RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 9 1 MARCH 1992-I

Quantitative theory of superconductivity in doped C_{60}

I. I. Mazin,* S. N. Rashkeev,* V. P. Antropov,† O. Jepsen, A. I. Liechtenstein,‡
and O. K. Andersen,
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart-80, Federal Republic of Germany

(Received 11 October 1991)

The electronic part η (the Hopfield factor) of the electron-phonon coupling constant λ for alkali-metal-doped fullerenes A_3C_{60} is calculated within the rigid muffin-tin-potential approximation. It is found that η is large for tangential atomic motions, while for the radial vibrations η is 20 times smaller. We have calculated η for three lattice constants (a = 14.1, 14.4, and 14.6 Å), corresponding approximately to those of C_{60}, Rb_3C_{60}, and (hypothetical) Cs_3C_{60}, and found η = 21, 32, and 36 eV/Å^2. Using semiempirical nearest-neighbor force constants we estimated λ = 0.49, 0.77, and 0.83, and $\langle\omega_{\log}\rangle = 870$ cm^{-1} for the average phonon frequency. The McMillan formula yields T_c = 5, 36, and 44 K for these lattice constants, in reasonable agreement with the available experimental data. The relatively high-temperature superconductivity in A_3C_{60}, as well as the strong dependence of T_c on the dopant, is fully explained within the framework of the conventional superconductivity theory.

Recently discovered[1–3] superconductivity in the alkali-metal-doped fullerene A_3C_{60} (A =K, Rb, Cs) posed the question whether this can be due solely to the conventional phonon mechanism, and, if so, which phonons are responsible for the relatively high T_c in these compounds. Several models have been suggested,[4–6] but they were either qualitative[4] or semiquantitative.[5,6]

The aim of this paper is to present an analysis of this system in terms of the traditional McMillan-Hopfield approximation,[7,8] using as parameters the results of a local-density approximation (LDA) band-structure calculation and available experimental data. In this approach the transition temperature is given by the McMillan formula

$$T_c = \frac{\langle\omega_{\log}\rangle}{1.2}\exp\left(\frac{-1.04(1+\lambda)}{\lambda-\mu^*-0.62\lambda\mu^*}\right), \tag{1}$$

where μ^* is the renormalized Coulomb pseudopotential and $\langle\omega_{\log}\rangle$ is the logarithmically averaged phonon frequency. We shall use a factorization of the electron-phonon coupling constant λ,[8] in terms of the force matrix Φ,

$$\lambda = \sum_{i,\alpha,\beta}\eta^i_{\alpha\beta}(\Phi^{-1})^{i\alpha,i\beta}, \tag{2}$$

where i labels the atoms, α and β are Cartesian indices, and η^i is the so-called Hopfield factor, which does not depend explicitly on the phonon spectrum but reflects the change of the electronic structure due to a displacement of the ith atom. The sum (2) can be grouped into sums over different types of atomic vibrations, which may not necessarily be associated with particular types of atoms. In A_3C_{60} these groups can be classified as alkaline phonons, rotations of the C_{60} molecules, acoustic phonons, tangential vibrations (with C atoms moving on the sphere surface), and radial vibrations with atoms moving perpendicular to the sphere surface. The following simple arguments show that the first two groups are of less importance for superconductivity: Several experiments[3,9,10] seem to indicate that the variation of T_c with different combinations of alkaline dopants is mostly due to the changes in lattice constant, thus eliminating the role of the alkaline phonons. The same follows from band-structure calculations,[11] which show a rigid band picture when doping with alkaline atoms. The three rotational phonons could be important because of their softness. However, since there are 174 intramolecular modes, it is unlikely that the electron-phonon coupling of the rotational phonons is so strong that they are important for superconductivity. Using the same argument we can discard the three acoustic phonons.

Therefore, it is likely that only the intramolecular tangential and radial vibrations are important for superconductivity. This has already been suggested by Martins, Troullier, and Schabel,[12] Schlüter *et al.*,[6] and Varma, Zaanen, and Raghavachari.[5] Before presenting our numerical results, we note that by radial vibrations the intramolecular bond lengths (b) are affected less than by tangential vibrations by a factor of about $b/2R \approx 0.2$. (R is the molecule radius.) The intermolecular bond lengths ($d \gtrsim 2b$) and thereby the conduction-band widths, however, are affected mostly by radial vibrations. Since only 24 of the 60 atoms participate in the bonds between the molecules, we expect the electrons to couple more strongly to the tangential phonons.

We now present our method and results. A standard approximation for obtaining the Hopfield factors using band-structure calculations is the rigid muffin-tin approximation (RMTA), i.e., the individual muffin-tin or, rather, atomic-sphere potentials are moving rigidly with atomic displacements. For an atom in a high-symmetry position a simple formula has be derived:[13]

$$\eta^i = \sum_l (l+1)N^i_l N^i_{l+1}(W^i_l)^2/N, \tag{3}$$

where N and N_l^i are, respectively, the total and partial angular-momentum decomposed densities of states at the Fermi level, and W_l^i is the radial matrix element of the gradient of MT potential, taken between the lth and $(l+1)$th partial waves. For a low-symmetry position, which we have in the fullerene, the generalized form of Eq. (3) is[14]

$$\eta^i_{\alpha\beta} = \sum_L \sum_{L_1} \sum_{L_2} \sum_{L_3} N^i_{LL_1} W^{i\alpha}_{L_1L_2} N^i_{L_2L_3} W^{i\beta}_{L_3L}/N, \qquad (4)$$

where $L \equiv lm$ is short for the angular momentum and magnetic quantum number, and $N^i_{LL_1}$ is the density-of-states matrix at the Fermi level. Equation (4) is not only valid for arbitrary symmetry, but it also represents η directionally decomposed, which is useful for identifying the most important phonon modes.

In general, the RMTA is a good approximation for systems where the screening is so effective that the effect on the one-electron potential of an atom's displacement vanishes outside its own atomic sphere. This is the case for transition metals, where the screening length is 3–7 times smaller than the atomic-sphere radius, and the RMTA is known to work well. In the fullerene this ratio is about a factor of 2 smaller, but presumably still sufficiently large that the RMTA is a reasonably good approximation.

The calculation of λ and T_c [Eqs. (1) and (2)] requires, in addition to the electronic (Hopfield) factor, the force matrix Φ, and the logarithmically averaged phonon frequency $\langle\omega_{\log}\rangle$. For the former, we have made use of the four force-constants fit suggested by Wu, Jelski, and George.[15] With a local coordinate system that has the x axis along an edge between two hexagons and the xz plane through the center of the molecule, we obtain the diagonal elements of the inverse force matrix, $\Phi^{-1}_{xx} = 0.025$ Å^2/eV, $\Phi^{-1}_{yy} = 0.022$ Å^2/eV, and $\Phi^{-1}_{zz} = 0.105$ Å^2/eV, which correspond to characteristic frequencies of 940, 1000, and 460 cm^{-1}, respectively. As expected, the fullerene molecule is relatively stiff (and isotropic) with respect to the tangential vibrations and soft with respect to the radial ones. Thus the radial modes (about 60 of the 180) are in this respect five times more efficient for superconductivity than the tangential ones. However, it will turn out that the radial movements have little effect on the electronic structure at the Fermi level, and their actual contribution to pairing is rather small.

We have calculated of the Hopfield factor according to Eq. (4) using the LDA. Since the calculations are quite time consuming, we were not able to make calculations for all known superconducting compositions. We only performed calculations for three lattice parameters, a = 14.1, 14.4, and 14.6 Å, corresponding roughly to pure C_{60}, Rb_3C_{60}, and (hypothetical) Cs_3C_{60}. The self-consistent band-structure calculations were performed for RbC_{60} and employed the linear muffin-tin orbital (LMTO) method in the atomic-spheres approximation[16] with carefully chosen interstitial spheres. The intramolecular bond length was taken as b=1.42 Å in all cases. The Brillouin-zone integrations were performed with 18 inequivalent k points and the tetrahedron method. The crystal structure used was the uni-directional fcc (space group $Fm\bar{3}$). The details of the band-structure calculations are described in Ref. 11, where it was shown that the effect of doping with different alkaline atoms is essentially due to the change of the lattice constant. Furthermore, the dopant concentration can be accounted for by a rigid shift of the Fermi level.

For a doping of three electrons per molecule and for the three different lattice constants we calculated the Hopfield matrix. The diagonal elements for the three types of carbon atoms are shown in Table I. The values for Rb are negligible and hence not shown. As expected, the radial part η_{zz} is small. It is slightly larger for the contact atoms, which contribute to the hopping between molecules than for the other atoms. The phonon modulation of the intermolecular C-C distance thus has relatively little effect on the conduction band (cf. Refs. 5 and 6). The important effect is that the intramolecular phonons mix in other molecular symmetries than t_{1u} to the conduction-band wave functions. This agrees with the conclusion of Varma, Zaanen, and Raghavachari,[5] who estimated the electron-phonon coupling for different phonons using a quantum-chemical approach and found that only phonons with $\omega > 1000$ cm^{-1} (which are essentially tangential[15]) have considerable coupling. On the contrary, the suggestion in Ref. 12 that the radial vibrations are the most important ones disagrees with our calculation.

One can check these findings by making frozen-phonon calculations for some phonon modes. We have done such calculations for two A_g modes for a = 14.1 Å and found the deformation potentials along the Γ-X line to be 0.3–0.8 and 1–3 eV/Å for the radial and the tangential mode, respectively.

From the values in Table I and taking into account

TABLE I. Diagonal Hopfield factors in eV/Å^2 for the three inequivalent carbon atoms defined as in Ref. 11.

a (Å)	Top-hexagon-edge atoms			Contact atoms			Remaining atoms		
	η_{xx}	η_{yy}	η_{zz}	η_{xx}	η_{yy}	η_{zz}	η_{xx}	η_{yy}	η_{zz}
14.1[a]	0.124	0.204	0.012	0.103	0.229	0.019	0.104	0.220	0.011
14.4[a]	0.181	0.316	0.017	0.163	0.353	0.025	0.159	0.340	0.018
14.6[a]	0.185	0.399	0.019	0.187	0.410	0.025	0.199	0.376	0.019
14.1[b]	0.336	0.360	0.015	0.237	0.308	0.016	0.235	0.378	0.016

[a] Three-electron doping into the t_{1u} band.

[b] Two-hole doping into the h_u band.

TABLE II. Calculated total Hopfield factors, η (eV/Å^2), electron-phonon coupling constants, λ, and T_c (K) for different lattice constants, a (Å) and a doping of three electrons. The experimental T_c values are linearly extrapolated from Fig. 2 of Ref. 2.

a	η	λ	T_c	T_c (Expt.)
14.1[a]	21	0.49	5	11
14.4[a]	32	0.77	36	27
14.6[a]	36	0.83	44	38
14.1[b]	37	0.85	45	

[a] Three-electron doping.
[b] Two-hole doping.

the number of atoms of each kind per molecule, we can calculate the trace of the Hopfield matrix (which is the total Hopfield factor, as it is usually defined[7,8]) $\eta = \sum_{i\alpha}\eta^{i}_{\alpha\alpha} = 21$ eV/Å^2 for $a = 14.1$Å and a doping of three electrons. For this lattice constant, the total λ calculated according to Eq. (2) (including off-diagonal terms) is 0.49. In order to estimate the superconducting transition temperature we adopt a simple three-peak model for the spectral function of the electron-phonon interaction, then $\langle\omega_{\log}\rangle$ for this system may be calculated[8] as $\langle\omega_{\log}\rangle = \omega_{xx}^{\lambda_{xx}/\lambda}\omega_{yy}^{\lambda_{yy}/\lambda}\omega_{zz}^{\lambda_{zz}/\lambda} = 870$ cm^{-1}. T_c calculated from Eq. (1) using these values and the Coulomb pseudopotential $\mu^* = 0.15$ (Ref. 17) is 5 K for $a = 14.1$ Å (Ref. 18).

For $a = 14.4$ and 14.6 Å and a doping of three electrons per molecule (corresponding to Rb_3C_{60} and to hypothetical Cs_3C_{60}), the density of states increases from about 13 to 21 and 24 states/eV spin molecule. As may be seen in Table I, the η's increase correspondingly. The results for η, λ, and T_c are shown in Table II together with the corresponding experimental T_c values linearly extrapolated from Fig. 2 of Ref. 2. The agreement is as good as in elementary transition metals,[7] and within the accuracy of the RMTA. An interesting possible cause of the overestimation of the slope of T_c versus the lattice constant is the fact that when the bandwidth, W, becomes comparable to the phonon frequencies the McMillan formula overestimates T_c (cf. Ref. 19) and fails completely when $W \simeq \omega_{\rm ph}\sqrt{\lambda}$. In Rb_3C_{60} the calculated $W \approx 0.3$ eV$\gtrsim 3\omega_{\rm ph}\sqrt{\lambda}$.

Recently[20] a very small bandwidth ($W \simeq 0.02$ eV) was estimated from the experimental coherence length $\xi = 26$ Å and penetration depth $\lambda_L = 2400$ Å, thus casting doubt on the LDA. Assuming the clean limit, we get from our LDA calculations $\lambda_L = c/\omega_{\rm pl} \approx 1300$ Å and $\xi = \hbar v_F/\pi\Delta(0) \approx 100$ Å [with $2\Delta(0)/k_BT_c = 4$]. We have used the average Fermi velocity for v_F, however, when the Fermi velocity varies over the Fermi surface, the value that enters the formula for ξ is closer to the minimal than to the average Fermi velocity. We have estimated the relevant value to be less than one half of the average v_F. The remaining discrepancy with the experiment may be due to the small mean free path.

Even though rumors that iodine-doped C_{60} is superconducting turned out to be incorrect, hole doping might be an interesting possibility. We have performed similar calculations for a material, doped with two holes per molecule and $a = 14.1$ Å, using a rigid band model. We find $N(0) = 24$ states/eV spin molecule, $\eta = 37.1$ eV/Å^2, $\lambda = 0.85$, and predict T_c to be about 45 K.

The physical picture we have described above can be illustrated with the help of a negative-U Hubbard model: Due to the small intermolecular hopping, an electron spends a long time on a particular molecule, where it is spread over the whole surface. Retarded interaction with the stretching (high-frequency) surface vibrational modes leads to a dynamical attraction with respect to another electron residing on the same molecule. Sufficient strength of this attraction is provided by the large number of the internal degrees of freedom (i.e., of the intramolecular vibrations). Since the size of this effective-negative-U center is large in comparison with the screening length, the Coulomb repulsion does not prevent the superconductivity.

In conclusion, we have performed calculations of the electron-phonon coupling using the LDA and the LMTO method for the band structure, the rigid muffin-tin approximation for the electron-ion scattering, and a semiempirical force matrix for the phonons. The results show that superconductivity in doped fullerenes can be completely explained by the conventional phonon mechanism. The relevant phonons are essentially the intramolecular tangential carbon vibrations. Calculations for different lattice constants confirm the expectation that the difference of T_c for different dopants is due to the chemical pressure. The reason for the relatively high transition temperature is that the corresponding phonons are very hard and still have moderate coupling constants. In fact this was the reasoning of Ginzburg and Kirzhnits[21] in 1977 for suggesting carbon compounds as potential high-temperature superconductors. While the fullerene is by no means the only material with phonon frequencies as high as about 10^3 cm^{-1}, it is probably the only material having at the same time moderate-sized λ.

We thank Dr. J. Zaanen, Dr. O. V. Dolgov, and Dr. O. Gunnarsson for helpful discussions. The support from Höchleistungsrechenzentrum (HLRZ), Jülich, FRG, where parts of the calculations have been performed, is gratefully acknowledged. One of us (A.I.L.) acknowledges support from the A. von Humboldt foundation.

---

* On leave from P.N.Lebedev Physical Institute, Moscow, U.S.S.R.

† On leave from Institute of Metal Physics, Ekaterinburg, U.S.S.R.

‡ On leave from Institute of Chemistry, Ekaterinburg, U.S.S.R.

[1] A.F.Hebard, M.J.Rossinsky, R.C.Haddon, D.W.Murphy, S.H.Glarum, T.T.M.Palstra, A.P.Ramirez, and A.R.Kor-

tan, Nature (London) **350**, 600 (1991).

[2] R.M.Fleming, A.P.Ramirez, M.J.Rossinsky, D.W.Murphy, R.C.Haddon, S.M.Zahurak, and A.V.Makhija, Nature (London) **352**, 787 (1991).

[3] S.P.Kelty, C.C.Chen, C.M.Lieber, Nature (London) **352**, 223 (1991).

[4] F.C.Zhang, M.Ogata, and T.M.Rice, Phys. Rev. Lett. **67**, 3452 (1991).

[5] C.Varma, J.Zaanen, and K.Raghavachari, Science **254**, 989 (1991).

[6] M.Schluter, M.Lanoo, M.Needels, G.A.Baraff, and D.Tomanek, Phys. Rev. Lett. **68**, 526 (1992).

[7] D.Rainer, Prog. Low Temp. Phys. **10**, 371 (1986).

[8] *The Problem of the High-Temperature Superconductivity*, edited by V.L.Ginzburg and D.A.Kirzhnits (Consultants Bureau, New York, 1982).

[9] G.Sparn, J.D.Thompson, S.-M.Huang, R.B.Kaner, F.Diederich, R.L.Whetten, G.Grüner, and K.Holczer, Science **252**, 1829 (1991).

[10] J.E.Schirber, D.L.Overmyer, H.H.Wang, J.M.Williams, K.D.Carlson, A.M.Kini, U.Welp, and W.-K.Kwok, Physica C **178**, 137 (1991).

[11] S.Satpathy, V.P.Antropov, O.K.Andersen, O.Jepsen, O.Gunnarsson, and A.I.Liechtenstein (unpublished).

[12] J.L.Martins, N.Troullier, and M.Schabel (unpublished).

[13] G.Gaspari and B.Gyorffy, Phys. Rev. Lett. **28**, 801 (1972).

[14] I.I.Mazin, S.N.Rashkeev, and S.Y.Savrasov, Phys. Rev. B **42**, 366 (1990).

[15] Z.C.Wu, D.A.Jelski, and T.F.George, Chem. Phys. Lett. **137**, 291 (1987).

[16] O.K.Andersen, Phys. Rev. B **30**, 3060 (1975).

[17] For transition metals μ^* usually lies in the range from 0.10 to 0.12. μ^* is related to the unrenormalized μ by $\mu^* = \mu/[1+\log(\omega_C/\omega_{\rm ph})]$, where ω_C characterize the frequency dependence of the Coulomb repulsion, and $\omega_{\rm ph}$ is a characteristic phonon frequency. Possible estimates for ω_C in A_3C_{60} are $\omega_{\rm pl} \approx 2$ eV or $E_{\rm gap} \approx 3.5$ eV. For elementary metals $\omega_{\rm pl}$ is an order of magnitude larger, and $\omega_{\rm ph}$ is several times smaller. One would therefore expect a weaker renormalization. However, it may very well be that the unrenormalized μ is smaller than in usual metals (cf. the Stoner-factor analysis in Ref. 11).

[18] The McMillan formula (MF) was originally derived for a particular (Nb) shape of the Eliashberg function $\alpha^2F(\omega)$; *a posteriori* microscopical justification of MF (Ref. 8) shows that particularly the prefactor and the coefficient to $\lambda\mu^*$ are dependent on the shape of $\alpha^2F(\omega)$. For these reasons it is possible that the MF is not very accurate for A_3C_{60}. However, the functional dependence given by the MF is rather universal (Ref. 8), and it was the meaning that was implied throughout the present paper.

[19] R.Michas, J.Ranninger, and S.Robaszkievics, Rev. Mod. Phys. **62**, 113 (1990).

[20] K.Holczer, O.Klein, G.Grüner, J.D.Thompson, F.Diederich and R.L.Whetten, Phys. Rev. Lett. **67**, 271 (1990).

[21] *The Problem of the High-Temperature Superconductivity* (Ref. 8), p. 28.