Mott transition and superconductivity in alkali-doped fullerides

O. Gunnarsson and E. Koch

Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

R.M. Martin

Department of Physics, University of Illinois, Urbana, Illinois 61801

Abstract. We study the effects of deviations from cubic symmetry on superconductivity and on Mott transitions by comparing A_3C_{60} and $NH_3K_3C_{60}$. The reduced frustration in $NH_3K_3C_{60}$ favours a Mott transition at a lower ratio U/W, where U is the Coulomb repulsion of two electrons on the same molecule and W is the width of the t_{1u} band. The closeness of $NH_3K_3C_{60}$ to a Mott transition may influence the superconductivity negatively, due to an inefficient screening of the Coulomb repulsion.

INTRODUCTION

The cubic alkali-doped fullerides A_3C_{60} (A= K, Rb) are superconductors with T_c growing with the lattice parameter a [1]. This is at least qualitatively well understood in terms of the electron-phonon coupling λ growing with a [1]. In contrast, many noncubic fullerides are not superconducting, or have a lower T_c than cubic fullerides with the same molecular volume. For instance, the orthorhombic $NH_3K_3C_{60}$ is believed to be an antiferromagnetic insulator at normal pressure and small T [2]. Under pressure the deviation from cubic symmetry is reduced, and the system becomes superconducting [2]. T_c is lower than for the cubic fullerides with the same molecular volume, but the difference is reduced as $NH_3K_3C_{60}$ becomes more cubic. Results like this have lead to the suggestion that deviations from cubic symmetry are bad for superconductivity. This is discussed below.

ELIASHBERG THEORY

To study the effects of noncubic symmetry, we have solved the Eliashberg equation [3] for systems with cubic and orthorhombic symmetries. We first calculate the hopping matrix elements of cubic A_3C_{60} and orthorhombic $NH_3K_3C_{60}$, using

a tight-binding formalism [4–6]. To make the two calculations as comparable as possible, we rescale the lattice parameters uniformly to obtain the band width $W = 0.62$ eV for both systems. Orientational disorder is introduced for both systems, although it is found experimentally only for A_3C_{60}. The orientational disorder smoothens the density of states and avoids the possibility that one system may have a large density of states $N(0)$ at the Fermi energy and therefore a large electron-phonon coupling λ. In this way we isolate the effects of the symmetry alone. The substantial difference in the lattice parameters ($a = 14.97$, $b = 14.90$ and $c = 13.69$ Å) in the orthorhombic system, leads to quite different hopping in the (110), (101) and (011) directions, with the largest hopping matrix element in the (011) direction about twice as large as the largest (110) element. A five-fold degenerate H_g Einstein phonon with the full Jahn-Teller character is included on each site. The coupling $\lambda/N(0) = 0.1$ (giving $\lambda \sim 0.6$) and the phonon frequency $\omega_{ph} = 0.2$ eV are used in both cases. The solution of the Eliashberg equation gives $T_c = 120 \pm 5$ K for both compounds. The large value of T_c is due to the neglect of the Coulomb pseudopotential in this calculation. The important point is that there is no difference in T_c between the two systems. We therefore conclude that at least within the Eliashberg framework and with everything else equal, the deviation from cubic symmetry does not hurt superconductivity.

MOTT TRANSITION AND FRUSTRATION

Several noncubic fullerides are insulators at normal pressure, for instance $NH_3K_3C_{60}$ and A_4C_{60}. We therefore study the effects of deviations from cubic symmetry on Mott transitions. In the cubic A_3C_{60} (A= K, Rb) the molecules sit on a fcc lattice. It is then possible to hop in a closed loop with an odd (three) number of hops. In analogy with the treatment of antiferromagnetism, we refer to this as frustration. The effects on the Mott transition are studied below. The orthorhombic lattice of $NH_3K_3C_{60}$ has the same topology as the fcc lattice, but the hopping in a triangular loop involves one hop with a matrix element which is only half as large as the other two. The frustration is therefore substantially reduced.

On dimensional grounds, it is expected that the Mott transition takes place when $U/W \sim 1$, where U is the Coulomb interaction between two electrons on the same molecule and W is the t_{1u} band width. In a system with an orbital degeneracy N this ratio tends to be increased by a factor of $\sqrt{N}$ [7]. Here we consider the effects of frustration [8] for a system with $N = 1$. In our earlier studies we found it useful to consider the limit when U is large. To find out about the Mott transition, this requires an uncontrolled extrapolation to intermediate values of U, but it nevertheless gives a quite useful indication of the ratio U/W at the transition.

The simplest system with frustration consists of three s-like orbitals on a triangle. We therefore study this system in more detail. The orbitals are connected by hopping matrix elements t, where t is assumed to be negative. A perfectly bonding state can then be formed by using the coefficient $1/\sqrt{3}$ for all orbitals. The

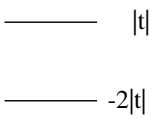

FIGURE 1. One-particle spectrum for three s-orbitals on a triangle and connected by hopping integrals t ($t < 0$).

corresponding energy is $-2|t|$. Due to the frustration, however, it is not possible to form a completely antibonding state. Therefore, the antibonding state only has the energy $|t|$ instead of $2|t|$ and the one-particle band width is only $W = 3|t|$ (see Fig. 1). This can be compared with a non-frustrated system, such as a square, which has $W = 4|t|$.

We consider the many-body case, assuming that there is no orbital degeneracy. To determine whether the system is an insulator, we calculate the band gap

$$E_g = A - I = E(M+1) + E(M-1) - 2E(M). \tag{1}$$

Here A is the affinity energy, I is the ionization energy and $E(K)$ is the energy of a system with K electrons. $M = 3$ is the number of electrons at half-filling. We now focus on the case of a large value of U. It is then very easy to calculate $E(3) = 0 + O(t^2/U)$, since hopping is suppressed for $K = 3$ and U large. We next consider the case of one extra electron, $K = 4$. We form the basis state number 1 in Fig. 2. In this state there is an extra electron on the upper left atom. This extra occupancy can hop clockwise around the triangle as illustrated by the states in the upper row. In state 4, the extra occupancy has returned to the original site. State 4 is, however, different from state 1, since the spins on the other two sites have been flipped. However, if the extra occupancy hops another lap around the triangle, the spins are flipped once more, and the resulting state is identical to state 1. This state was reached after an even number (six) hops. In the large U limit we then obtain a 6×6, problem with the extreme eigenvalues $\pm 2t$. The same result is obtained for the case of an extra hole ($K = 2$). Thus in the many-body case the effects of frustration are not noticed for this model. The gap then becomes

$$E_g = U - 4|t| = U - \frac{4}{3}W. \tag{2}$$

The prefactor $4/3$ results from the frustration, e.g., that W has been reduced by frustration while in this case the reduction of band gap due to hopping is completely

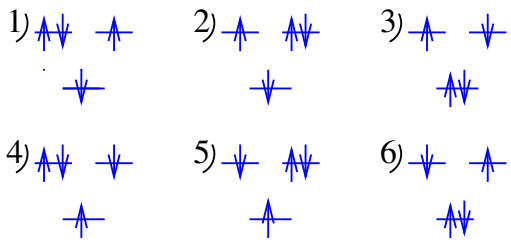

FIGURE 2. Basis states for treating the $(M+1)$-electron case for a triangle.

unaffected by frustration. If the same calculation is performed for a square, we obtain $E_g = U - 4|t|$ again, but since $W = 4|t|$ in this case, we find $E_g = U - W$, e.g., with the prefactor 1. In more general cases, the effects of frustration are more complicated [8], but the prefactor in front of W in Eq. (2) is nevertheless larger than one in all cases studied [8].

To test these ideas for intermediate values of U, we have performed $T = 0$ fixed node projection quantum Monte Carlo calculations [9,7] for models of A_3C_{60} and $NH_3K_3C_{60}$. These models describe the three-fold degenerate, partly occupied t_{1u} level. We include the on-site Coulomb interaction U and the hopping integrals $t_{im,jm'}$ between the molecules. This leads to the Hubbard-like model

$$H = \sum_{i\sigma} \sum_{m=1}^{3} \varepsilon_{t_{1u}} n_{i\sigma m} + \sum_{<ij>\sigma mm'} t_{ijmm'} \psi^{\dagger}_{i\sigma m} \psi_{j\sigma m'} + U \sum_{i} \sum_{\sigma m<\sigma' m'} n_{i\sigma m} n_{i\sigma' m'}, \quad (3)$$

where the sum $< ij >$ is over nearest neighbor sites. The hopping integrals $t_{imjm'}$ have been obtained from a tight-binding parametrization [4,5], taking the appropriate lattice structure into account. The orientational disorder is included for A_3C_{60} but not for $NH_3K_3C_{60}$ in accordance with experiment, and the hopping integrals are chosen accordingly [6]. We have performed calculations for clusters with up to 64 molecules and extrapolated the calculated gap E_g to infinite cluster size. We then find that the Mott-Hubbard transition takes place for

$$\frac{U}{W} \sim \begin{cases} 2 & \text{for} \quad NH_3K_3C_{60} \\ 2.5 & \text{for} \quad A_3C_{60} \end{cases} \quad (4)$$

$NH_3K_3C_{60}$ has the same volume per molecule as the superconducting Rb_2CsC_{60}, which has the A_3C_{60} lattice. Since superconductivity has only been observed for A_3C_{60} systems with a slightly larger lattice parameter than Rb_2CsC_{60}, this system is probably close to a Mott transition. According to tight-binding calculations, the band widths for $NH_3K_3C_{60}$ and Rb_2CsC_{60} are similar, with the width of $NH_3K_3C_{60}$ slightly larger ($\sim 10\%$). In view of the different ratios U/W for a Mott transition in these two types of systems, it is then not surprising that $NH_3K_3C_{60}$ is on the insulating and Rb_2CsC_{60} on the metallic side of a Mott transition.

SUPERCONDUCTIVITY

We now address the superconductivity and the unusual T_c versus a dependence in $NH_3K_3C_{60}$ [2]. The electron-phonon interaction induces a weak (~ 0.1 eV) attractive interaction between the electrons. This is counteracted by a strong Coulomb repulsion (~ 1.5 eV). For conventional systems it is believed that the Coulomb repulsion is strongly reduced by retardation effects, allowing the electron-phonon interaction to drive the superconductivity. For the fullerides it has been argued that the retardation effects from the higher subbands are weak [10], but that within RPA

the screening is so efficient that superconductivity nevertheless becomes possible [10]. This, however, raises questions about the accuracy of the RPA approximation. Recently, this accuracy has been studied within a quantum Monte Carlo approach for a model of the type described above (Eq. (3)). It was found that RPA is surprisingly accurate until the system gets close to the Mott transition, where the screening becomes inefficient in the more accurate QMC calculation [11].

This suggests the following picture. At normal pressure $NH_3K_3C_{60}$ is a Mott insulator. As pressure is applied the system becomes a metal, but at first the screening is poor and T_c is reduced or superconductivity may be completely suppressed. As the pressure is increased the system moves away from the Mott transition and the screening becomes more efficient. The corresponding reduction of the Coulomb interaction leads to an increased T_c. This is contrary to the behavior for the A_3C_{60}, where the screening probably already is efficient, and the dominating effect is the reduction of the electron-phonon coupling as the lattice parameter is reduced.

SUMMARY

We have studied the effects of deviations from cubic symmetry on superconductivity and on Mott transitions by comparing A_3C_{60} and $NH_3K_3C_{60}$. We find that the reduced frustration in $NH_3K_3C_{60}$ leads to a Mott transition for a lower ratio of U/W than for the cubic system. It is then not surprising that $NH_3K_3C_{60}$ is a Mott insulator, while Rb_2CsC_{60} is a metal although the two systems have similar band widths. By solving the Eliashberg equation, we find that deviations from cubic symmetry is not by itself bad for superconductivity. It may, however, harm superconductivity indirectly by putting the system closer to a Mott transition, which may lead to a less efficient screening of the Coulomb repulsion.

REFERENCES

1. Fleming, R.M. *et al.*, Nature **352**, 787 (1991).
2. Rosseinsky, M.J. *et al.*, Nature **364**, 425 (1993); Zhou, O. *et al.*, Phys. Rev. B **52**, 483 (1995); Iwasa, Y.*et al.*, Phys. Rev. B **53**, R8836 (1996).
3. Eliashberg, G.M., Zh. Eksp. Teor. Fiz. **38**, 966 [Sov. Phys. JETP **11**, 696 (1960)].
4. Gunnarsson, O. *et al.*, Phys. Rev. Lett. **67**, 3002 (1991).
5. Satpathy, S. *et al.*, Phys. Rev. B **46**, 1773 (1992).
6. Mazin, I.I. *et al.*, Phys. Rev. Lett. **26**, 4142 (1993).
7. Gunnarsson, O., Koch, E., and Martin, R.M., Phys. Rev. B **54**, R11026 (1996).
8. Gunnarsson, O., Koch, E., and Martin, R.M., Phys. Rev. B **56**, 1146 (1997).
9. ten Haaf, D.F.B. *et al.*, Phys. Rev. B **51**, 353 (1995); van Bemmel, H.J.M. *et al.*, Phys. Rev. Lett. **72**, 2442 (1994).
10. Gunnarsson, O., and Zwicknagl, G., Phys. Rev. Lett. **69**, 957 (1992); Gunnarsson, O., Rainer, D., and Zwicknagl, G., Int. J. Mod. Phys. B **6**, 3993 (1992).
11. Koch, E., Gunnarsson, O., and Martin, R.M., (to be publ.).