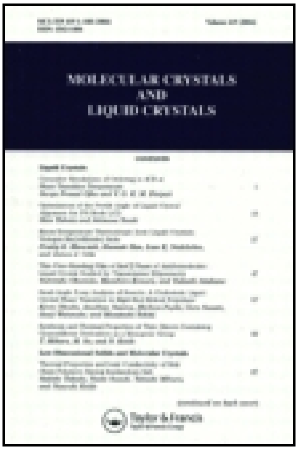

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electronic Properties of Ba-Intercalated Fullerides

Y. Iwasa [a] , X. H. Chen [b] , T. Takenobu [a] & T. Mitani [a]

[a] Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa, 923-1292, Japan

[b] Department of Physics, The University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

Version of record first published: 24 Sep 2006

To cite this article: Y. Iwasa, X. H. Chen, T. Takenobu & T. Mitani (2000): Electronic Properties of Ba-Intercalated Fullerides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 583-586

To link to this article: http://dx.doi.org/10.1080/10587250008025529

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 583-586
Reprints available directly from the publisher
Photocopying permitted by license only

Electronic Properties of Ba-Intercalated Fullerides

Y. IWASA[a], X. H. CHEN[b], T. TAKENOBU[a] and T. MITANI[a]

[a]*Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923–1292, Japan and* [b]*Department of Physics, The University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

(Received May 30, 1999; In final form July 5, 1999)

Raman spectra have been measured on Ba_xC_{60} binary systems for x=3, 4 and 6. The pentagonal pinch Ag(2) mode exhibits a softening in an approximately proportional manner to the formal valence of C_{60} molecule. This result suggests that the valence of C_{60} in Ba doped systems are understood by the naive ionic crystal model based on Ba^{2+}. The broader Raman peaks in superconducting Ba_4C_{60} indicates that the electron-phonon interaction is considerably large comparing to those for Ba_3C_{60} and Ba_6C_{60}.

Keywords: C_{60}; Ba intercalated fullerides; Raman spectra

INTRODUCTION

Fullerene intercalation chemistry has afforded a vast variety of compounds [1]. One of the unique aspects of fullerenes as a building block of solids is a large capacity of electrons. In the alkali doped C_{60}, for example, the molecular valence was found to be controlled from 0 to 6 by changing the chemical compositions. This valence change has been confirmed by a number of experiments, among which Raman spectroscopy has been known to be the best probe to detect the valence state of C_{60} molecules [2]. Fullerene molecules can be viewed as electron sponges, whose properties should be more investigated. Particularly, the alkaline earth intercalated fullerides are of significant importance from this point of view, because much higher reduction state could be achieved due to the divalent nature of alkaline earth ions.

In this paper, we focus on Ba intercalated fullerides where more than six electrons are transferred to C_{60}. The charge states of the Ba-C_{60} binary systems have been investigated by means of Raman spectroscopy. The pentagonal pinch mode shows a continuous softening depending on the charge state of C_{60} molecules, suggestive of almost complete charge transfer from Ba to C_{60}

molecules. The larger Raman linewidths in Ba_4C_{60} than those for Ba_3C_{60} and Ba_6C_{60} indicates that the electron-phonon interaction plays an important role in Ba_4C_{60}, which might be relevant to the occurrence of superconductivity in this compound [3].

EXPERIMENTAL

The structural sequence of Ba-intercalated compounds are established by the isolation of Ba_4C_{60} [4], which turned out to be a true superconducting phase. Since the first discovery of the superconducting Ba-C_{60} binary , it has been believed that the superconducting phase is Ba_6C_{60} [5]. Table 1 summarizes the structures and properties of Ba-C_{60} binaries. One is able to synthesize Ba_3C_{60} and Ba_6C_{60} in a rather good quality by one or two annealings of mixed powders of Ba and C_{60} at about 600℃. Ba_4C_{60}, however, requires more than five times of annealing with intermediate grindings to synthesize phase pure samples, and this is the reason why it took a long time to identify the superconducting phase. Raman spectra were measured on pelletized samples in sealed Pyrex tubes using a 632.8 nm line of a He-Ne laser in the Brewster angle backscattering geometry. The scattered light was detected with a Dilor xy multichannel spectrometer with a spectral resolution of 3 cm^{-1}.

Ba_xC_{60}	Structure	Properties
x=3	cubic (A15), a=11.34Å	semiconductor
x=4	orthorhombic, a=11.610Å, b=11.235Å, c=10.883Å	superconductor , Tc=6.5K
x=6	bcc, a=11.20Å	semimetal

TABLE I: Structural and electronic properties of Ba-intercalated C_{60}

RESULTS AND DISCUSSION

The left panel of Fig. 1 shows the Raman spectra for three materials Ba_xC_{60} (x=3, 4, and 6). Each Ag(2) mode located at about 1400 cm^{-1} exhibits a single peak, indicating that the materials measured are prepared in a single phase . The Ag(2) mode shows an enormous softening upon the increase of Ba concentration x. The right panel displays the relation between the position of the Ag(2) mode and the nominal charge transfer simply derived from the chemical formula Ba_xC_{60} assuming that Ba ion is divalent. In this figure, the data for K_xC_{60} are also plotted for comparison. The plots for Ba_xC_{60} approximately fall on an extrapolation of the lines for K_xC_{60}, indicating that the charge transfer is from Ba

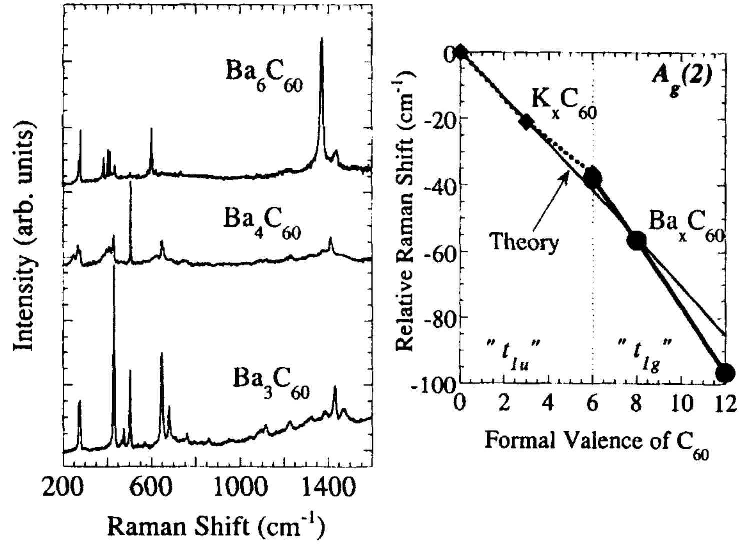

FIGURE 1: Raman spectra for B_3C_{60}, Ba_4C_{60} , and Ba_6C_{60} (Left). A relation between the position of the Ag(2) mode and the nominal valence of C_{60} molecule (Right).

to C_{60} is close to complete. In other words, the valence states for Ba_xC_{60} are regarded as -6, -8, and -12, respectively.

The two lowest unoccupied molecular orbitals (LUMO's) are both triply degenerate, which are so called t_{1u} (LUMO) and t_{1g} (LUMO+1) levels. According to a naive band picture, the hexa- and dodeca-valence state should provide semiconducting states, while the octavalent state should be metallic because the t_{1g} band is partially filled. In this sense, the occurrence of superconductivity in Ba_4C_{60} looks in accord with the simple band model. However, it should be pointed out that, in such an orthorhombic structure, superconductivity never occurs in the case of alkali doped materials. Superconductivity of alkali doped fullerides is extremely selective: It appears only when the valence state is half full of the t_{1u} band, and at the same time the structure should be fcc or related structures. The superconductivity of noncubic and non half-full Ba_4C_{60} is raising an interesting question on the criteria for fullerene superconductivity. The naive band picture predicts that Ba_6C_{60} is semiconducting, since the t_{1g} band is completely full. However, a recent magnetic susceptibility measurement revealed that both Ba_6C_{60} and Sr_6C_{60} show Pauli paramagnetic behaviors, indicative of metallic (semimetallic) natures in these compounds [6]. The observed semimetallic property can be explained by the hybridization of C and Ba orbitals, which causes a band broadening and, as a result, an overlap of the LUMO+1 and upper bands.

Another notable feature of the Raman spectra for Ba_xC_{60} is the linewidths of the Hg modes. For example, the five-fold degenerate Hg(1) mode is split into two or three components. Of particular interest is the linewidth of each peak. According to Allen's theory [7], the linewidth of Raman spectra is related to the electron-phonon interactions. We observed that the linewidths of the Hg modes are commonly larger in Ba_4C_{60} than in Ba_3C_{60} and Ba_6C_{60}. Thus, we conclude that the electron-phonon interaction in Ba_4C_{60} is considerably stronger than those in Ba_3C_{60} and Ba_6C_{60}. In fact, the electron-phonon coupling constant λ derived from the analysis of Raman spectra is comparable to that of K_3C_{60}. The absence of superconductivity in Ba_6C_{60}, despite the metallic behavior, is possibly understood by this small electron-phonon interactions.

In summary, we have measured Raman spectra on Ba intercalated C_{60} and showed that the molecular valence of C_{60} is approximately understood by a naive ionic crystal model. A considerably large electron-phonon interactions are suggested from the broad Raman lines for the superconducting Ba_4C_{60}.

Acknowledgments

This work has been supported by Grant from the Japan Society for Promotion of Science (RFTF96P00104, MPCR-363/96-03262), and also by Grant-in-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science, and Culture. YI and XHC thank Inoue Science Foundation for their support.

References

[1] M. J. Rosseinsky, Chem. Mater. **10**, 2665 (1998).
[2] P. C. Eklund et al., J. Phys. Chem. Solids **53**, 1391 (1992).
[3] X. H. Chen, S. Taga, and Y. Iwasa, to be published in Phys. Rev. B.
[4] M. Baenitz et al., Solid State Commun. 96, 539 (1995). C. M. Brown et al., preprint.
[5] A. R. Kortan et al., Nature **360**, 566 (1992).
[6] B. Gorgia et al., Phys. Rev. B**58** 1077 (1998).
[7] P. B. Allen, Solid State Commun. **14**, 937 (1974).