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Electronic structures and Jahn-Teller effects in alkali metal fullerides

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Electronic structures of alkali metal fullerides A_xC_{60} (A=Na, K, Rb, and x=1,2,3,4,6) have been investigated by means of optical reflection spectroscopy and electron paramagnetic resonance measurements. Optical spectra and spin susceptibilities for K_3C_{60} and Rb_3C_{60} can be understood in the framework of the band picture. However, the magnetic properties of A_xC_{60} can bot be explained by the simple band theory: The odd x compounds, Rb_1C_{60} and K_3C_{60} exhibit almost temperature-independent Pauli-like spin susceptibilities, whereas for the even x compounds, Na_2C_{60}, K_4C_{60}, and K_6C_{60}, temperature-dependent Curie-like spin susceptibilities were observed. As an explanation for this even-odd effect, the Jahn-Teller instability of doped C_{60} molecules is suggested.

1. INTRODUCTION

Since the discovery of superconductivity in alkali metal doped C_{60}, a large amount of experimental efforts have been made to clarify the nature of superconductivity of alkali metal fullerides (A_xC_{60}). As well as the investigation of the physical properties of the superconducting compounds, many kinds of alkali metal fullerides have been synthesized and their structures have been determined. Such material scientific studies [1] have revealed that most of alkali metal fullerides form line phase compounds rather than solid solutions, and that the compounds of integer x (=1, 2, 3, 4, 6, and 11) exist for A=Na, K, Rb, and Cs. Table 1 shows the crystal structures at room temperature of the already known A_xC_{60}'s for 1≤x≤6.

A \ x	*1*	2	3	4	5	6
Na		fcc	fcc			fcc
K	rhb		fcc	bct		bcc
Rb	rhb		fcc	bct		bcc
Cs	rhb			bct		bcc

Table 1. Identified alkali metal fullerides A_xC_{60}. "rhb" means rhombohedral. Superconductivity is observed only in hatched materials.

Among these compounds, superconductivity was found to occur only in x=3 phase such as K_3C_{60}, Rb_3C_{60} and the binary compounds $A_xA'_{3-x}C_{60}$ [1]. Molecular orbital calculations show that thelowest unoccupied molecular orbital (LUMO), into which the electrons are introduced, has a t_{1u} symmetry and is triply degenerate. Since the alkali metals are fully ionized in A_xC_{60}, the x value directly corresponds to the number of electrons occupying the t_{1u} LUMO. Therefore, the superconducting x=3 phase is half-filled. The metallic behavior and occurrence of superconductivity in the half-filled system is in sharp contrast to the high T_c cuprate superconductors.

According to a naive band picture, metallic states are predicted for x=1,2,3, and 4 compounds, and there is nothing particular in x=3 phase. In fact, many experimental results suggest that the electronic structure of the superconductors, K_3C_{60} and Rb_3C_{60} can be qualitatively understood in the framework of the simple band picture. Therefore, questions such as why the superconductivity occurs only in the x=3 phase, or what is particular of the x=3 are not understood yet and remain to be solved. One of the possible means to solve this puzzle is to investigate the electronic structures of A_xC_{60} other than x=3, and compare the electronic structures of these compounds with those of the x=3 materials. In this paper, we report the optical reflection spectra for K_3C_{60} and Rb_3C_{60} and show that the band picture semiquantitatively holds in these x=3 superconducting compounds. We also report the results of electron paramagnetic resonance (EPR) study for Rb_1C_{60}, Na_2C_{60}, K_3C_{60}, K_4C_{60}, and K_6C_{60}. We show that the EPR properties are strongly dependent on the parity of x, and that the band picture can not explain the whole features of the magnetic properties. As a plausible explanation for the failure of the band picture, the Jahn-Teller instability of doped C_{60} is suggested.

2. EXPERIMENTAL

For reliable optical measurements, we need samples with optically flat surfaces and minimum phase separations. For this purpose, we have grown samples of K_3C_{60} and Rb_3C_{60} by a so-called cosublimation method following the literature [2]. Obtained samples were characterized by the measurements of X-ray diffraction and Raman spectra. These data show that the cosublimation grown samples are sufficiently pure with no detectable phase separation.

Samples for EPR measurements were synthesized by a standard reaction of alkali vapors and C_{60} powders [1]. Obtained samples were found to be in single phase by X-ray diffraction measurements at room temperature. EPR measurements were made at various temperatures in a range from 5 to 290K. The g-values were determined by comparing the resonance position of Li-TCNQ (g=2.0026). The spin susceptibilities χ_s were calculated by integrating the EPR curves, and the absolute values of susceptibilities were calibrated using the signal of standard specimen. We have also made SQUID measurements, and obtained susceptibilities showing similar temperature dependence to those from the EPR measurements. The absolute values of χ_s determined from EPR and SQUID measurements coincided with each other within a factor.

3. OPTICAL REFLECTION SPECTRA FOR K_3C_{60} and Rb $_3C_{60}$

Figure 1 shows the optical reflection spectra for K_3C_{60} and Rb_3C_{60}. Typical metallic reflection with the plasma edge at about 0.7eV was observed for both samples. We also observe a small peak at around 1eV which is attributable to the interband transition. The reflection spectra for both samples resemble to each other, indicating that the electronic structures of these compounds are very similar. It should also be pointed out that no corresponding structures were observed for the undoped C_{60}. This implies that the observed reflection structures in the photon energy region measured are attributed to the contribution from the electons transfered from alkali metals. Therefore, the reflection peak at about 1eV is assigned to the transition from the t_{1u} LUMO band to the t_{1g} band. This energy agrees with that from the molecular orbital or band calculations [3].

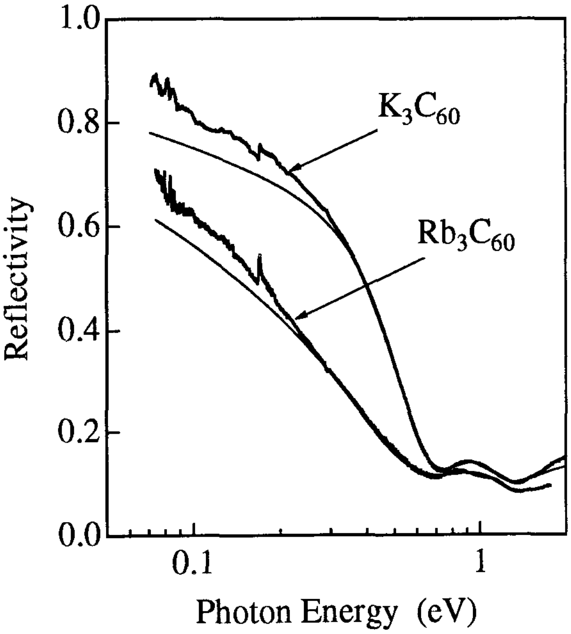

Figure 1. Optical reflection spectra of K_3C_{60} and Rb_3C_{60}. The thin solid lines show the calculated curves using the Drude-Lorentz model.

A Drude analysis was made to derive more quantitative information on the t_{1u} conduction band. The best-fit curves are plotted by the thin solid lines. Since it was difficult to fit the whole spectra by the simple Drude formula, the fitting procedure was done so as to reproduce the spectra around the plasma edge. Using this method, we can derive reliable plasma energies. The plasma energy ω_P was determined to be 1.5 and 1.2eV for K_3C_{60} and Rb_3C_{60}, respectively. Using the free electron model, the density of states at Fermi energy $N(\varepsilon_F)$ were calculated to be 23 and 36 eV^{-1} per C_{60}, respectively. The band calculation, on the other hand, show that the $N(\varepsilon_F)$ values are 24 and 31 eV^{-1} per C_{60} [4]. This agreement strongly suggests that the band picture is applicable to the x=3 phase compounds.

4. MAGNETIC PROPERTIES OF A_xC_{60} (x=1,2,3,4,6)

Figure 2 summarizes the temperature dependence of the spin susceptibilities χ_s's obtained from the EPR measurements for Rb_1C_{60}, Na_2C_{60}, K_3C_{60}, and K_4C_{60}. A notable feature of this figure is that the χ_s's for the odd x compounds Rb_1C_{60}, and K_3C_{60} are almost temperature-independent, while the χ_s's for the even x compounds Na_2C_{60} and K_4C_{60} exhibit a temperature dependence which approximately obeys the Curie law. Such an even-odd effect in the spin susceptibilities of A_xC_{60}'s are related to the underlying electronic structures in A_xC_{60}. A naive interpretation for the temperature independent susceptibility is the Pauli paramagnetism, indicating that the the odd x compounds are metallic. The Curie-like susceptibility suggest that the electrons in the even x compounds are localized, indicating that the even x compounds are insulating.

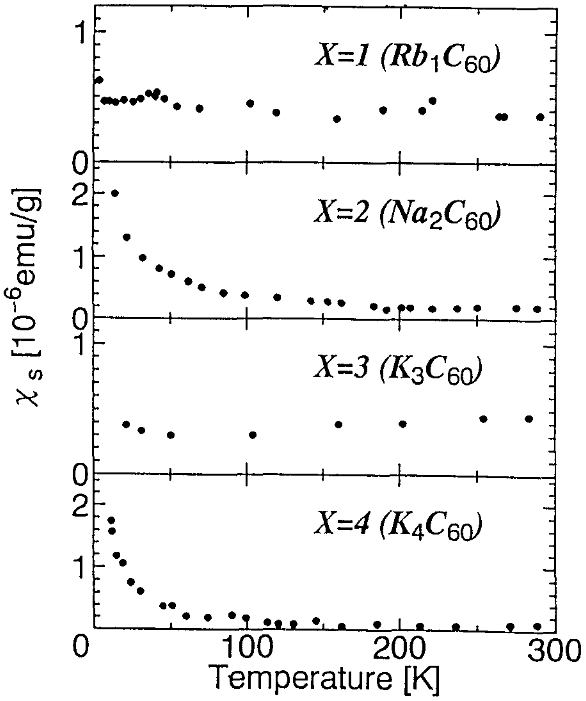

Figure 2. Temperature dependence of spin susceptibilities for Rb_1C_{60}, Na_2C_{60}, K_3C_{60}, and K_4C_{60}.

In order to clarify the nature of the Curie-like spin susceptibilities, we have plotted χ_s^{-1} as a function of temperature for Na_2C_{60}, K_4C_{60}, and Rb_6C_{60} in Fig.3. For all samples, almost Curie-like χ_s's are observed at low temperatures. Assuming that S=1/2, the spin densities were estimated to be 1/11, 1/22, and 1/36 per C_{60} molecule for Na_2C_{60}, K_4C_{60}, and Rb_6C_{60}, respectively. The values seem to be too small to be attributed to an intrinsic origin. It is to be noted that even K_6C_{60}, which is apparently a band insulator, exhibits a Curie paramagnetism. This indicates that the spins in K_6C_{60} are due to the paramagnetic impurities associated with the non-stoichiometry of alkali metals. In fact, the estimated error of the nominal values of x is about 0.3. Since the observed spin densities in Na_2C_{60} and K_4C_{60} are in the same order as that in K_6C_{60}, the spins in the former two compounds are also likely to arise from the nonstoichiometry. This implies that the intrinsic ground states of x=2 and 4 compounds are nonmagnetic insulators.

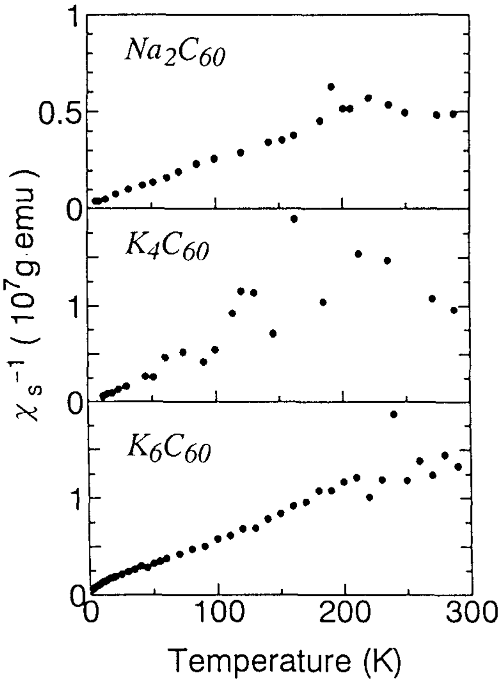

Figure 3. $\chi_s{}^{-1}$-T plot for the even x compounds, Na_2C_{60}, K_4C_{60}, and K_6C_{60}.

The observed even-odd effect is a clear evidence for the failure of the band picture in A_xC_{60}'s. The failure of the band picture and insulating nature of x=2 and 4 phases are very unique, since many experiments including present results show that the band picture holds for the superconducting x=3 phase. As an underlying mechanism of the breakdown of the band picture, one can consider the effect of electron-electron interaction and the electron-phonon interaction which are not taken into account in the simple band picture.

In order to consider the effect of electron-electron interactioon, let me compare the present results with those for the 3d transition metal oxides. This system is known to be a typical example of a failure of the band picture due to the strong electron-electron interaction. In Perovskite-type 3d transition metal oxides AMO_3 (A=La or Y, and M=Ti, V, Cr, Mn, Fe, Co, Ni, Cu), the number of electrons in the five-fold degenerate 3d orbitals can be controlled by changing the 3d transition metal elements M. In this sense, the problem is very similar to that for A_xC_{60}. According to Torrance et al. [5], most of these compounds are Mott insulators. The nature of this insulating state is magnetic, undergoing dramatic magnetic phase transitions.

There is no even-odd effect. These features are completely different from those for A_xC_{60}'s, indicating that the electron-electron interaction does not play a dominant role in A_xC_{60} compounds.

The second possibility is the electron-phonon interaction. One of the unique features of C_{60} molecule is its high symmetry. Therefore, the doped molecule is unstable to the Jahn-Teller type distortion. Here, we assume that the C_{60} ball is deformable rather than rigid. Since the LUMO is triply degenerate, the doped C_{60} is deformed from the I_h symmetry so as to stabilize the electronic energy. When such a Jahn-Teller distortion takes place in a static fashion, the ground state of C_{60} molecule will be spin singlet for the even number of electrons accommodated, and the spin doublet for the odd number of electrons. These molecular properties will naturally reflected in the ground state of solids, leading to a nonmagnetic insulator for the former case, while to a metallic phase for the latter case. This is consistent with the observed even-odd effect in the A_xC_{60}.

In this context, the x=3 phase is quite anomalous, because it is located between the insulating x=2 and 4 phases, which should be matallic according to the band model. The x=3 phase compounds are also unstable to the Jahn-Teller distortion. Nonetheless, no experimental evidence for the failure of the simple band theory was found for the x=3 materials. Therefore, the Jahn-Teller effect for the x=3 phase is expected to be dynamical, if it exists. It is interesting to point out that Varma et al. [6] proposed a mechanism of the superconductivity assuming such a dynamical Jahn-Teller effect plays a dominant role.

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