Mott-Hubbard-like Behavior of the Energy Gap of A_4C_{60} (A = Na, K, Rb, Cs) and $Na_{10}C_{60}$

Martin Knupfer and Jörg Fink
Institut für Festkörper- und Werkstofforschung Dresden, D-01171 Dresden, Germany

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We have studied the low energy electronic excitations of A_4C_{60} (A = Na, K, Rb, Cs) and $Na_{10}C_{60}$ using electron energy-loss spectroscopy in transmission. Our results provide evidence for a Mott-Hubbard ground state in these compounds together with a Jahn-Teller distortion of the fullerene molecules. The behavior of the energy gap as a function of lattice parameter and crystal symmetry could be successfully modeled within this framework. We conclude that a comprehensive understanding of the A_4C_{60} and A_3C_{60} materials requires the consideration of both a Jahn-Teller distortion owing to strong electron-phonon coupling and electron correlation effects. [S0031-9007(97)04198-7]

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The intercalated fullerene compounds A_3C_{60} and A_4C_{60} (A = alkali metal) exhibit a variety of intriguing physical properties. One of the most striking differences between them is their electronic ground state. While the A_3C_{60} compounds are metals [1] and even superconductors [2,3], A_4C_{60} compounds are insulators [4–6], although both formally have a partly filled conduction band and are thus expected to be metals within a one-electron description. This demonstrates that a complete understanding of the electronic properties of these materials requires the consideration of phenomena such as electron-phonon and electron-electron interactions that can significantly alter the electronic structure of solids from the expectations of one-electron theory. Indeed, it has been shown that both types of interaction are present in fullerene compounds and have considerable impact on various properties [7]. Consequently, these materials are also of general interest because, through their study, one can gain important insight into the interplay of different quasiparticle interactions which plays an important role in many correlated systems such as, e.g., the high temperature superconductors. Furthermore, fullerenes are ideal model compounds for investigating electron correlation effects in degenerate systems.

Despite a large number of experimental and theoretical studies, the relative importance of electron-phonon and electron-electron interactions as regards the ground state of A_3C_{60} and A_4C_{60} is still under discussion. The range of proposed scenarios reaches from the conclusion that stoichiometric A_3C_{60} and A_4C_{60} are Mott-Hubbard insulators due to strong electronic correlations [8,9], via descriptions of A_3C_{60} as a correlated metal and A_4C_{60} as a Mott-Hubbard [10,11] or band [12] insulator, to the inference that A_4C_{60} is a Jahn-Teller insulator owing to strong electron-phonon coupling [13,14].

In order to elucidate these points we have carried out a systematic study of the low-lying electronic excitations in A_4C_{60} (A = Cs, Rb, K, Na) using electron energy-loss spectroscopy (EELS) in transmission. We have also examined $Na_{10}C_{60}$ as this compound also has a conduction band which is partly filled with an even number of electrons [15] and its loss function is strikingly similar to those of the A_4C_{60} materials [16]. We show that the energy gap of the compounds studied is strongly dependent on both the lattice constant and the crystal symmetry. This behavior can be understood by taking electron correlation effects into account, which indicate a correlated ground state for these compounds. In addition, higher-lying excitations indicate the presence of a Jahn-Teller distortion of the molecules. Thus, a combination of both Jahn-Teller and correlation effects is probably responsible for the different ground states of A_4C_{60} and A_3C_{60}.

The preparation of thin fullerene films is described elsewhere [17]. Alkali metals were added from an SAES getter source under ultrahigh vacuum conditions while the film was held at 550 K until A_6C_{60} (A = Na, K, Rb, Cs) stoichiometries were reached, as determined from $C1s$ core excitation and electron diffraction spectra. In order to obtain films with A_4C_{60} stoichiometry, the films were then heated to 570 K (130 h), 670 K (27 h), 680 K (26 h), and 690 K (12 h) for A = Na, K, Rb and Cs, respectively, in order to distill A_4C_{60} films [18]. Recently, we have shown that vacuum distillation can be used to prepare single phase samples for transmission EELS studies [19]. The films were characterized using electron diffraction. The K_4C_{60}, Rb_4C_{60}, and Cs_4C_{60} samples were found to be body-centered tetragonal (bct), while for Na_4C_{60} a face-centered cubic (fcc) diffraction profile was observed, consistent with x-ray diffraction data in the literature [20,21]. We emphasize that with our preparation procedure we do not obtain the body-centered polymeric Na_4C_{60} phase which has been reported recently [22] but that our Na_4C_{60} film clearly has fcc symmetry. No indication of other phases could be observed. For Cs_4C_{60}, Rb_4C_{60}, and K_4C_{60} further annealing at the abovementioned temperatures did not lead to further changes in film composition or structure, demonstrating that the vacuum distillation process was carried out to completion. In contrast, under similar conditions, the sodium concentration in Na_4C_{60} decreased, consistent with a solid solution behavior. $Na_{10}C_{60}$ films have been prepared by subsequent Na addition and annealing at 420 K for several cycles. Further details are described in Ref. [16].

The electron diffraction and EELS measurements were performed in transmission at room temperature using a 170 keV spectrometer described elsewhere [23]. The energy and momentum resolutions were chosen to be 115 meV and 0.05 Å^{-1}. The raw data have been corrected for contributions from the elastic line. In order to obtain the optical conductivity from the measured loss functions we have performed a Kramers-Kronig analysis. Our results for K_4C_{60} are in very good agreement with those obtained from reflectivity measurements [24] and EELS in reflection [25].

In Fig. 1 we show the optical conductivity σ of the compounds studied in an energy range of 0–2.2 eV. When compared to the optical conductivity of A_6C_{60} materials [24], the curves shown in Fig. 1 are rich in structure. Four features at about 0.6, 1.0, 1.3, and 1.6 eV are visible. Going to $Na_{10}C_{60}$, K_4C_{60}, and Na_4C_{60} a broadening of the structures is observed and the first feature shifts to lower energies. To explore this behavior further we have modeled the optical conductivity using a sum of Lorentz oscillators,

$$\sigma(\omega) = \epsilon_0 \sum_j \frac{\omega^2 f_j \gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}\,. \qquad (1)$$

The results of this fit are given in Table I.

The crystal structures of the compounds under investigation differ in both their lattice parameters and symmetry, i.e., the number of nearest neighbors. Both these quantities determine the volume of the primitive unit cell V_p which is also given in Table I. In Fig. 2 we show the energy positions and relative oscillator strengths of the first four transitions as a function of V_p. As can be seen, the energy position of the three higher-lying transitions (open squares, circles, and triangles) is almost independent of V_p, and their oscillator strength also hardly varies. In contrast, the first transition (filled squares), which represents the energy gap, significantly shifts to higher energies with increasing V_p while its oscillator strength considerably decreases. In a solid consisting of relatively weakly interacting molecules, one has to distinguish between electronic excitations that are confined to a molecule and those which involve a transfer of the excited electron to a neighboring molecule. While the latter strongly depends upon the

TABLE I. Parameters derived from a Lorentz fit of the curves shown in Fig. 1 (ω_j equals oscillator position, γ_j equals oscillator width, and f_j equals oscillator strength). Also given is the volume of the primitive unit cell V_p (Å^3).

	Cs_4C_{60}	Rb_4C_{60}	K_4C_{60}	Na_4C_{60}	$Na_{10}C_{60}$
ω_1	0.61	0.61	0.5	0.25	0.38
γ_1	0.3	0.3	0.4	0.3	0.35
f_1	0.3	0.4	1.2	1.3	0.58
ω_2	0.98	0.98	0.92	0.92	0.94
γ_2	0.3	0.3	0.4	0.5	0.5
f_2	1.0	1.08	1.06	1.15	1.25
ω_3	1.28	1.28	1.25	1.15	1.27
γ_3	0.3	0.3	0.4	0.5	0.5
f_3	0.37	0.38	0.4	0.6	0.67
ω_4	1.59	1.59	1.56	1.6	1.62
γ_4	0.3	0.3	0.4	0.5	0.5
f_4	0.33	0.48	0.35	0.39	0.46
V_p	831	788	758	713	778

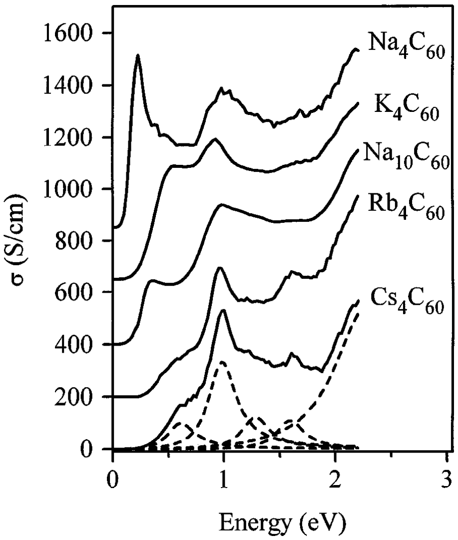

FIG. 1. The optical conductivity σ of A_4C_{60} and $Na_{10}C_{60}$ compounds as derived via a Kramers-Kronig analysis of the measured loss function. The curves are offset in the y direction. For Cs_4C_{60} we additionally show the decomposition of σ into the four Lorentz oscillators and the background due to higher-lying excitations.

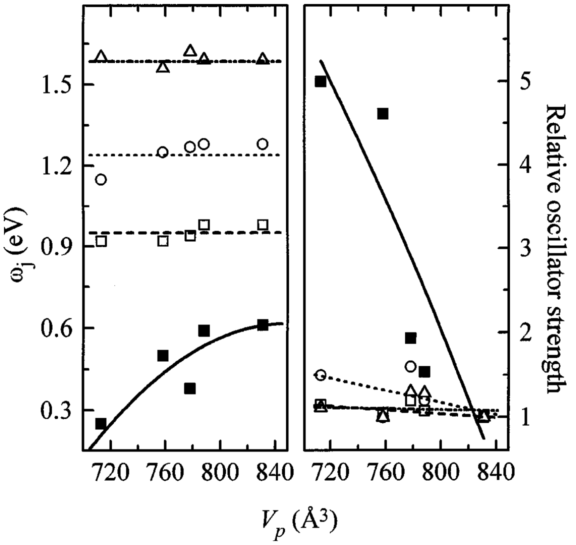

FIG. 2. The energy position ω_j and oscillator strength [relative to that of Cs_4C_{60} (see also Table I)] of the four low-lying excitations shown in Fig. 1 plotted as a function of the volume of the primitive unit cell V_p.

interaction of the molecules, i.e., their distance and coordination, the first is only weakly influenced by these parameters. We therefore conclude from Fig. 2 that the optical gap in A_4C_{60} and $Na_{10}C_{60}$ is defined by an excitation to an adjacent C_{60} molecule. The higher-lying excitations, however, are intramolecular transitions between different electronic levels. Comparing the data in Fig. 1 to those of A_6C_{60} [24,26] (which exhibit only one structure centered at about 1.1 eV arising from $t_{1u} \rightarrow t_{1g}$ transitions), it is clear that the highly degenerate electronic levels of C_{60} must be split in A_4C_{60} and $Na_{10}C_{60}$. The most likely mechanism for such a splitting is a Jahn-Teller distortion of the molecules, which has been predicted to be of the order of 0.2 eV for the t_{1u} and t_{1g} derived levels of a C_{60}^{4-} molecule [27,28], consistent with the energy separation of the observed structures in Fig. 1. For $Na_{10}C_{60}$, is has been shown that the charge transfer from sodium to C_{60} is incomplete, resulting in C_{60}^{8-} [15,16], and it is reasonable to assume a similar Jahn-Teller splitting for these C_{60}^{8-} molecules. Our interpretation is supported by resonant Raman [29] and nuclear magnetic resonance [14] experiments in which an (optically forbidden) excitation has been observed at about 0.2 eV for A_4C_{60} compounds which can be attributed to transitions between the split t_{1u} derived states. Furthermore, optical studies [24] have reported a splitting of the $T_{1u}(4)$ vibrational mode in A_4C_{60}, and a significant broadening of the $C1s$ excitation edges has been observed using EELS for A_4C_{60} [26] and $Na_{10}C_{60}$ [16] which is also fully consistent with a Jahn-Teller distortion of the fullerene molecules.

The insulating ground state of A_4C_{60} and the observed behavior of the energy gap, however, cannot be understood within a Jahn-Teller scenario. Firstly, the Jahn-Teller splitting of the molecular levels is considerably smaller than the calculated one-particle bandwidth [30], from which one would therefore expect the system to remain metallic. Secondly, the calculated bandwidths for fcc and bct fulleride systems are very similar [30,31]. It is thus impossible to rationalize the observed difference in the magnitude of the gap between K_4C_{60} (bct) and Na_4C_{60} (fcc) on the basis of a Jahn-Teller model because the gap then would depend solely on the Jahn-Teller splitting and the bandwidths, both of which hardly change. The energy shift of the gap as a function of V_p indicates transitions to adjacent molecules, and one should therefore seriously consider electron correlation effects. For C_{60} it has been shown that the on-site correlation energy U in the solid is about 0.8–1.6 eV [7,8] and thus comparable to the bandwidth of these materials. We therefore attribute the first peak observed in Fig. 1 to transitions from the lower to the upper Hubbard band. These are dipole allowed as they involve states on different molecules.

In the following, we explore this idea further and show that the size and the shift of the energy gap in the materials studied here can be satisfactorily explained within a simple Mott-Hubbard description. The gap Δ in a half-filled correlated fulleride system roughly behaves as [11]

$$\Delta \sim (U_0 - \delta U) - \sqrt{N}\,W\,. \tag{2}$$

The parameters are the bare on-site correlation energy $U_0 \sim 2.9$ eV [7], the screening of this energy is due to polarization $\delta U \sim 1.58$ eV for a bct lattice with lattice constants $a = 11.886$ Å and $c = 10.774$ Å, and $\delta U \sim 1.69$ eV for an fcc lattice with $a = 14.1$ Å [32], the orbital degeneracy N of the molecular t_{1u} levels which form the conduction band ($N = 3$), and the conduction bandwidth W. For systems with fourfold occupied t_{1u} states, $\sqrt{N}$ is reduced to $\sqrt{N_{\mathrm{eff}}} = (\sqrt{2} + \sqrt{3})/2$ [33,34].

The lattice dependence of Δ enters via those parameters which are a function of the nearest neighbor distance d: $\delta U \propto d^{-4}$ (Ref. [8]) and $W \propto d^{-2}$ (Ref. [35]). Furthermore, band-structure calculations give a width of the t_{1u} derived bands of $W = 0.61$ eV for K_3C_{60} ($d = 9.927$ Å) [31] and 0.56 eV for K_4C_{60} ($d = 9.969$ Å) [30]. With the figures given above we obtain the gap as a function of d, $\Delta(d)$, ($d_0 = 9.969$ Å):

$$\Delta(d) \sim U_0 - \delta U\,\frac{d_0^4}{d^4} - \sqrt{N_{\mathrm{eff}}}\,W\,\frac{d_0^2}{d^2}\,. \tag{3}$$

In Fig. 3 we show the d dependence of Δ for crystals with bct (A_4C_{60}, A = K, Rb, Cs) and fcc symmetry (Na_4C_{60}, $Na_{10}C_{60}$). Additionally depicted are the gap values as derived from the optical conductivities shown in Fig. 1. The agreement between the expectation derived from the simple model in Eqs. (2) and (3) and the measured gap values is remarkably good. This strongly indicates that

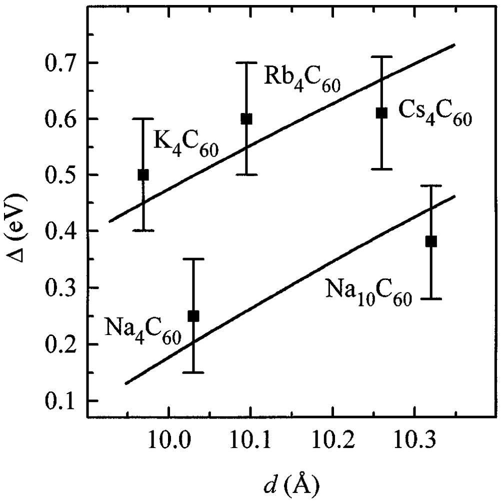

FIG. 3. The experimentally determined energy gap Δ of A_4C_{60} and $Na_{10}C_{60}$ compounds as a function of the nearest neighbor distance d (symbols). The error bars give an estimate of the uncertainties arising from the normalization procedure in the Kramers-Kronig analysis and the elastic line subtraction. The solid lines show the expected behavior for fcc (lower line) and bct phases (upper line) within a simple Mott-Hubbard model (see text).

alkali metal intercalated fullerene compounds with conduction bands that are partly filled with an even number of electrons have a correlated ground state, i.e., they are Mott-Hubbard insulators. This seems to be in contradiction to the observation that A_4C_{60} compounds are nonmagnetic [4], whereas Mott-Hubbard insulators are usually magnetic having local magnetic moments, i.e., a local high-spin configuration. On the other hand, our results above also indicate a Jahn-Teller splitting of the C_{60} molecular electronic levels and such a splitting could stabilize a low-spin (nonmagnetic) ground state if the Jahn-Teller splitting overcomes the Hund's rule exchange energy. Thus, both the Jahn-Teller effect *and* electronic correlations are important in understanding the ground state of A_4C_{60} and $Na_{10}C_{60}$, and one is led to the conclusion that these materials deserve the name *nonmagnetic molecular Jahn-Teller Mott insulators* [36].

The question now arises whether the A_3C_{60} compounds are metallic, although electronic correlations are strong and render the A_4C_{60} materials insulating. A relatively small but important difference between these two classes of compounds is the Jahn-Teller contribution to the correlation energy U_{JT} [28]. While in A_4C_{60} it provides a positive contribution, thus stabilizing an insulating ground state, U_{JT} is negative for A_3C_{60} ($U_{JT} \sim -0.2$ eV) [28] which helps to reduce correlation effects. Considering the observed gap for fcc Na_4C_{60} of $\sim$0.25 eV and the reduction of U due to the Jahn-Teller contribution [28], one would expect the A_3C_{60} compounds to be metallic although still correlated. This has also been concluded from theoretical considerations [11].

To summarize, we have shown that a complete description of the electronic properties of alkali metal intercalated fullerides requires the inclusion of both electron correlation and Jahn-Teller effects. A combination of these two mechanisms most likely stabilizes an insulating correlated ground state of the A_4C_{60} compounds, while in A_3C_{60} they partly cancel, which places these phases on the metallic side of the Mott metal insulator transition.

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