Bipolaronic model and critical fields in the superconducting state of K_3C_{60}

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A model of "Fullerene" T_c's is proposed on the basis of a strong electron–phonon coupling, which forms a charged Bose-liquid of small bipolarons. The experimental H_{c1} and H_{c2} data suggest that the bipolaronic picture can be used to describe M_xC_{60}. Some anomalous properties of these compounds are predicted.

In an interesting Letter[1] Holczer *et al.* presented measurements of the temperature dependence of the lower critical field H_{c1} and upper critical field H_{c2} in superconducting K_3C_{60} and claimed that "experiments on the critical magnetic fields in K_3C_{60} show a strong type-II superconducting state *with the temperature dependence of the parameters well described by the mean-field theory.*"

Contrary to the last remark, I intend to show that the temperature dependence of

H_{c2} and H_{c1} measured by Holczer *et al.*[1] clearly contradicts the canonical mean-field BCS description and can be explained in terms of the bipolaron theory of superconductivity.[2]

The conclusion by Holczer *et al.*[1] is based on a groundless assertion that "a linear dependence adequately fits the temperature dependence of H_{c2}." However, an unbiased observation of the experimental curves (Figs. 3 and 4 in Ref. 1) clearly reveals a nonlinear (upward) temperature dependence of H_{c2} in the temperature region comparable to that used in Ref. 1 for a linear fit. The upward temperature dependence can hardly be attributed to the sample's inhomogeneity or to the fluctuations, because "the magnetic transition, as pointed out in Ref. 1, is narrow (less than 1 K), suggesting that the superconducting transition is relatively homogeneous."

My point is that because of its cluster structure, K_3C_{60} is a system in which real-space electron pairs (small bipolarons) are formed as they do in a variety of other compounds: Ti_4O_7, $Na_xV_2O_5$, WO_3, Chevreul phases, and in high-T_c metal oxides. The ground state of carriers is a charged, narrow-band Bose liquid[2] with the non-BCS temperature dependences of H_{c2} (Ref. 3) and H_{c1} (Ref. 4):

$$Hc_2 = H_2 \left(\frac{1 - t^{3/2}}{t} \right)^{3/2}, \tag{1}$$

$$Hc_1 \simeq H_1 (1 - t^2), \tag{2}$$

where $t = T/T_c$, and H_2 and H_1 are temperature-independent constants.

As one can see from Fig. 1, the non-mean-field temperature dependence of the upper critical field of a charged Bose gas scattered by impurities [Eq. (1)] fits the experiment[1] much better than the linear mean-field curve (dashed line).

As for H_{c1}, it was already shown in Ref. 1 that the quadradic law [Eq. (2)] describes the experimental data but not the two-fluid or BCS temperature dependence of H_{c1}.

Thus the quadratic temperature dependence of H_{c1}, which was used in Ref. 1 as an empirical law, has a clear microscopic explanation as the temperature dependence of the lower magnetic field of small bipolarons.

Using the magnetic penetration depth for charged bosons (charge $2e$) $\lambda_H^2(0) = (8\pi ne^2/m^{**}c^2)$[2,3] with the electron concentration $n = 5.7 \times 10^{21} 1/\text{cm}^3$ and $\lambda_H(0) = 2400$ Å,[1] we obtain the bipolaron mass $m^{**} = 24\, me$, which gives for the bipolaron bandwidth $D = z\hbar^2/a^2m^{**} \simeq 200$ K, where $z = 6$ is a coordination lattice number, and $a \simeq 10$ Å is the lattice constant. Our formula for the critical temperature of the superconducting transition of small bipolarons [Eq. (3.26) in Ref. 3] gives $T_c < D/6 \simeq 33$ K, which agrees rather well with the experimental values $T_c = 18$ K (K_3C_{60}) (Ref. 5) and $T_c = 30$ K (Rb_3C_{60}) (Ref. 6).

In conclusion, the experimental data of Ref. 1 do not support the claim mentioned at the beginning of this Letter and suggest that the bipolaronic picture better describes the superconducting K_3C_{60}. The coherence length $\xi = 26$ Å, estimated in

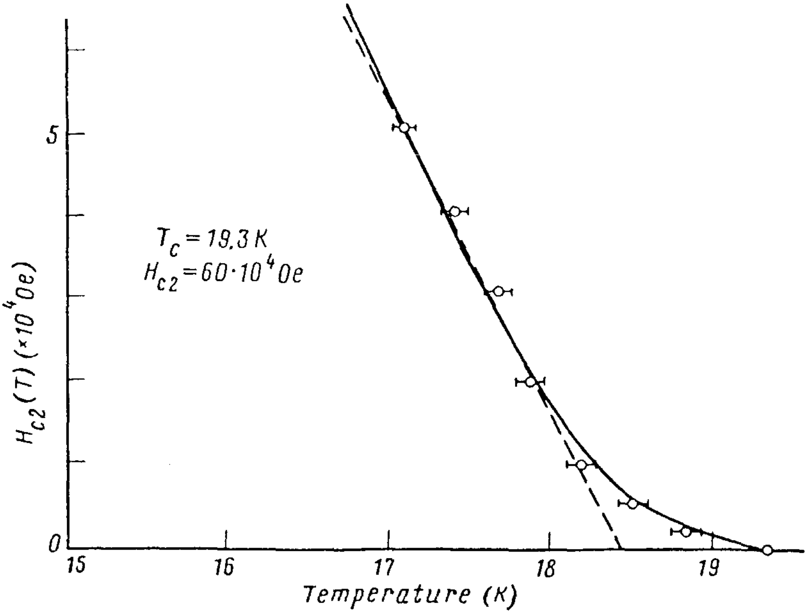

FIG. 1. Temperature dependence of the upper critical field. The solid line is a fit with Eq. (1), the dashed line is a linear fit, used in Ref. 1.

Ref. 1, is not large enough compared with $a = 10$ Å to apply the mean field theory (in Al, which is a classical BCS superconductor, $\xi/a = 10^4$). Of course, more experimental evidence is necessary before a definitive conclusion about the nature of the carriers in K_3C_{60} can be made. On the basis of the bipolaronic picture I predict: a λ-like heat capacity jump at T_c as in He^4, a strong pressure dependence of T_c, and two gaps, the largest of which is the temperature-independent gap which exists *above* T_c.

I would also like to mention that the Coulomb repulsive interaction in M_xC_{60} might be strongly suppressed by a high value of the dielectric constant, as in the metal oxides, where the high-frequency ϵ is larger than 10. On the other hand, the characteristic phonon frequency might be high ($\gtrsim 0.2$ eV). These factors allow the existence of mobile bipolarons with a reasonable value of the effective mass, in contradiction of Anderson's objection.[7]

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