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W. Victoroff, M. Héritier. From Weakly to Strongly Correlated Electrons in the Alkali Fulleride Family. Journal de Physique I, 1996, 6 (12), pp.2175-2180. 10.1051/jp1:1996213 . jpa-00247305

HAL Id: jpa-00247305

<https://hal.science/jpa-00247305v1>

Submitted on 4 Feb 2008

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From Weakly to Strongly Correlated Electrons in the Alkali Fulleride Family

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(Received 26 June 1996, received in final form 12 July 1996, accepted 13 August 1996)

PACS.71.20.Tx – Fullerenes and related materials; intercalation compounds
PACS.71.27.+a – Strongly correlated electron systems; heavy fermions
PACS.74.70.Wz – Fullerenes and related materials

Abstract. — We discuss the effect of strong electron-vibron interaction and static or dynamic Jahn-Teller distortion on the electronic properties of the A_nC_{60} family, where A is alkali metal and $0 \leq n \leq 6$. Repulsive electron-electron correlations are expected for even n , but attractive ones for odd n . Such a model seems able to make compatible weak electron correlations for $n = 3$, fairly strong correlations for $n = 1$ and an insulating behavior for $n = 2$ or 4.

An important clue for understanding the electronic properties of the Alkali Fulleride family is the answer to the following question : how large are the electron-electron correlations compared to the one-electron energy bandwidth W ? The C_{60} molecule forms, with the alkali metal series, salts with chemical formula A_nC_{60} where A is an alkali metal and n an integer ($0 \leq n \leq 6$). In icosahedral symmetry, the LUMO of the C_{60} molecule is a three-fold degenerate t_{1u} orbital, giving rise, in the crystal, to a narrow band of about 0.5-0.6 eV. If there is a general agreement about this order of magnitude for W , the value of the intramolecular electron-electron repulsion (U in the Hubbard model) is rather controversial. The experimental estimations are indirect and range from more than 1 eV (from photoemission) [1] to values much smaller than the bandwidth (from analysis of Fermi liquid properties). This question is conceptually important since the relevant theoretical description of the Alkali fullerides could be either a weakly correlated Fermi liquid or a strongly correlated one, or even a (possibly doped) Mott insulator, depending on the strength of the ratio U/W .

As far as we know, there is no reliable *ab initio* calculation of U , taking into account many-electron effects. The effective value of U is certainly smaller than the bare carbon atom on-site electron-electron Coulomb repulsion, typically a few eV's. It is certainly strongly reduced by electronic screening and by the delocalization of the electron wave function over the 60 atoms. However, given the order of magnitude of W , it seems difficult to believe, at first sight, that U can be much smaller than the bandwidth W . It is, therefore, important to discuss the possible effects of electron correlations on the electronic properties.

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The first indication of strong correlations is the failure of the rigid band model in the A_nC_{60} family when n varies from 0 to 6. The three-fold degenerate t_{1u} LUMO can accommodate the electrons transferred from the cations. In the cases $n = 0$ and $n = 6$, one expects an insulating behaviour in any model, for vanishing as well as strong correlations. Except in these two cases, for any other value of n ($0 < n < 6$), in a rigid band model, the partial filling of the band would confer a metallic behaviour and provide the possibility of a superconducting state. This is in obvious contradiction with the experimental data: up to now, the superconductivity seems restricted to the immediate vicinity of $n = 3$; more importantly, several counter-examples of semiconducting compounds, such as Na_2C_{60} , K_4C_{60} or Rb_4C_{60} prove the failure of the non interacting picture [2].

For that reason, many authors have discussed the superconductivity in A_3C_{60} in the context of large Coulomb correlations, similarly to the case of cuprates. Exotic mechanisms have been proposed to interpret the relatively high superconducting critical temperatures (up to $T_c = 40$ K in Cs_3C_{60}). For example, a positive electron-electron binding energy, due to an over screening effect at large values of the intermolecular Coulomb energy has been suggested on the basis of a second order perturbation calculation [3]. However, this attractive effect is now recognized as an artifact of the perturbation calculation [4]. Theoretical models of superconducting doped Mott insulators, as proposed in the cuprate oxides, are at variance with the data. They would imply no superconductivity at exactly $n = 3$, since Mott localization and a fixed number of electrons on each site are incompatible with superconducting phase coherence. In such models, one would expect a superconducting critical temperature T_c vanishing at $n = 3$ and increasing on both sides of this integer value as n is varied. On the contrary, experiments show that the T_c strongly decreases when one departs from $n = 3$ [5]. Moreover, the properties of the normal phase of A_3C_{60} seem compatible with a weakly correlated Fermi liquid picture. Furthermore, the effect of Coulomb repulsion in a correlated Fermi liquid on the BCS transition temperature T_c has been studied as a function of U/W , where W is the electron bandwidth. The results of this calculation are as follows: at small values of U/W , T_c is an increasing function of the density of states at the Fermi level and, therefore, of U/W at constant U , as expected in a weakly interacting picture ; but at larger U/W , the Coulomb repulsion has a dramatic effect on T_c , which strongly decreases with U/W , at variance with the data [6]. The experimental fact that T_c is a monotonous increasing function of the cubic lattice parameter, up to the highest observed value in Cs_3C_{60} , restricts the possible range for U/W to a fairly weak value, certainly smaller than half the bandwidth, that is to say about 0.25 eV. However, it is not obvious to explain how the effective intramolecular electron-electron repulsion can be so small, even if electron delocalization on the large C_{60} molecule as well as the core and conduction electron screening are taken into account.

The case $n = 1$ also deserves attention. The properties of Rb_1C_{60} , for example, exhibit interesting features. It forms, at temperature lower than 300 K, a polymeric phase with a pseudo-body-centered-orthorhombic lattice [7, 8]. RPE [7] and NMR data seem to indicate a strongly correlated Fermi liquid behaviour. For example, the magnetic susceptibility is strongly decreased under pressure, by a factor of 30% under 6 kbar (*i.e.* about 5 times more than in the $n = 3$ compound) [9]. This can be understood only if the ambient pressure susceptibility is strongly enhanced by correlations. A magnetic transition is observed below 50 K. Well above the transition temperature, NMR data reveal large fluctuations [10], rapidly disappearing under pressure [9]. The quasi-one-dimensional nature of this transition, as well as of these fluctuations (in relation with the crystal structure) is still controversial [7, 10, 11]. In any case, electron correlations in this phase seem quite strong, much stronger than in A_3C_{60} .

The compounds $n = 2$ or 4, such as Na_2C_{60} or Rb_4C_{60} are insulating at ambient pressure. A pressure induced insulator-metal transition is observed at a critical pressure of a few kilobars.

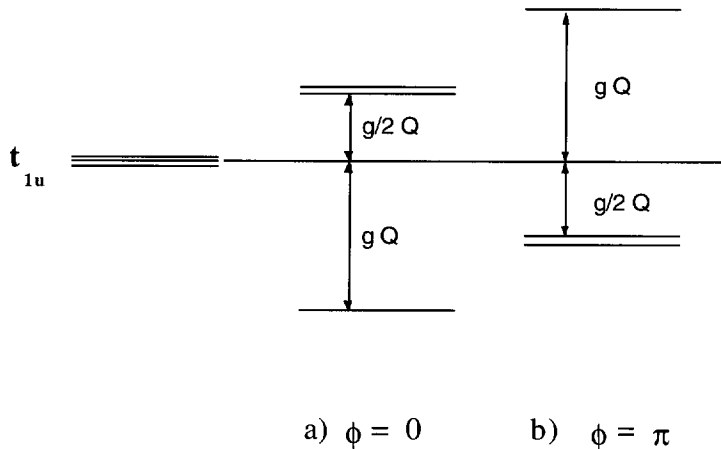


Fig. 1. — Splitting of the t_{1u} triplet by Jahn-Teller distortions of the C_{60} molecule with opposite phases.

Although one cannot exclude a one electron effect to interpret such an insulating behaviour at ambient pressure, these data are indicative of strong correlations, of the order of the electron bandwidth in these even - n compounds.

The effects of electron correlations seem, at first sight surprising and contradictory. While the bandwidths do not seem to vary appreciably with n in the A_nC_{60} , and keep the same order of magnitude (0.5-0.6 eV), correlations seem weak for $n = 3$, strong but preserving a Fermi liquid character for $n = 1$, and even larger than the bandwidth for $n = 2$ or 4. Usually, electron-electron correlations are interpreted as an effect of Coulomb repulsion. At first sight, it seems difficult to understand how the Coulomb repulsion between two electrons on the same molecule can vary on a large scale as a function of n , even though one can admit that screening effects may reduce U in a different manner, to a certain extent. We propose here, to interpret the data, that another source of electron correlation, due to strong coupling of electrons with intramolecular modes of vibration of the C_{60} molecule should be included. It is generally accepted that superconductivity in A_3C_{60} is mediated by a strong electron-phonon interaction. It seems likely that the phonon modes involved in superconductivity imply intramolecular vibrations of the C_{60} molecule [3].

The three-fold degeneracy of the t_{1u} orbitals is lifted by any quadrupolar deformation that makes the Cartesian axes inequivalent. The relevant modes are those having the H_g symmetry. These eight five-fold degenerate modes can give rise to a static or dynamic Jahn-Teller effect on the three-fold t_{1u} state. This degeneracy lifting can induce strong electron correlations. Let us consider the molecular limit. We consider two molecules occupied by $2n$ electrons in the limit of zero intermolecular transfer integral between neighboring molecules t_{ij} . This Jahn-Teller problem of a three-fold degenerate electronic state interacting with a five-fold degenerate vibration mode has been solved already [12]. A further decrease of the ground state energy of the molecule might be obtained by a bimodale distortion lifting the degeneracy of the lowest doublet. We have not considered here this possibility.

The triplet splits according to Figure 1a for one phase of the vibration and to Figure 1b for the opposite phase. Then, we calculate the energy $E(n)$ of a molecule occupied by n electrons in the limit of vanishing t_{ij} . The energy of a pair of neighboring molecules depends on the way the $2n$ electrons occupy the molecular levels. The Jahn-Teller distortion induces a correlation

energy U_{JT} which we can define in the following way [13]:

$$U_{JT} = E(n+1) + E(n-1) - 2E(n).$$

Figure 2, where C is the elastic stiffness constant, gives the variation of U_{JT} as a function of n . U_{JT} has not a constant sign over the range $0 \leq n \leq 6$. It is positive for even values of $n = 2, 4$ and negative for odd values $n = 1, 3, 5$.

Positive values of U_{JT} imply a tendency of localizing an equal number of n electrons on each molecule. In that case, U_{JT} and U_C the intramolecular Coulomb repulsion between electrons add their effects to localize the electrons. These localization terms compete with the energy band term, which favors an itinerant state. A sort of Mott-Hubbard metal-insulator transition occurs when $U_{\text{eff}} = U_{JT} + U_C$ exceeds a critical value, which can be estimated in the Gutzwiller approximation [14]:

$$(U_{\text{eff}})_c = \alpha \langle \varepsilon(k) \rangle$$

where the brackets $\langle \dots \rangle$ mean averaging over the independent electron energy band, $\varepsilon(k)$ is the one electron dispersion law, Fourier transform of t_{ij} and α is a numerical constant of order unity. It has been argued recently [15], to interpret new experimental data of NMR under pressure in Rb_4C_{60} , that the semiconducting character presented by this compound is indeed due to a Jahn-Teller distortion. When a pressure is applied to Rb_4C_{60} the electron bandwidth increases. A transition to a metallic state, exhibiting a Korringa law, occurs above a critical pressure of a few kbars [15]. Rb_4C_{60} seems a favorable case to such a situation for two reasons: i) $n = 4$ corresponds to the largest positive value of U_{JT} ; ii) the less effective screening of Coulomb interaction, due to a lower electron density, increases U_C , compared to the case $n = 3$. However, on the other hand, the body-centered tetragonal structure probably leads to larger intermolecular overlaps than the fcc structure of A_3C_{60} , which should therefore contribute to increase U_{eff} .

An important feature of Figure 2 is the negative values of U_{JT} at odd values of n , the most negative one occurring at $n = 3$. Such negative values indicate a tendency to superconducting pairing. In the molecular limit $U_{JT} \gg t_{ij}$, a local pair would form on a given molecule, the doublet state being occupied by 4 electrons, while the neighboring molecules would be occupied by 2 electrons. A static Jahn-Teller distortion would occur on each molecule, with a difference of phase of π between neighboring molecules. However, it seems plausible that the correct limit is rather $U_{JT} \leq t_{ij}$. In that case, the electron tunnels to a neighboring molecule before the local pair has time to be formed. The molecular limit is not the relevant one. The Hubbard Hamiltonian discussed above must be written and studied in the reciprocal space, with an effective intramolecular electron-electron interaction $U_{\text{eff}} = U_{JT} + U_C$.

The fact that U_{JT} is negative for odd values of n implies superconducting correlations for $n = 1, 3, 5$. It seems that no static Jahn-Teller distortion have been observed experimentally in the ground state. It is more likely that the U_{JT} term in the Jahn-Teller-Hubbard Hamiltonian is too small to induce a static distortion, but that dynamic Jahn-Teller effect induce superconducting correlations for odd values of n . It has been found experimentally that the superconducting transition temperature T_c in A_nC_{60} is strongly peaked at $n = 3$ [5]. It reaches 33 K in $\text{Cs}_2\text{RbC}_{60}$, which corresponds to the highest lattice parameter of the Alkali Fulleride family and therefore to the largest density of states. The maximum at $n = 3$ is not easily understood in an usual BCS theory, since band structure calculations do not predict a maximum of the density of states at $n = 3$. Our model provides a natural interpretation of the data since we propose that the effective repulsion potential μ^* appearing in the BCS-Eliashberg expression for T_c increases linearly with $|n - 3|$ on both sides of $n = 3$. We therefore expect that $T_c(n)$ decreases exponentially on both sides of its maximum.

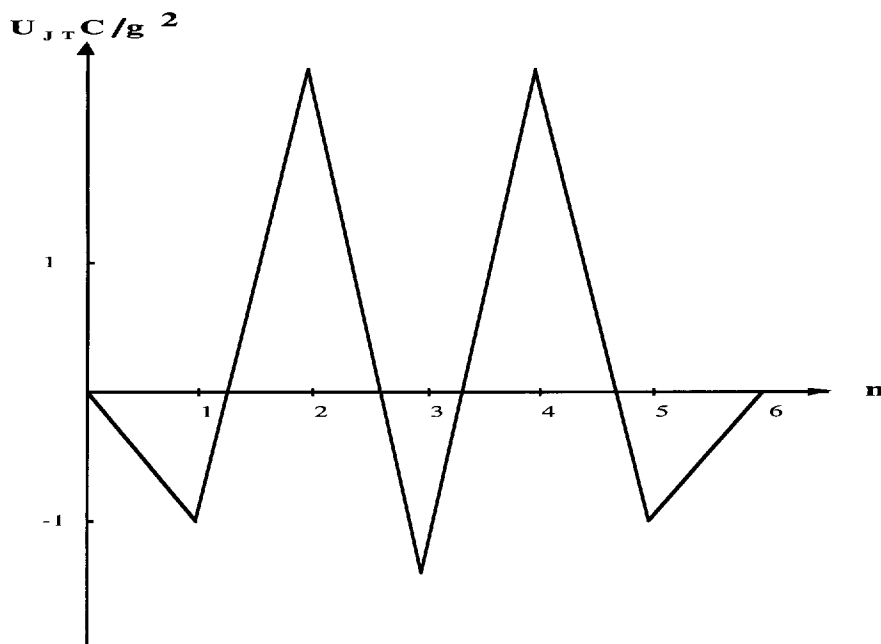


Fig. 2. — Correlation energy induced by the Jahn-Teller distortion as a function of the number of electrons in the t_{1u} band.

The experimental data suggest that U_{eff} almost vanishes for $n = 3$ as a result of a cancellation between a positive value of U_c , of the order of 0.5 eV and a negative value of U_{JT} (~ -0.5 eV). This is not incompatible, nevertheless, with a fairly strong correlation in Rb_1C_{60} , with $U_{\text{eff}} \sim +0.2$ eV. Since U_{JT} is definitely less negative for $n = 1$ than for $n = 3$, we are left with a non vanishing positive U_{eff} for $n = 1$, the order of magnitude of which cannot be very different from a few tenths of eV. Then, even though the case $n = 3$ corresponds to a limit of weak correlations, $n = 1$ might correspond to a limit of strong correlations, since the relevant dimensionless parameter is $U_{\text{eff}}N(E_F)$. This picture might be able to interpret the observed properties of this compound. Our discussion is based on the LDA calculation of the band structure given by Erwin *et al.* [8]: the three-fold LUMO of C_{60} is splitted by the orthorhombic distortion. This gives rise to three weakly overlapping energy bands. The lowest one is quite three-dimensional, as pointed out by Erwin *et al.*, and nearly half-filled, with a bandwidth of 0.6 eV. The second one is rather low-dimensional and anisotropic and only weakly filled. In that case, below 300 K but well above a magnetic ordering temperature, the electrons would behave as a strongly correlated liquid, with strong magnetic fluctuations. However this band should play an important role, because the Fermi level corresponds to a density of states singularity. The associated peak in the density of states $N(E_F)$ is enough to induce a nearly ferromagnetic character to the normal phase up to relatively high temperature, with $U_{\text{eff}}N(E_F) \approx 1$ even for moderate values of U_{eff} . However, at lower temperature, the low-dimensional character of the second band induces a maximum of $\chi(q)$ at finite q , due to a Fermi surface geometry effect. One should, therefore, obtain a crossover to antiferromagnetic fluctuations and eventually a three-dimensional antiferromagnetic ordering. These effects should be strongly pressure dependent and could account for the large relaxation rates observed in Rb_1C_{60} by NMR experiments.

Acknowledgments

We are particularly grateful to D. Jérôme and H. Alloul for communicating their data prior to publication and for very helpful and stimulating discussions.

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