

EPR test of the resonating-valence-bond theory of superconductivity in $C_{60}K_n$

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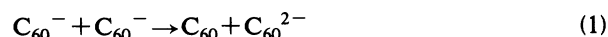
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EPR experiments on powder samples of $C_{60}K_n$ are presented. The results contradict the basic assumption of a negative Hubbard U , which has been used to explain the superconductivity in fullerenes. The apparent orbital nondegeneracy of the observed state is explained in terms of a generalized dynamic Jahn-Teller effect.

Electron paramagnetic resonance (EPR) of singly negatively charged ions of C_{60} molecules in several diamagnetic organic solvents has previously been reported.¹⁻⁷ These several studies have shown that disproportionation reactions such as



do not occur in solution. Recently, Chakravarty and Kivelson⁸ have proposed that reaction (1) may occur in the solid state. In this paper we report EPR observations on powder sample of $C_{60}K_n$ precipitated from solution which demonstrate that less than 3% of the radical anions disproportionate according to reaction (1).

The detailed description of the sample preparation is given elsewhere.⁴ Briefly, our samples of $C_{60}K_n$ were prepared by reduction of C_{60} by metallic potassium in dry tetrahydrofuran (THF). This solution had nearly the same g factor as was reported for other solutions of C_{60}^- with various cations in other solvents.¹⁻⁷ It also exhibited the same near-infrared absorption of C_{60}^- at $1.075 \mu\text{m}$ (molar absorptivity $\epsilon \sim 20\,000 \text{ mol}^{-1} \text{ cm}^{-1}$), which was reported by Kato *et al.*^{5,9} and confirmed in our laboratory by coulometric reductions. Evaporation of the THF left a reddish black powder. The EPR spectrum of this powder had the same integrated signal intensity and nearly the same g factor as that of its THF solution. The derivative of the X-band EPR absorption spectrum of the powdered sample, shown in Fig. 1, consists of a single approximately Lorentzian line with a temperature-independent $g = 1.9982 \pm 0.0004$. The Lorentzian line shape implies delocalization of the observed electron over the molecule. The temperature dependence of the linewidth, shown in Fig. 2, is similar to those in previous reports on solid solutions of singly ionized fullerene molecules in various diamagnetic organic solvents.¹⁻⁷ The temperature variation of the inverse EPR signal intensity for $C_{60}K_n$, shown in Fig. 3, implies that the signal is coming from the ground state and not from an excited state. The inverse intensity shows a Curie-Weiss dependence in the observed temperature region. Extrapolation of the inverse intensity (assuming a linear temperature dependence) to zero gives a large ferromagnetic Curie-Weiss

temperature $\Theta \sim 147 \text{ K}$, in contrast to the copper-oxide superconductors and related insulators where the interactions between copper ions are typically antiferromagnetic.

The number of unpaired electrons in each sample was estimated to about 10% accuracy by comparison of the magnitude of its EPR signal with that of a standard sample. Since the optical-absorption spectrum and peak molar absorptivity¹⁰⁻¹² are known and since it does not form diamagnetic ion clusters in dilute solutions in polar solvents¹³ such as THF, the radical anion of anthracene,¹⁴ prepared by electrolytic reduction, was chosen to be the standard. The number of unpaired electrons determined in this manner agreed to within 10% with the number determined from the optical density at $1.07 \mu\text{m}$ of the reduced C_{60} solutions. For greater (or less) than $n \sim 1$, the EPR intensity decreases. When the $n \leq 1$ powdered samples were redissolved, no evidence of the dianion ($\epsilon \sim 18\,000 \text{ mol}^{-1} \text{ cm}^{-1}$ at 945 nm) was observed in the optical-absorption spectrum of the sample; this observation sets an upper limit of 3% on the fraction of radical which disproportionates in the solid state.

Free radicals in general and those of aromatic hydro-

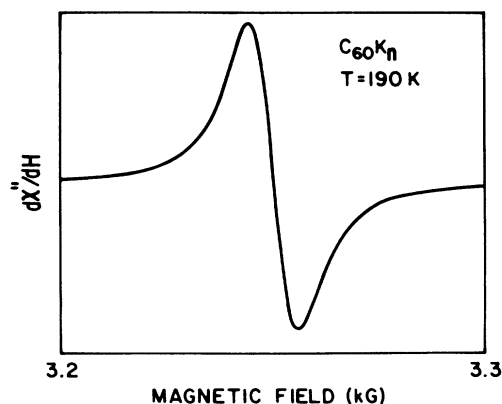


FIG. 1. Magnetic-field derivative of the EPR absorption spectrum of $C_{60}K_n$ powder at 190 K.

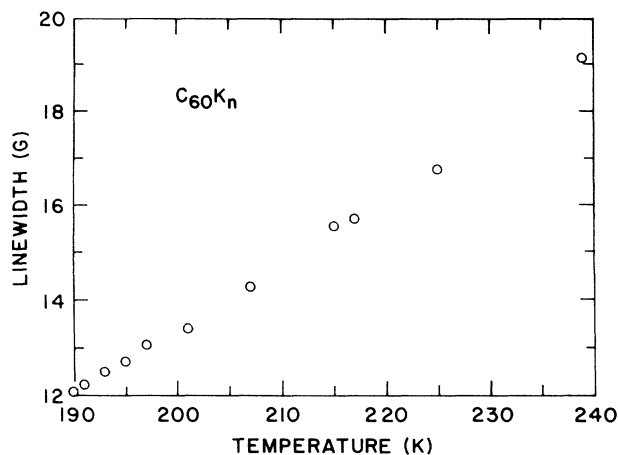


FIG. 2. Temperature dependence of the EPR linewidth in $C_{60}K_n$ powder.

carbons in particular have g factors close to 2 due to orbital quenching; i.e., the orbital states in these compounds are effectively nondegenerate. However, it is known that the lowest unoccupied electronic state in neutral C_{60} is an orbital triplet¹⁵ T_{1u} , where T_{1u} is an irreducible representation of the icosahedral point group. In the singly ionized molecule, the electron occupies this state, and because of the triplet orbital degeneracy, it should have an effective orbital angular momentum $L = 1$. When spin is included, the total angular momentum $J = \frac{1}{2}$ would have a Landé g factor of $\sim \frac{2}{3}$, which is far from the pure spin g value of 2.0023. The close proximity of the observed $g \cong 1.998$ to the free-spin value and the fact that the signals are observable at relatively high temperatures indicate that the electron is in an orbitally singlet and not in an orbitally triplet state. (The small difference between the observed g and free-spin values may be attributed to second-order spin-orbit interactions with excited states.) Although it is possible that this apparent orbital nondegeneracy is produced by purely electrostatic crystal fields that lower the icosahedral symme-

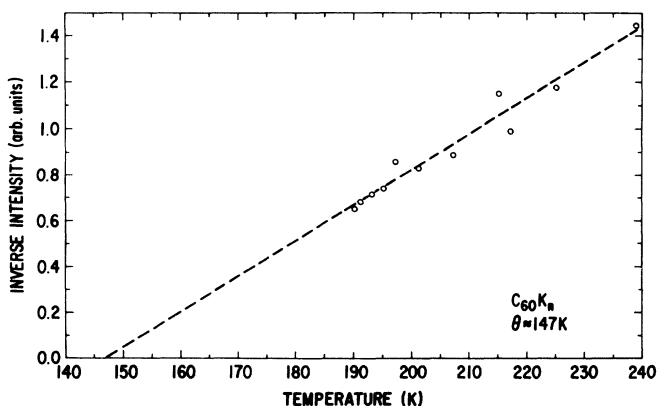


FIG. 3. Temperature dependence of the inverse EPR signal intensity in $C_{60}K_n$ powder.

try in the lattice, a *static* Jahn-Teller effect could also remove the degeneracy, even for a single molecule in free space. A generalized *dynamic* Jahn-Teller effect,¹⁶ which couples electronic motion to rotation or vibration, preserves icosahedral symmetry. A group-theoretical analysis shows that the rotational mode T_{1g} (a triplet) and the vibrational mode H_g (a quintuplet) are the only nontrivial nuclear modes that couple to the orbital electronic T_{1u} triplet state since

$$T_{1u} \times T_{1u} = A_g + T_{1g} + H_g . \quad (2)$$

The breathing mode A_g is, of course, trivial. The cross product of the electronic T_{1u} and the quintuplet vibrational mode H_g results in

$$T_{1u} \times H_g = T_{1u} + T_{2u} + G_u + H_u , \quad (3)$$

where the states on the right-hand side of (3) are the *vibronic* states and consist of two triplets T_{1u} and T_{2u} , a quadruplet G_u , and a quintuplet H_u . Therefore this coupling would not produce a singlet vibronic state. However, it has been shown¹⁷ that the C_{60} molecules in solids rotate even faster than in liquids. It is possible to explain the apparent orbital nondegeneracy of the orbital state by a rotational-electronic (*rotonic*) effect, since the T_{1g} rotational mode has a cross product with the electronic state T_{1u} :

$$T_{1u} \times T_{1g} = A_u + T_{1u} + H_u , \quad (4)$$

which includes the rotonic singlet A_u . If this singlet is the ground state of the rotonic Hamiltonian and if the triplet T_{1u} and quintuplet H_u are the excited states, the rotonic g factor of the ground state would be close to 2, as observed. Another possibility is that the ground rotonic state is the rotonic T_{1u} triplet, but the orbital factors are drastically reduced from their purely electronic values. This would be caused by the rotonic analogs of Ham's reduction factors¹⁶ in vibronic states, which would bring the g values closer to 2 and make the signals easier to detect at high temperatures. This alternative would be more appealing from a *continuity* point of view; i.e., the rotonic ground state remains a T_{1u} since we start from an electronic T_{1u} ground state. However, the signal in this case is expected to be anisotropic. The isotropy of the observed signal (Fig. 1) thus favors the singlet rotonic A_u to be the ground state. Nevertheless, the possibility of the ground state being either a rotonic or a vibronic T_{1u} cannot be completely ruled out because relaxation processes can, in principle, produce an *apparent* isotropy in a basically anisotropic line.¹⁶

Chakravarty and Kivelson⁸ have recently proposed a theory for the superconductivity in fullerenes that is a variation of the short-ranged resonating-valence-bond (RVB) theory.¹⁸ Their theory, which has been shown to be consistent with pressure experiments,¹⁹ is based on the following two fundamental assumptions.

(a) It is easier, in the solid, to add an electron to a singly negatively charged molecule than to a neutral molecule: i.e., the Hubbard U is negative.

(b) Each electron on the molecule breaks up into a

chargeless spinon and a spinless charged particle. For two electrons on a molecule, the two spinless charged particles repel each other and the two spinons form a spin singlet.

If assumption (a) is correct, for $n \sim 1$ about half of the molecules will be doubly charged and the rest will be neutral. The powder EPR results for $n \sim 1$, however, are not indicative of doubly ionized (or neutral) molecules.

For $n > 1$ the EPR signal intensity diminishes, implying that the doubly charged ions are probably diamagnetic. Therefore EPR data are consistent with assumption (b). However, since we have shown above that the orbital ground state in the solid is most probably a singlet, the two spins would be paired anyway if the first excited state is high enough to prevent Hund's rules from being applicable. Even if the orbital state is a triplet, Hund's rules predict that the total angular momentum for two electrons in an orbital triplet state is zero and no resonance should be observed. The separation between the spinon and spinless charged particle is thus not necessary to account for the diamagnetism of the doubly charged molecules, whether or not Hund's rules are applicable.

From our measurements and observations, we conclude that a phase separation²⁰ such as



has not occurred in the time scale of the experiments (\sim hours). Although we have not established the thermodynamic stability of $C_{60}K$, it is possible that it exists as a stable low-temperature phase. However, if the phase separation (5) had occurred, our conclusion, refuting a negative Hubbard U , would be, *a fortiori*, valid for $C_{60}K_3$, as neither a doubly charged nor a quadruply charged molecule (arising from a negative U in $C_{60}K_3$) would have EPR signals similar to those that have been observed, whereas a triply charged molecule would have an orbital-singlet spin-quadruplet state and could be responsible for the observed signal if no fine structure is resolved. This possibility would also eliminate the need for invoking the rotonic effect to explain the orbital non-degeneracy. On the other hand, it would imply that the observed signals in solutions¹⁻⁷ also arise from triply (not singly) ionized molecules, since their EPR characteristics are similar to those for the solid. However, a recent report²¹ on $C_{60}K_3$ shows different EPR characteristics from those reported in this paper and supports our conclusion that our results are due to singly (not triply) ionized molecules.

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