DYNAMICS OF METHYLAMINE GROUPS IN (CH$_3$NH$_2$)K$_3$C$_{60}$ UNDER HIGH PRESSURE

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Introduction

Superconductivity in alkali fullerides (A_3C$_{60}$ where A = alkali metal) was for many years discussed within the BCS formalism where the small bandwidth is comparable to the effective on-site Coulomb repulsion or the phonon energies.[1] This view has been challenged recently with the discovery of body-centered cubic Cs$_3$C$_{60}$,[2] which retains the threefold degeneracy of the active t_{1u} orbitals, but has a largely expanded unit cell compared to other known face-centered cubic A_3C$_{60}$. In this compound, the electronic correlations win over the kinetic energy due to the electronic delocalisation and are responsible for the antiferromagnetic insulating ground state with $T_N = 46$ K.[3,4] With the application of pressure, Cs$_3$C$_{60}$ undergoes a metal-insulator transition (MIT) and the superconductivity is restored at the surprisingly high temperature of $T_C = 38$ K at 0.79 GPa.[2]

The alkali fullerides with large unit cell volumes are so close to MIT that even slight deviation from the cubic symmetry immediately destroys the superconductivity by shifting the MIT boundary to smaller volumes. NH$_3$K$_3$C$_{60}$ and (CH$_3$NH$_2$)K$_3$C$_{60}$ both adopt face-centered orthorhombic structures and are antiferromagnetic (AFM) insulators with Néel temperatures of $T_N = 41$ and 11 K, respectively.[5,6] A comparison of the T_N temperatures shows that the latter compound has a substantially lower ordering temperature, although they both have similar interfulleride distances. It has been suggested that close proximity of the CH$_3$NH$_2$ protons with C$_{60}^{3-}$ anions might affect the electronic properties below the structural phase transition at $T_s = 220$ K, where the (CH$_3$NH$_2$)-K$^+$ discrete Markovian-type jump motional dynamics freeze out.[7] In this communication, we investigate the dynamics of the (CH$_3$NH$_2$)-K$^+$ units employing ^{2}D NMR T_1 measurements on the deuterated sample, (CD$_3$ND$_2$)K$_3$C$_{60}$ at high hydrostatic pressures. Comparison of the ambient and high pressure data indicates that the (CD$_3$ND$_2$)-K$^+$ units may interact with the C$_{60}^{3-}$ units via formation of weak hydrogen bonds. This interaction may explain the reduced Néel temperature in (CH$_3$NH$_2$)K$_3$C$_{60}$.

Experimental

The deuterated (CD$_3$ND$_2$)K$_3$C$_{60}$ (hereafter called MAK$_3$C$_{60}$) powder sample was prepared by reaction of the K$_3$C$_{60}$ powder with CD$_3$ND$_2$ vapour, as described elsewhere.[8] Phase purity was confirmed by synchrotron X-ray diffraction with the high-resolution powder diffractometer on beamline ID31 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

The deuteron NMR measurements were performed in a 9 T magnetic field at the Larmor frequency, $\omega_L/2\pi = 58.3363$ MHz. A home-made clamped-type high pressure (HP) cell made of a nonmagnetic beryllium bronze (BeCu) was used in the experiments. Paraffin oil was used as a pressure transmitting medium. The deuteron NMR spin-lattice relaxation rate, $1/T_1$, was studied using an inversion recovery pulse sequence with $\pi/2$ pulse length of 4.5 μs. The nuclear magnetisation recovery curves were measured over four decades and were in all cases found to be single exponentials.

Results and Discussion

The deuteron spin-lattice relaxation rate, $1/T_1$ as a function of temperature is shown in the inset of Fig. 1. At ambient pressure, the relaxation rate decreases with decreasing temperature from 14.5 s^{-1} at room temperature and reaches a shallow minimum of 2.8 s^{-1} at 200 K. On further cooling, $1/T_1$ increases with decreasing temperature and approaches 10 s^{-1} at 130 K. The minimum coincides with the structural phase transition observed before at $T_s = 220$ K.[7] Application of pressure has a large effect on $1/T_1$. Namely, $1/T_1$ at room temperatures drops to 8.9 s^{-1} at 0.4 GPa and then to 4.5 s^{-1} at 1.0 GPa (up and down triangles, respectively in the inset of Fig. 1). The temperature dependence of $1/T_1$ at 0.7 GPa shows that the relaxation rate minimum is shifted to ~220 K and has a value of ~1.0 s^{-1} smaller than that at ambient pressure. We thus propose that under the applied pressure of 0.7 GPa the structural phase transition temperature increases by ~20 K.

Remarkably, the slope of $1/T_1$ when plotted in a logarithmic scale as a function of inverse temperature (Fig. 1) does not change with pressure. This means that the activation energy for the correlation times that define local field fluctuations is not very sensitive function of pressure. In our recent ambient pressure deuterium NMR measurements, deuteron NMR lineshape simulations indicated two thermally activated processes associated with the MAK dynamics.[7] Therefore, in order to simulate the $1/T_1$ data, we employ a two-relaxation channels model, where both relaxation rates follow a Bloembergen-Purcell-Pound (BPP) relaxation expression:

$$\frac{1}{T_1} = \frac{1}{T_1^1} + \frac{1}{T_1^2} = A\frac{\tau_1}{1+(\omega_L\tau_1)^2} + B\frac{\tau_2}{1+(\omega_L\tau_2)^2}.$$

Here A and B are the fitting constants, and $\tau_{1,2}$ are correlation times for the two thermally-activated processes given by the Arrhenius equation

$$\tau_{1,2} = \tau_{1,2}^\infty e^{E_a^{1,2}/k_BT}.$$

We introduced two activation energies, $E_a^{1,2}$ with $\tau_{1,2}^\infty$ being the corresponding correlation times at infinite temperature. k_B is the Boltzmann constant. Unconstrained fittings of $1/T_1$ using the above model are shown as solid lines in Fig. 1 and the obtained parameters are summarised in Table 1. The ambient pressure activation energies are in a good agreement with the two previously reported ambient pressure activation energies ($E_a = 236(51)$ meV at high temperatures and $E_a = 23(7)$ meV at low temperatures).[7] From this we conclude that the deuteron spin-lattice relaxation mechanism is indeed governed by the thermally activated MAK motional dynamics.

Table 1. Fitting parameters for the $(CD_3ND_2)K_3C_{60}$ deuteron spin-lattice relaxation data obtained from the double BPP relaxation model (see text for details).

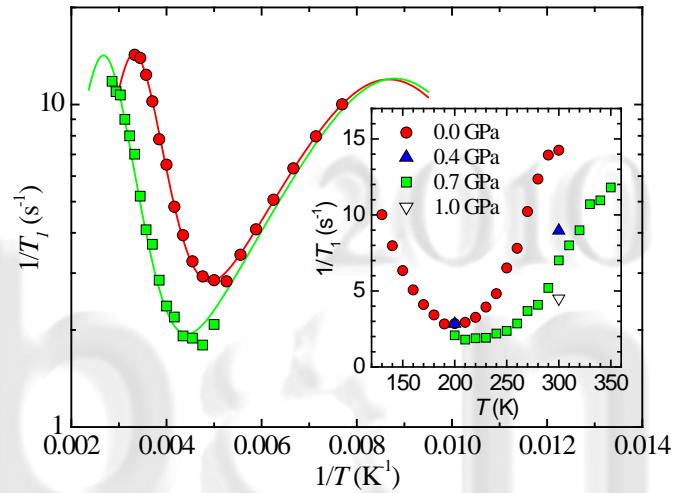|	Ambient pressure	0.7 GPa
A	$1.6(1)\times10^9$	$1.6(1)\times10^9$
τ_1^∞	$6.0(1)\times10^{-12}$ s	$3.0(2)\times10^{-11}$ s
E_a^1	203(8) meV	205(8) meV
B	$1.4(1)\times10^9$	$1.4(1)\times10^9$
τ_2^∞	$7.4(1)\times10^{-11}$ s	$6.8(8)\times10^{-11}$ s
E_a^2	55(3) meV	55 meV

High pressure data can be equally well fitted using the same two-relaxation channels model. We find that the extracted 0.7 GPa high-temperature activation energy, $E_a^1 = 205$ meV is nearly identical to that at ambient pressure (E_a^2 was fixed to the ambient pressure value of 55 meV because of the lack of low-temperature data). This implies that the energy barrier for the thermally activated process does not depend much on the size of the octahedral voids where the MAK units reside. In order to understand this surprising finding, we recall that a weak hydrogen bond was suggested in the crystallographic study where close contacts between the protons of the MAK units and the C_{60}^{3-} anions were found at 2.25 Å – 2.32 Å.[8] We thus suggest that the obtained activation energy, $E_a^1 = 205(15)$ meV in fact represents the hydrogen-bond energy between the C_{60}^{3-} and the CD_3 deuterons of MAK groups and therefore does not depend on the unit cell volume. The correlation times at infinite temperature on the other hand changed significantly with pressure in the high temperature regime, i.e. by a factor of ~5 at 0.7 GPa. In the Arrhenius expression, τ^∞ is the inverse of the attempt frequency, which is typically determined by the lattice dynamics. In fullerenes the lattice dynamics are governed by several vibrational modes such as C_{60} librations, C_{60}-C_{60} vibrations, K-C_{60} phonons or intramolecular vibrations. Since in MAK$_3$C$_{60}$, the C_{60}^{3-} molecules are static below room temperature, we suggest that it is the C_{60} librational modes which are mainly affected by the application of pressure. We note that weak hydrogen bonding between the ammonia D atoms and C_{60}^{3-} anions has been suggested also in $(ND_3)_xNaA_2C_{60}$.[9]

The experimental evidence for the formation of weak hydrogen bonds between MAK protons and C_{60}^{3-} anions is also important for our understanding of magnetic properties in MAK$_3$C$_{60}$. Such bonding is expected to (i) lead to larger band width and thus stabilize the Mott insulating state and (ii) influence the t_{1u} orbital ordering, which determines the interfulleride exchange interactions. Then the significantly suppressed Néel temperature in MAK$_3$C$_{60}$ is a direct consequence of the interaction between the host C_{60}^{3-} ions and the co-intercalated (CD_3ND_2) groups.

Conclusions

We measured the temperature and pressure dependence of the deuteron $1/T_1$ in MAK$_3$C$_{60}$. The activation energies for the thermally activated processes only weakly depend on the applied pressure, supporting the suggested weak hydrogen bond formation between MAK deuterons and C_{60}^{3-} anions. We suggest that this interaction is responsible for the severely suppressed Néel temperature in MAK$_3$C$_{60}$.

Fig. 1 Deuteron spin-lattice relaxation rate, $1/T_1$ (logarithmic scale) versus $1/T$ for powdered $(CD_3ND_2)K_3C_{60}$ measured at ambient pressure and 0.7 GPa. Solid lines are fits to the two-relaxation channel model (see text for details). Inset: $1/T_1$ versus temperature for different pressures.

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