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Intercalation and high temperature superconductivity of fullerides

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Abstract. Intercalation of polyatomic molecules into a superconductor can drastically affect the properties of the compound. A mechanism responsible for a large increase in T_c for such systems is proposed. It explains the recent remarkable observation of high T_c superconductivity in the hole-doped C_{60}/CHX_3 (X≡Cl, Br) compounds and the large shift in their T_c upon Cl→Br substitution. The increase in T_c is due to contribution to the pairing arising from the interaction of electrons with the vibrational manifold of the molecule. The proposed mechanism opens up the possibility to observe a site-selective isotope effect. We also suggest that intercalating CHI_3 would further increase the critical temperature to $T_c \simeq 140$ K.

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This paper is concerned with the impact of intercalation by polyatomic molecules on the properties of superconductors. The study has been motivated by the recent remarkable observation of high T_c caused by intercalation of $CHBr_3$ (bromoform) and $CHCl_3$ (chloroform) molecules into hole-doped fullerides [1] (see also description of [1] in Ref. [2]). The discovery of high temperature superconductivity [1] in these systems ($T_c = 117$ K for $C_{60}/CHBr_3$; $T_c = 80$ K for $C_{60}/CHCl_3$) has attracted a lot of attention and raises the fundamental question about the nature of this phenomenon.

The usual superconducting fullerides (see, *e.g.*, the reviews [3,4]) are chemically electron-doped compounds (*e.g.*, Rb_3C_{60}, K_3C_{60}). It is believed that their superconductivity is due to the coupling of electrons to the intramolecular vibrational modes. The vibrational spectrum spreads over a broad region ($\Omega_L \simeq 270$ cm^{-1} $\rightarrow \Omega_H \simeq$ 1500 cm^{-1}). Strictly speaking, all modes contribute to the pairing but the question of which region of the vibrational spectrum plays a major role is still controversial (see, *e.g.* [4]).

A new exciting development was described in [5]; with the use of gate-induced doping, a hole-doped fulleride compound was created without chemical dopant. As a result a major increase in T_c to 52 K(!) was observed. This is caused by the different properties of the valence band relative to the conduction band such as the density of states. Recently, this technique was complemented by intercalating the molecules $CHBr_3$ and $CHCl_3$ into the crystal [1]. These molecules are placed in regions near the C_{60} units. This has resulted in a dramatically higher T_c again: $T_c \simeq 117$ K(!). It was indicated in [1] that the change in lattice spacing may be responsible for the increase in T_c. This is an interesting scenario which needs to be studied in detail. Here we propose another additional mechanism. It is of interest in its own right; furthermore, it can provide for a quantitative explanation of the drastic increase in T_c observed in [1].

It is very essential to note that the experimentalists [1] observed not only a remarkable high T_c for the C_{60}/CHX_3 compound (X≡ Br, Cl), but also a large difference in the value of T_c for X≡ Br *vs.* X≡ Cl. Whereas $T_c \equiv T_C^{Br} \simeq 117$ K was observed for X≡Br, the value of T_c for X≡ Cl turned out to be much smaller ($\simeq 80$ K), although still very high. The structures of the bromoform and chloroform molecules are similar and therefore a microscopic explanation of the strong change in the critical temperature is also of definite interest.

The picture we propose is that the intercalated molecules themselves actively, and importantly, participate in the pairing. The internal vibrational modes of the molecules provide for an additional attraction which leads to higher T_c. Such a mechanism was considered by one of the authors in [6]. Therefore, our major focus is on the vibrational spectra of these molecules.

Let us start with the parent hole-doped fulleride ($T_c =$ 52 K). The order parameter for this superconductor is described by the equations:

$$\Delta(\omega_n)Z(\omega_n) = \pi T \sum_{\omega_{n'}} \left[\lambda_1 D(\omega_n - \omega_{n'}; \tilde{\Omega}_1) - \mu^\star\right] \frac{\Delta(\omega_{n'})}{|\omega_{n'}|} \quad (1)$$

$$Z(\omega_n) = 1 + \lambda_1 \pi T \sum_{\omega_{n'}} D(\omega_n - \omega_{n'}; \tilde{\Omega}_1) \frac{\omega_{n'}}{|\omega_{n'}|} \cdot \quad (2)$$

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Here λ_1 is the electron-phonon coupling constant, $\tilde{\Omega}_1$ is the characteristic (average) intramolecular vibration frequency ($\tilde{\Omega}_1 = \langle \Omega^2 \rangle^{1/2}_{\text{intra}}$; see, *e.g.*, Ref. [4]), $D = \tilde{\Omega}_1^2 \left[\tilde{\Omega}_1^2 + (\omega_n - \omega_{n'})^2 \right]^{-1}$ is the phonon Green's function, $\omega_n = (2n+1)\pi T$, $T = T_{\text{c}}$, Z is the renormalization function, and $\mu^\star$ is the Coulomb pseudopotential. We are employing the temperature Green's functions formalism (see, *e.g.* [7]).

Equations (1, 2) correlate the value of T_{c} with the values of the parameters $\tilde{\Omega}_1$, λ_1, $\mu^\star$. It is natural to assume that hole-doped fullerides [5] differ from electron-doped compounds obtained by chemical doping in the magnitude of the coupling constant λ_1, whereas the values of the characteristic phonon frequency $\tilde{\Omega}_1$ and $\mu^\star$ should remain similar. Following reference [4], let us take as an estimate $\tilde{\Omega}_1 \simeq 0.1$ eV and $\mu^\star = 0.15$. Then, the value of $T_{\text{c}} = 52$ K observed in [5] implies the value $\lambda_1 \approx 0.75$. We would like to emphasize that if we were to adopt a different value of $\tilde{\Omega}_1$ (*e.g.*, $\tilde{\Omega}_1 = 80$ meV, or even 50 meV), this would affect some intermediate parameters (see below), but the final result, namely the value of T_{c} for the C_{60}/CHBr$_3$ compound, would not be affected in any noticeable way.

In the intercalated C_{60} compound, polyatomic molecules CHX$_3$ (X = Cl, Br) are added at interstitial sites. (see, *e.g.*, Fig. 1 in Ref. [2]). As indicated above, their presence is found to result in two phenomena: 1. A remarkable high T_{c} ($T_{\text{c}} \simeq 117$ K) for X≡Br; 2. A very high, but significantly lower T_{c} ($\simeq 80$ K) for intercalation by chloroform (X≡Cl).

The molecules have a relatively complex vibrational spectra (see, *e.g.*, Ref. [8]), but it can be modeled as an additional phonon mode. Then, instead of equations (1, 2) we have:

$$\Delta(\omega_n) Z(\omega_n) = \tag{3}$$

$$\pi T \sum_{\omega_{n'}} \left[\sum_{i=1,2} \lambda_i D(\omega_n - \omega_{n'}; \tilde{\Omega}_i) - \mu^\star \right] \frac{\Delta(\omega_{n'})}{|\omega_{n'}|}$$

$$Z(\omega_n) = 1 + \pi T \sum_{i=1,2} \lambda_i \sum_{\omega_{n'}} D(\omega_n - \omega_{n'}; \tilde{\Omega}_i) \frac{\omega_{n'}}{|\omega_{n'}|} \cdot \tag{4}$$

The values of λ_1 and $\tilde{\Omega}_1$ correspond to the parent, non-intercalated state (see Eq. (1)). We assume that the value of $\mu^\star$ is also essentially unchanged, although the presence of molecules and their electrons might lead to an effective decrease in $\mu^\star$ (see below).

The presence of the second term ($\sim \lambda_2$) in the sum on the right-hand side of equation (3) leads to an increase in T_{c} relative to that of the parent compound ($T_{\text{c}}^0 \simeq 52$ K). The magnitude of this increase depends on the values of $\tilde{\Omega}_2$ and λ_2.

As is known, the value of the coupling constant λ is described by the McMillan relation [9]:

$$\lambda = \frac{\nu \langle I^2 \rangle}{M \langle \Omega^2 \rangle}, \tag{5}$$

where ν is the density of states, I is the matrix element, and M and Ω describe the vibrational spectrum. We will show that the differences in the vibrational spectra of the CHX$_3$ molecules can account quantitatively for the observed large difference in T_{c} upon chemical substitution (Cl→Br). Let us now turn to quantitative analysis.

The vibrational spectrum of the CHCl$_3$ molecule (see, *e.g.* [8]) contains five major modes which can contribute to the pairing. These modes are $\Omega^{(1)\text{Cl}} \simeq 262$ cm^{-1}, $\Omega^{(2)\text{Cl}} \simeq 366$ cm^{-1}, $\Omega^{(3)\text{Cl}} \simeq 668$ cm^{-1}, $\Omega^{(4)\text{Cl}} \simeq 761$ cm^{-1}, $\Omega^{(5)\text{Cl}} \simeq 1216$ cm^{-1} (the notation Ω^{Cl} means that we consider the chloroform molecule; the modes $\Omega^{(1)\text{Cl}}$, $\Omega^{(4)\text{Cl}}$, $\Omega^{(5)\text{Cl}}$ are degenerate). All these modes are Raman active and can couple to the conduction electrons [4,8].

Consider now the CHBr$_3$ molecule. It has the same configuration and a similar set of modes, but all of them are noticeably softened. Indeed, according to reference [8], $\Omega^{(1)\text{Br}} \simeq 154$ cm^{-1}, $\Omega^{(2)\text{Br}} \simeq 222$ cm^{-1}, $\Omega^{(3)\text{Br}} \simeq 539$ cm^{-1}, $\Omega^{(4)\text{Br}} \simeq 656$ cm^{-1}, $\Omega^{(5)\text{Br}} \simeq 1142$ cm^{-1}. As a result, it can be expected that the well-known "softening" mechanism (*cf.*, *e.g.* [10]) manifests itself. That is, T_{c} is expected to increase as a result of the substitution.

The effective coupling constants (see Eq. (5)) also contain the mass (M) factor. It is crucial that all these modes in CHX$_3$ molecule correspond, mainly, to the motion of the light carbon ion relative to the heavy X$_3$ (X≡ Cl, Br) unit. As a result, $M \approx M_{\text{C}}$ and the difference in coupling strength between the two compounds is mainly determined by the aforementioned frequency shift ($\lambda_i \sim \Omega_i^{-2}$). Note that the hydrogen stretching mode is not essential since it lies much higher in energy and, if desired, can be singled out by isotope substitution.

Let us consider the C_{60}/CHCl$_3$ system first. Using the above mentioned vibrational modes taken from literature [8], we determine the average frequency to be $\tilde{\Omega}_2 \equiv \Omega_2^{\text{Cl}} = 85$ meV (care should be taken of the degeneracy of the modes). Performing a numerical calculation with equations (3, 4) and the derived frequency $\tilde{\Omega}_2$, we obtain that the observed value $T_{\text{c}} = 80$ K [1] implies the value $\lambda_2^{\text{Cl}} \approx 0.2$. Such a value is small and perfectly realistic, confirming that the observed rise upon intercalation can be assigned to the action of the added intramolecular modes.

Let us now substitute Cl→Br and compare C_{60}/CHCl$_3$ and C_{60}/CHBr$_3$. This comparison is an important step in our analysis. As was stressed above, the total coupling constant λ_2^{Br} changes relative to λ_2^{Cl} primarily as a result of the vibrational frequency shifts. Using the literature values for the vibrational frequencies Ω_i^{Br} and Ω_i^{Cl} (see above), we calculate that $\lambda_2^{\text{Br}} \approx 2.65 \lambda_2^{\text{Cl}}$. Therefore, the "softening", indeed, leads to a noticeable increase in the coupling constant.

Since $\lambda_2^{\text{Cl}} \approx 0.2$ (see above), we obtain $\lambda_2^{\text{Br}} \approx 0.55$. Using this value for λ_2^{Br} and the frequency $\Omega_2^{\text{Br}} \simeq 70$ meV infered from the above vibrational spectra, we solve equations (3) and (4) and obtain $T_{\text{c}} \simeq 110$ K for the C_{60}/CHBr$_3$ compound. It is important to emphasize once more that during this last step the value of T_{c}^{Br} has been obtained without any additional adjustable parameter. Table 1 summarizes our numerical results. The derived value $T_{\text{c}} \simeq 110$ K is close to the experimentally observed

Table 1. Calculation of λ_2^{Cl}, λ_2^{Br} and T_c for C_{60}/$CHBr_3$. λ_1: coupling to intramolecular vibrations of C_{60}, λ_2: additional coupling to the vibrational modes of $CHCl_3$ or $CHBr_3$. The coupling constant λ_2 for $CHBr_3$ is fixed by the other set of parameters (see text).

	hole-doped C_{60}	C_{60}/$CHCl_3$	C_{60}/$CHBr_3$
λ_1	0.75	0.75	0.75
λ_2	0	0.2	0.55
T_c [K]	52 [5]	80	110

one $T_\mathrm{c} \simeq 117$ K [1]. Since our calculation made use of some approximations, the agreement can be considered as rather good.

References [1] and [11] also describe the study of electron-doped systems. We first note that doped electrons are filled into the conduction band made of orbitals with T_{1u} symmetry (at the Γ point), whereas doped holes fill in the valence band which has H_{1u} symmetry (see, *e.g.*, Ref. [12].) A group theoretical analysis shows that in the former case, electrons couple to intramolecular vibrations of the C_{60} cluster belonging to the five-fold degenerate h_g irreducible representation. In the hole-doped case, on the other hand, the higher symmetry of the valence band allows for coupling of holes to additional vibrational modes. Both h_g and the four-fold g_g vibrations are Jahn-Teller active in hole-doped systems. One can therefore expect that the overall coupling is larger for holes than for electrons, thereby enhancing T_c.

The procedure described above for hole-doped C_{60}/CHX_3 can be applied to the electron-doped case and reproduce the results obtained in reference [1] as well. Indeed, from equations (1, 2) we conclude that the observed value $T_\mathrm{c} = 11$ K [11] is reached for $\lambda_1 \approx 0.5$. Since the frequencies of the h_g and g_g modes are in the same range [13], we take the same value of $\tilde{\Omega}_1$ for electron- as for hole-doped systems. From equations (3, 4) we further obtain the experimentally observed $T_\mathrm{c} = 18$ K for C_{60}/$CHCl_3$ with an additional coupling $\lambda_2^{\mathrm{Cl}} \approx 0.07$. The scaling relation $\lambda_2^{\mathrm{Br}} \approx 2.65\lambda_2^{\mathrm{Cl}}$ then leads to $\lambda_2^{\mathrm{Br}} \approx 0.2$. As a result we obtain $T_\mathrm{c} \approx 30$ K for electron-doped C_{60}/$CHBr_3$. This is in good agreement with the experimental value $T_\mathrm{c} \simeq 26$ K [1].

We have focused on the vibrational spectra of the intercalated molecules. Note that an additional contribution to the pairing could also come from the Coulomb interaction and the corresponding polarization of the electronic systems of the molecules, virtual transitions between electronic levels (see Ref. [15]). This additional attraction would correspond to the electronic energy scale and can be described as an effective decrease of $\mu^\star$ (*cf.* Ref. [16]). Note that the polarizability $\alpha^{\mathrm{Br}} \equiv \alpha_{\mathrm{CHBr_3}}$ is much larger than α^{Cl} [17]. This question will be considered elsewhere. Another factor indicated in [1] is the increase in "ionic" radius upon intercalation and Cl→Br substitution. However, recent experiments indicate that lattice stretching resulting from the intercalation cannot account for the increase in T_c [18]. It thus remains an open question whether this effect by itself is capable of producing such a giant impact on T_c.

We propose also the following experiment directly related to our approach. Namely, one can observe site selective isotope effect by substituting $^{12}\mathrm{C}\leftrightarrow{}^{13}\mathrm{C}$ on the intercalated molecules. Such substitution will affect T_c because the vibrational manifold of these molecules contribute to the pairing. From equations (3, 4) and the experimentally observed shift in $\Omega^{(j)\mathrm{Cl}}$ $j = 1, \ldots, 5$ for $CHCl_3$ [19] we obtain that $\Delta T_\mathrm{c} = T_\mathrm{c}(^{12}\mathrm{C}) - T_\mathrm{c}(^{13}\mathrm{C}) \simeq -0.2$ K. Though small, such a shift can be measured experimentally (*cf.* [20]). The corresponding isotope coefficient $\alpha_\mathrm{C}^{\mathrm{Cl}} \equiv -(M_\mathrm{C}/\Delta M_\mathrm{C})(\Delta T_\mathrm{c}/T_\mathrm{c})$ is of order 0.03. If, in addition, one also substitutes $^{35}\mathrm{Cl}\leftrightarrow{}^{37}\mathrm{Cl}$ a shift in T_c of about ~ -0.35 K can be observed.

A more precise numerical treatment would require proper use of tunneling spectroscopy, similar to that described in reference [14], in order to obtain the accurate form of $\alpha^2(\Omega)F(\Omega)$[1]. Our aim was to identify the mechanism responsible for the strong increase in T_c for the intercalated compounds. We argued that this mechanism involves the vibrational manifolds of the intercalated molecules. We demonstrated that this mechanism can naturally lead to high values of T_c, as observed in reference [1].

Finally, we would like to propose to carry out the same experiment as in reference [1] with the compound C_{60}/CHI_3. The corresponding modes are $\Omega^{(1)\mathrm{I}} \simeq 110$ cm^{-1}, $\Omega^{(2)\mathrm{I}} \simeq 154$ cm^{-1}, $\Omega^{(3)\mathrm{I}} \simeq 425$ cm^{-1}, $\Omega^{(4)\mathrm{I}} \simeq 578$ cm^{-1}, $\Omega^{(5)\mathrm{I}} \simeq 1068$ cm^{-1} [21]. Our analysis shows that such intercalation leads to $T_\mathrm{c} \simeq 140$ K(!) Note also that the site selective isotope effect $^{12}\mathrm{C}\leftrightarrow{}^{13}\mathrm{C}$ for CHI_3 molecules has the additional advantage that iodine has no natural isotopes.

The mechanism of pairing proposed here and connected with the interaction of electrons with vibrational manifolds of intercalated molecules can provide for a drastic increase in T_c. The search for new systems which would similarly permit the intercalation by appropriate polyatomic molecules is an exciting and promising direction in the quest of new high temperature superconductors.

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Note added in proof

Recent tunneling measurements [22] have shown the appearance of additional peaks upon intercalation. This additional structure corresponds to the vibrational manifold of the molecules, and Cl→Br substitution leads to the "softening". The data of reference [22] support our theory.

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[1] Note that the analysis of $\alpha^2 F$ has to be made with considerable care, as the vibrational manifold of the intercalated molecules partially overlaps with that of the C_{60} intramolecular modes.

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