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Rotational dynamics of C_{60} in superconducting $K_3Ba_3C_{60}$

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Abstract

The orientational dynamics of C_{60} in superconducting $K_3Ba_3C_{60}$ are studied by neutron inelastic scattering. Low-energy excitations are present near ~ 6 meV between 150 and 320 K and are assigned to small-amplitude librations of the C_{60}^{9-} ions. They are harder and broader than those measured in K_3C_{60}, reflecting the existence of a stronger and more anisotropic orientational potential. The anisotropy and dispersion effects are also larger than those in isostructural Rb_6C_{60}, as a result of positional disorder of the Ba^{2+} and K^+ ions, which reside in distorted tetrahedral interstices. The estimated barrier of the hindrance potential, E_a, is ~ 1.4 eV.

1. Introduction

The study of the intercalation compounds of solid C_{60} with electron donors has been an active research field in recent years. Prominent among these systems have been the alkali fullerides, A_3C_{60} ($A =$ alkali metal) which adopt face-centred cubic (*fcc*) structures and exhibit superconductivity with T_c as high as 33 K at ambient pressure [1]. Intercalation of solid C_{60} to saturation leads to compositions A_6C_{60} with body-centred cubic (*bcc*) structures, which are insulators, as the conduction band, arising from the lowest unoccupied molecular orbital (LUMO) of C_{60} of t_{1u} symmetry is full. Doping of C_{60} to even higher charge state ($n > 6$) can be achieved when divalent alkaline earth metals are used as intercalants [2,3]. In such cases, the conduction band derives from the next unoccupied molecular orbital (LUMO $+ 1$) of C_{60} of t_{1g} symmetry and superconductivity is found for the orthorhombic compositions AE_4C_{60} ($AE =$ Ba, Sr), in which the conduction band is not half-filled [4]. This is in contrast to the A_4C_{60} fullerides, which are insulating. Half-filling of the t_{1g} band can be formally achieved for the mixed alkali-alkaline earth fullerides, $A_3Ba_3C_{60}$ ($A =$ K, Rb, Cs) [5,6]. This family also displays superconductivity but in marked difference to its alkali antecedents, T_c decreases with interfullerene separation. The origin of this behaviour is not as yet understood but it may be related to the presence of strong interaction between Ba and C_{60} and hybridisation of Ba 5*d* and C_{60} t_{1g} orbitals [4,7,8]. The crystal structure of $K_3Ba_3C_{60}$ has been determined as *bcc* ($a =$ 11.21661(7) Å at 10 K, space group $Im\bar{3}$), isostructural with that of the A_6C_{60} fullerides. The K^+ and Ba^{2+} cations are disordered in the same distorted tetrahedral interstitial sites, $(0, \frac{1}{2}, \frac{1}{4} + \delta)$. However, they are displaced by a different distance from the

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centre of the site ($\delta = 0.034(2)$ and $\delta = 0.0265(8)$ for K^+ and Ba^{2+}, respectively), resulting in different coordination environments with the C_{60} units [7]. Short Ba–C and K–C distances (~ 3.08 Å), close to the sum of the ionic radii and the van der Waals radius of C are also noticeable.

Low-energy neutron inelastic scattering (NIS) measurements have been extensively used to probe the rotational dynamics of pristine C_{60} [9] as well as of C_{60}^{3-} and C_{60}^{6-} ions in a variety of fullerides [10–16]. In all cases, the excitations observed at low temperatures at non-zero energy transfer are due to fullerene molecules, librating about their equilibrium orientations. It is of particular interest to see how the introduction of the Ba^{2+} ions in the lattice and the consequent increase in the charge of the C_{60} units modify the interfullerene orientational potential. For this reason, we performed neutron inelastic scattering (NIS) measurements of the low-energy rotational excitations in $K_3Ba_3C_{60}$ between 150 and 320 K. The momentum-transfer, Q dependence of the intensity of the broad low-energy excitations in $K_3Ba_3C_{60}$ leads to their assignment as librational modes whose energies are substantially higher than those in the parent material K_3C_{60} [10], indicating a considerable change in the orientational potential between the two fullerides. Softening of the librational peaks is observed on heating, while their substantially increased widths indicate a very anisotropic rotational potential and/or rotation-translation coupling. Considerable similarities with the behaviour of isostructural Rb_6C_{60} [10] are also encountered.

2. Experimental details

The $K_3Ba_3C_{60}$ sample used in the present work was synthesized by intercalation of K into preformed Ba_3C_{60} [5,6]. Stoichiometric amounts of potassium metal and Ba_3C_{60} powder were loaded in a tantalum cell sealed under 500 mmHg of helium in a Pyrex tube and heated at 260°C for seven days. Phase purity was confirmed by X-ray diffraction with a Siemens D5000 diffractometer. SQUID magnetometer measurements established the onset of superconductivity below $T_c = 5.4$ K.

The neutron scattering measurements were performed at the Center for Neutron Research, National Institute of Standards and Technology (NIST) using the BT4 triple-axis spectrometer with fixed incident neutron energy, E_i, of 35 meV. 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 1.527 meV full width at half maximum (FWHM). For the present experiment, 0.576 g of powder sample were loaded in an indium-wire-sealed aluminium cylindrical can and placed inside a closed-cycle helium refrigerator. In the analysis of the NIS measurements [17], background runs were first subtracted, the intensities were corrected for changes in the scattered energy contribution to the spectrometer resolution, and then the spectra were symmetrised. The corrected data were subsequently fitted using the measured resolution function at zero energy transfer ($\hbar\omega = 0$) and two Lorentzians centred at non-zero energy transfer, and convoluted with the instrumental resolution function.

3. Results and discussion

NIS measurements for $K_3Ba_3C_{60}$ were performed as a function of Q and ω at several temperatures. Fig. 1 shows representative spectra at temperatures between 150 and 320 K at a scattering vector, $Q = 5.5$ Å^{-1}. The solid circles are the corrected experimental data and the lines are the fits described in the previous section. Well-defined peaks are observed at non-zero energy transfer at all temperatures and may be assigned to librational modes of the C_{60}^{9-} ions from the dependence of their integrated intensity on the scattering vector, Q. This is apparent from Fig. 2, where the integrated intensity of the librational peaks is shown as a function of Q at 300 and 320 K, together with Monte Carlo calculations for uncorrelated isotropic molecular librations with root-mean-square amplitudes, $\theta_{rms} = 5.7°$ (solid line) and 6.7° (dashed line). In Fig. 2, both calculations were scaled to the measured intensity at $Q = 5.9$ Å^{-1} and 320 K and a constant background was added to the calculated values. Its origin may be related to the presence of multiphonon contributions to the scattering [16] and/or rotation-translation coupling [15]. The latter should become more significant in the

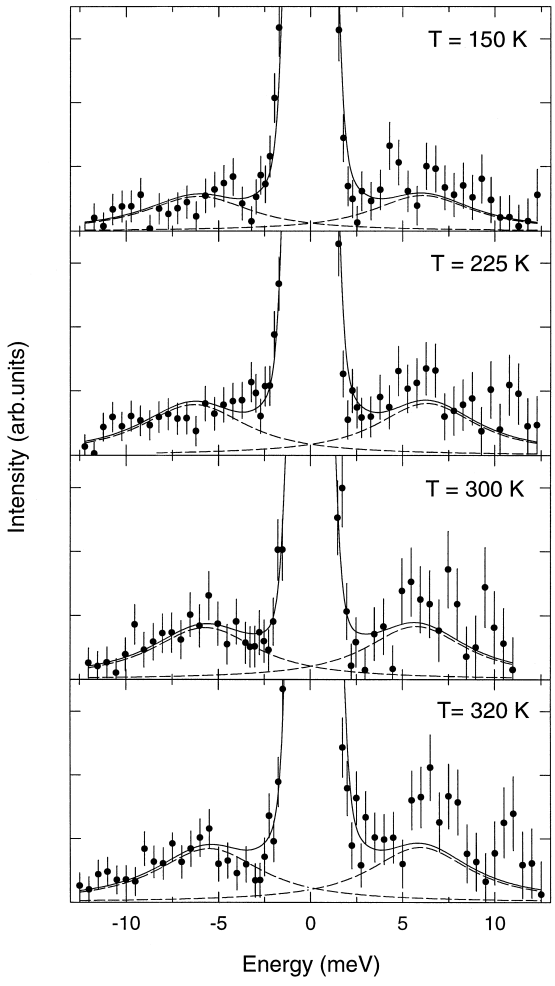

Fig. 1. Representative NIS spectra of $K_3Ba_3C_{60}$ in the temperature range 150–320 K at constant $Q = 5.5$ Å^{-1}. The solid circles are experimental points and the solid lines are best fits, as discussed in the text. The dashed lines show the individual Lorentzian components at non-zero energy transfer.

present system due to the large mass of the Ba^{2+} ion, which should shift the optic vibrations to low energies. Otherwise there is good agreement between the experimental data and the librational model calculations at these temperatures, confirming the assignment of the low-energy inelastic scattering peaks as arising from molecular librations.

A comparison of the temperature evolution of the energies of the librational modes in $K_3Ba_3C_{60}$ with those reported before in Rb_6C_{60} and K_3C_{60} [10] is

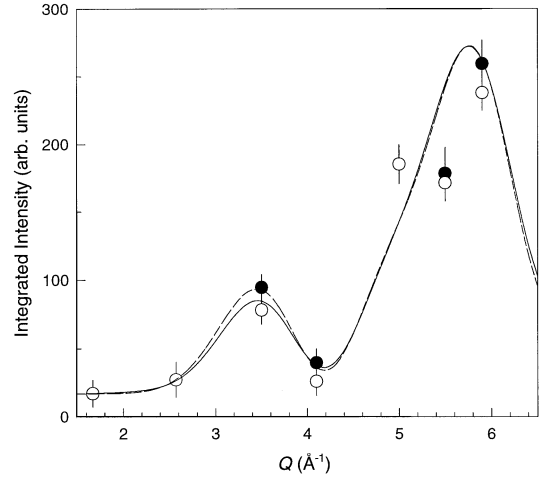

Fig. 2. Q dependence of the intensity of the librational peaks in $K_3Ba_3C_{60}$ at 320 (solid circles) and 300 K (open circles). The lines represent the intensity variation calculated for uncorrelated isotropic librations with root-mean-square amplitude of 5.7° (solid line) and 6.7° (dashed line) with an added constant background.

shown in Fig. 3. At low temperatures, the librational energy in $K_3Ba_3C_{60}$ (5.7(3) meV at 300 K) is comparable to that in the isostructural Rb_6C_{60} fulleride (5.5(4) meV), but larger than that measured in K_3C_{60} (3.59(3) meV) at the same temperature. The energy of the librational modes increases as the ionicity of the C_{60} unit increases and the strong

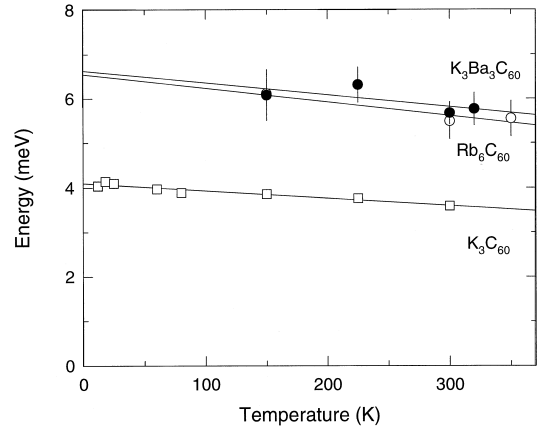

Fig. 3. Temperature evolution of the librational energy for $K_3Ba_3C_{60}$ (solid circles). Earlier results for Rb_6C_{60} (open circles) and K_3C_{60} (squares) [10] are included for comparison. Lines are linear fits to the data.

Coulomb forces between highly charged ions dominate the potential. An estimate of the rotational barrier in $K_3Ba_3C_{60}$ can be made assuming that a simple sinusoidal hindrance potential is sufficient to describe the rotational motion of the librating group. For small amplitudes of libration,

$$E_a = \left(E_{lib}^2/B\right)\left(\theta/2\pi\right)^2, \quad (1)$$

where E_a is the potential barrier, θ is the hopping angle between neighbouring potential minima, $B = 0.346$ μeV is the rotational constant for C_{60} and E_{lib} is the librational energy at a given Q and temperature. Assuming a reorientational motion in $K_3Ba_3C_{60}$, similar to that of K_3C_{60} we obtain an estimate of the activation barrier of the hindrance potential, $E_a \sim 1.4$ eV. In agreement with the increased charge of the C_{60} units, this is much larger than the value, $E_a \sim 0.5$ eV calculated for K_3C_{60}. It is however comparable to the energy barrier in Rb_6C_{60}, as the effect of the increased charge appears to be compensated by the larger radius of the Rb^+ ion. The librations in $K_3Ba_3C_{60}$ also soften as the temperature increases (Fig. 3) in agreement with the behaviour of the other systems studied. The softening in $K_3Ba_3C_{60}$ ($\sim 12\%$ by extrapolation to low temperatures) is comparable to those in Rb_6C_{60} ($\sim 12\%$) and K_3C_{60} ($\sim 11\%$).

The widths of the librational peaks in $K_3Ba_3C_{60}$ (~ 6.4 meV) are not resolution limited and are considerably larger than those encountered in both Rb_6C_{60} (~ 3.4 meV) and K_3C_{60} (~ 1 meV). This observation, together with the small amount of softening observed with increasing temperature, indicate the presence of substantial anisotropies in the rotational potential. Such effects arise naturally as a result of the strongly anisotropic coordination of the intercalants to the C_{60} units. In comparison to Rb_6C_{60}, they are further enhanced by the occupancy of distinct tetrahedral sites by Ba^{2+} and K^+, as revealed by the structural work [7]. Finally, the somewhat short Ba^{2+}–C and K^+–C contacts (~ 3.08 Å) encountered in the structure should also favour mixing of the intermolecular modes of C_{60}^{9-} with the Ba^{2+} optic modes, thus resulting in increased dispersion effects and increased linewidths.

4. Conclusions

In conclusion, we have measured the low-energy NIS spectra of $K_3Ba_3C_{60}$ as a function of the scattering vector, Q at temperatures between 150 and 320 K. The fulleride units are found to undergo small-amplitude librations about their equilibrium position, giving rise to librational peaks near 6 meV. The librational energy is larger than in the parent K_3C_{60} salt and the peaks are much broader, reflecting a stronger and more anisotropic orientational potential. While there are similarities in the magnitude of the hindrance potential between $K_3Ba_3C_{60}$ and the isostructural Rb_6C_{60} salt, anisotropy and dispersion effects are much more pronounced in the former. This is consistent with the positional disorder of the Ba^{2+} and K^+ ions and a stronger interaction between the Ba^{2+} and K^+ and the C_{60} orbitals.

Acknowledgements

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