temperatures higher than $\sim 250 \text{ K}$. A better representation of the experimental data is achieved by associating the measured librational intensity, I_{lib}, with *all* of the inelastic scattering rather than with just the one-phonon scattering. In such a case, I_{lib}/I_{tot} is equal to: $1 - \exp[-2W]$, where $\exp[-2W]$ is the librational Debye-Waller factor [20]. In the incoherent approximation $2W$ is identical to the one-phonon scattering intensity ratio given above, with $C = (4/3)BQ^2R^2$, where $R = 3.5 \text{ Å}$ is the radius of a C_{60} molecule; at $Q = 5.5 \text{ Å}^{-1}$ this yields $C = 0.18 \text{ meV}$. The resulting solid line in fig. 5 is in good agreement with experiment at all temperatures. Monte Carlo simulations which assume isotropic librations of C_{60} molecules have also been employed [15] to calculate I_{lib}/I_{tot} as a function of the root-mean-square librational amplitude, $\theta_{r.m.s.}$, at given values of Q. The results are well represented by the function $1 - \exp[-2W]$ with $2W = (1/3)Q^2R^2\theta_{r.m.s.}^2$. From the experimental value of I_{lib}/I_{tot} we estimate that at 350 K, $\theta_{r.m.s.}$ is about 8°. In C_{60} this quantity is at least 7° at the orientational order-disorder transition temperature. Thus it is reasonable to predict that a similar transition will occur in Na_2RbC_{60} in this temperature range.

Conclusions. – We have measured the low-energy NIS spectra of superconducting Na_2RbC_{60} fulleride at various temperatures. The C_{60}^{3-} ions are found to undergo small-amplitude librations about their equilibrium positions, giving rise to well-defined librational peaks near 2.8 meV at low temperature. The librational energy is comparable to that found in C_{60} but lower than in K_3C_{60}, reflecting a considerable softening in the reorientational potential that can be understood as due to the reduced repulsive A^+-C interaction due to the smaller tetrahedral cation. This allows the C_{60}^{3-} ions in Na_2RbC_{60} to adopt orientations [8] favoured by the Coulomb part of the A^+-C interaction [17] where each Na^+ ion has a coordination number of 12, facing three C-C bonds and one hexagonal face of the neighbouring C_{60}^{3-} ions [7]. This orientation is also favoured by the C-C interactions as evidenced by the structure of pure C_{60}. The change in orientational potential from K_3C_{60} to Na_2RbC_{60} should have profound consequences for the superconducting behaviour of alkali fullerides containing small cations [7] as the change in dominant intermolecular interactions will influence the magnitude of the density of states at the Fermi level ($N(\varepsilon_F)$). It may also affect the intramolecular electron-phonon coupling strength as well as open the way for increased contributions from intermolecular modes. Finally, the librations soften drastically and their amplitudes increase as the temperature increases, signalling the approach to an order-disorder transition.

Additional Remark.

Differential scanning calorimetry (DSC) measurements [21] performed on Na_2RbC_{60} between 100 and 450 K have now revealed the existence of an order-disorder phase transition at 304.5 K ($\Delta H = 3.1 \pm 0.5 \text{ J/g}$). The corrected NIS data (fig. 1) at $Q = 5.5 \text{ Å}^{-1}$ at 300 and 350 K (as well as a low-statistics run at 325 K) were also fitted using a delta-function and a Lorentzian at zero energy transfer ($\hbar\omega = 0$), each convoluted with the measured Gaussian instrumental resolution function. The librational model of the second section is clearly superior to such a quasi-elastic model at 300 K, but only marginally so at 325 and 350 K. Higher-resolution NIS measurements are required to clarify the situation. We note that the quasi-elastic linewidths extracted from the fits at 5.5 Å^{-1} are 4.99(16) meV at 325 K and

5.26(14) meV at 350 K, comparable to the value of ~ 5 meV for pristine C_{60} [15] just above the phase transition at 260 K.

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