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A correlation between ionization energies and critical temperatures in superconducting A_3C_{60} fullerides

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ABSTRACT

Buckminster A_3C_{60} fullerides (A = alkali metal) are usually superconductors with critical temperatures T_c in the range 2.5–40 K. Although they are very similar in size, structure and many other aspects, the effect of the alkali atoms on T_c has generally been understood in terms of the variation of the lattice constant. Here we show that there seems to be a direct correlation between the sum of the ionization energies of the three alkali atoms in the superconducting A_3C_{60} compounds and the corresponding critical temperatures. A linear fit of the correlation implies a certain limit for the sum, below which superconductivity should not occur. Ionization energies have so far not been connected to superconductivity.

1. Introduction

Many conventional superconductors show different critical temperatures (T_c) depending on their structure. The pure material gallium (Ga) is superconducting in four different crystal structures with a transition temperature range from 1 K to 8 K. In contrast, niobium and tantalum have identical crystal structure (bcc) with the same lattice constant $a = 0.330$ nm, but their transition temperatures differ by a factor of two. Obviously, both the structure of the solid and the electron configuration are important for the phenomenon of superconductivity.

In the following we will examine 14 different alkali metal doped C_{60} compounds, exhibiting similar crystal structures with relatively similar lattice parameters, but a variation in T_c from 2.5 K to 40 K [1,2].

The solid state structure of pure C_{60} molecules corresponds to a truncated icosahedron, consisting of 12 pentagonal and 20 hexagonal faces [3]. The unit cell of a C_{60} crystal may be described as face centered cubic (fcc) with a large lattice constant of $a = 1.417$ nm and Fm$\bar{3}$m symmetry [1]. Van der Waals forces are responsible for the bonding.

The C_{60} lattice allows several ways to incorporate other atoms, usually alkali or earth alkali metals, into its structure. The stoichiometry of these A_xC_{60} variations may range from $x = 0$ to 6 and even higher [1]. The C_{60} buckyballs are semiconductors and

are considered as moderately effective electron acceptors. But the compounds with $x = 3$ become metallic and are, with few exceptions, superconducting [1].

The lattice structure of these A_3C_{60} compounds is usually fcc at room temperature, with the alkali metals occupying the tetrahedral and octahedral interstitial vacancies in the lattice (see Fig. 1). The tetrahedral sites are close in size to the Na$^+$ ion, while the octahedral site is larger than any alkali atom [1].

The lattice constant varies with the different size of the intercalated alkali metals from $a = 1.4092$ nm for Na$_2$RbC$_{60}$ to $a = 1.4761$ nm for Cs$_3$C$_{60}$ [4–12]. The latter exhibits superconductivity only at high pressure, with a two phase mixture of the bct and A15 structures [11], or an fcc structure, with slightly different critical temperatures [12].

The ionic character of these A_3C_{60} compounds is assumed to be $[A_3]^{3+}[C_{60}]^{3-}$, with charge transfer nearly complete [1]. The critical temperatures range from around 2.5 K to 33 K at ambient pressure, and are as high as 40 K for Cs$_3$C$_{60}$ at high pressure [1,2,4]. The metallic character is provided by the electrons of the alkali metals. The resistivity at T_c is relatively high, typically e.g. for K$_3$C$_{60}$ $\rho \approx 2 \times 10^{-5}$ Ωm [13,14], which is comparable with the resistivity of optimum doped high temperature superconductors (HTSC) [15].

2. Motivation

It has been shown for a wide number of materials that the different T_c values of superconducting A_3C_{60} are correlated to the lattice parameter a [16,17]. Expansion of the lattice usually leads

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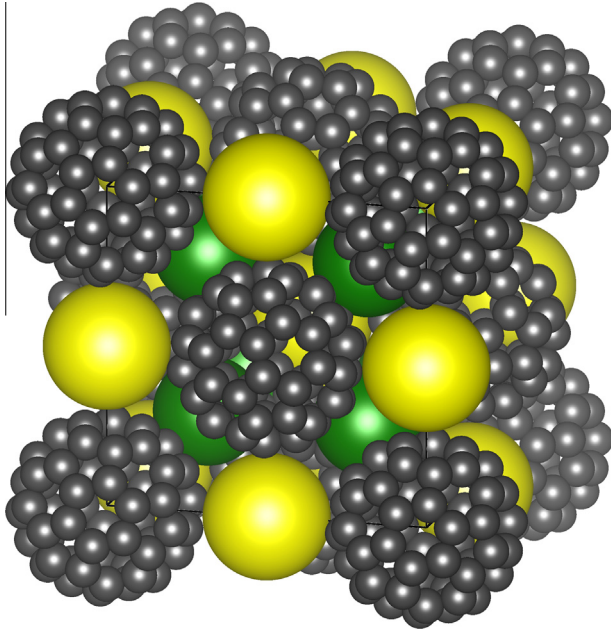
Fig. 1. A_3C_{60} fcc structure. The octahedral sites are displayed in yellow, the tetrahedral sites in green. Only one orientation of the C_{60}^{3-} anions is displayed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to higher critical temperatures. An explanation for this empirical "T_c–a" correlation would be that by intercalating alkali metals of different size into the C_{60} lattice the distance between the atoms (and so their band structure) is altered. Recent papers have connected the influence of the lattice parameter to the ratio U/W, where U is the on-site Coulomb repulsion, and W is the bandwidth of the conducting band [18]. This ratio can be understood as a form of density of states (DOS), in accordance with the BCS theory. It also controls the metal–insulator transition. By expanding the lattice, the bandwidth is narrowed [12], leading to slightly different electronic properties and thus different critical temperatures [19].

Here, we present a new approach. The alkali s^1 electrons provide half filling of the t_{1u} conducting band of the C_{60} molecule. This seems to be the optimal configuration, in terms of the highest critical temperature, for superconductivity in these materials [1]. An examination of the electronic properties of the alkali s^1 electrons seemed then reasonable to us. For compounds with identical crystal structure and very similar lattice parameters the density of states and the resulting band structure might be affected by the molecular bonding. This bonding is, in turn, dependent on the ionization potential of the species involved. This was a motivation to investigate the sum of the ionization energies ΣE_{ion} of the three alkali atoms per C_{60} buckyball. Of course, given that there exists a correlation between the lattice constant and the critical temperatures, it is reasonable to expect the ionization energies to also correlate, since they depend on the ionic/atomic radii, which in turn ultimately determine the lattice constant. Through the use of the ionization energies, we are presenting a new perspective on the matter.

3. Results and discussion

Table 1 is a summary of 14 different fullerides with their lattice parameters at room temperature, T_c and ΣE_{ion}, including Cs_3C_{60} under pressure and the Na_3C_{60} and Li_3C_{60} compounds. It should be noted that it has not been possible so far to produce Li_3C_{60} in a stable form and Na_3C_{60} might partly transform into Na_2C_{60} and Na_6C_{60} [20]. Also, at low temperatures, Na_2KC_{60}, Na_2RbC_{60},

Table 1
Physical properties and ΣE_{ion} in A_3C_{60}. The Li_3C_{60} compound does not form a stable crystal under normal pressure conditions. Data are from Refs. [4–12,16,21].

| Material	Lattice		T_c (K)	ΣE_{ion} (eV)
	Structure	a (10^{-10} m)		
Li_3C_{60}	–	–	–	−16.173
Na_3C_{60}	fcc	14.191	–	−15.417
ΣE_{ion} = 0.0882 eV/K · T_c − 14.9 eV				
Na_2KC_{60}	fcc	14.122	2.5	−14.619
Na_2RbC_{60}	fcc	14.092	3.5	−14.455
$Na_2Rb_{0.5}Cs_{0.5}C_{60}$	fcc	14.114	8.4	−14.314
Na_2CsC_{60}	fcc	14.126	12	−14.172
K_3C_{60}	fcc	14.240	19	−13.023
K_2RbC_{60}	fcc	14.299	21.8	−12.859
K_2CsC_{60}	fcc	14.292	24	−12.576
Rb_2KC_{60}	fcc	14.336	24.4	−12.695
Rb_3C_{60}	fcc	14.384	29	−12.531
Rb_2CsC_{60}	fcc	14.431	31	−12.248
$RbCs_2C_{60}$	fcc	14.555	33	−11.965
Cs_3C_{60}	fcc	14.761	35	−11.682

$Na_2Rb_{0.5}Cs_{0.5}C_{60}$ and Na_2CsC_{60} undergo a structural change from face centered cubic to simple cubic lattice [4,16].

Fig. 2 shows the sum of the ionization energies ΣE_{ion} for different alkali atoms plotted versus the transition temperature T_c. Using a linear regression, a straight line fits the data in the range $2\ K \leqslant T_c \leqslant 40\ K$ with a slope of 88.2 meV/K and an ordinate intercept value of −14.9 eV.

T_c increases with lower bonding energies of the outer electron of the alkali atoms. But the ordinate intercept demonstrates that there is an ionization threshold of −14.9 eV to obtain superconductivity. Below this value, the bonding may be too strong to allow the formation of Cooper pairs. We would expect this for stable low temperature phases of the materials Li_3C_{60} and Na_3C_{60}. It is interesting to note that the third ionization energy of C_{60} has been measured in the same order of magnitude (−14.8 eV/−16.6 eV [22]). One possible explanation for this could be that below $|14.8\ eV|$ C_{60} can only attract electrons from atoms other than buckyball neighbors.

The slope of the correlation has a value of approximately 88 meV/K or 1024 k_B. It might be a measure for the pairing force or coupling mechanism in the A_3C_{60} compounds. The reason could be the direct influence of the ionization on the density of states and the band structure. The ionization sums, except for the Cs_3C_{60} material, range from −14.619 eV to −11.965 eV, spanning about 2.65 eV. The electron affinity of the C_{60} molecule lies, incidentally, around this same value of 2.6 eV [23].

The calculation of ionization energies in a molecule is usually rather complex. Given the relatively large separation between the alkali atoms in the molecule and the uniform background
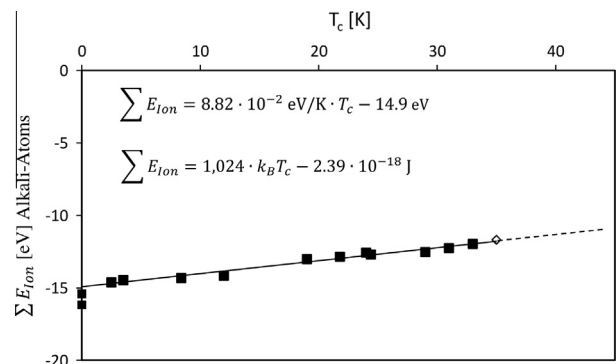
Fig. 2. Relationship between ionization energy sum and critical temperature. Data points are from Table 1, the open data point refers to Cs_3C_{60}. The slope is calculated from all data points, with the exception of pressurized Cs_3C_{60}.

provided by the C_{60}^{3+} anions, we use the sum of the first ionization energies of the isolated atoms.

It is worth noticing that the importance of considering the ionization energies of the outermost electrons has already been mentioned by the authors in an earlier paper on HTSCs [24].

The compound $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ fits the linear behavior quite well; the "$\Sigma E_{ion} - T_c$" correlation seems not to be limited by the number of participating dopants. It covers simple cubic and face centered cubic structures, and also the pressure dependent Cs_3C_{60} (with an fcc structure), which seems to confer it a broad generality. Additionally, from this new perspective, a threshold for the appearance of superconductivity in these compounds has been identified.

Next steps would be to examine more combinations of alkali atoms at optimum pressure and doping, and to apply this type of analysis to other superconducting families.

Author contributions

Acknowledgements

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