

Pressure dependence of superconductivity in simple-cubic $\text{Na}_2\text{CsC}_{60}$

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The pressure dependence of the superconducting transition temperature T_c of simple-cubic $\text{Na}_2\text{CsC}_{60}$ is studied by an ac susceptibility method with a Swenson-type piston-cylinder apparatus. The observed value of dT_c/dP is -12.5 ± 0.2 K/GPa, significantly larger than the values of -7.8 and -9.7 K/GPa reported earlier for K_3C_{60} and Rb_3C_{60} , respectively. Using the compressibility available (that of K_3C_{60}), we find that the evolution of T_c with interfullerene spacing in $\text{Na}_2\text{CsC}_{60}$ is significantly different from that established for merohedrally disordered face-centered-cubic superconductors $M_3\text{C}_{60}$ (M = alkali metal), but in excellent agreement with the ambient pressure data for the simple cubic superconductors $\text{Na}_2\text{RbC}_{60}$ and $\text{Na}_2\text{CsC}_{60}$. The present results provide an additional dimension to the existing features of fulleride superconductors, establishing the importance of the relative orientation of C_{60}^{3-} ions in affecting the electronic and conducting properties of these materials.

Since the discovery of relatively high-temperature superconductivity in alkali-metal-doped $M_3\text{C}_{60}$ compounds,¹⁻³ a large amount of experimental and theoretical work⁴ has been devoted to the understanding of the properties of these novel molecular solids. At present, the highest reported superconducting transition temperature T_c stands at 33 K, observed in the $\text{RbCs}_2\text{C}_{60}$ compound.⁵ Such a high T_c is only surpassed by the cuprate superconductors. What is most striking for the superconductivity in these systems is the existence of a simple monotonic relation between T_c and the unit cell size (or intermolecular spacing), observed both at ambient pressure for a number of mixed metal $M_{3-x}M'_x$ salts⁶ and at elevated pressures for Rb_3C_{60} (Ref. 7) and K_3C_{60} .⁸ These results suggested that T_c depends principally only on the overlap between near-neighbor C_{60} molecules, which modulates the electronic density of state at the Fermi level $N(E_F)$. Thus, it is generally believed that a relation between T_c and $N(E_F)$ is more fundamental than between T_c and the lattice constant. Indeed, local-density-approximation calculations with varying lattice constant by Oshiyama and Saito⁹ showed that T_c scales well with $N(E_F)$.

Recently, however, studies based on the stoichiometric approach discovered deviations from such a simple empirical linear relation between T_c and the lattice constant for fulleride salts which contained small alkali met-

als Li and Na.^{10,11} While $\text{Na}_2\text{CsC}_{60}$ appeared to show "normal" behavior, all other $\text{Na}_2M'\text{C}_{60}$ and $\text{Li}_2M'\text{C}_{60}$ salts showed either anomalously low T_c or no superconducting transition down to 50 mK. For example, $\text{Na}_2\text{RbC}_{60}$ has a T_c of 3.5 K, far less than that of K_3C_{60} (~ 10 K) at high pressure at the same lattice spacing.⁸ Of importance then is the observation in the diffraction profile of $\text{Na}_2\text{RbC}_{60}$ by high-resolution synchrotron x-ray diffraction of weak Bragg peaks, which could be indexed on a primitive cubic (space group $Pa\bar{3}$) unit cell.¹² The crystal structure of this compound differed from the one adopted by the $M_{3-x}M'_x\text{C}_{60}$ ($M, M' = \text{K, Rb, Cs}$) superconductors, namely merohedrally disordered fcc (space group $Fm\bar{3}m$),¹³ implying the possibility of detrimental effects to the superconductivity arising from the modified crystal structure. However, a subsequent high-resolution powder neutron-diffraction study¹⁴ revealed that the structure of $\text{Na}_2\text{CsC}_{60}$, for which the T_c and the lattice constant lie on the universal curve of fcc fullerides, was also simple cubic, isostructural with $\text{Na}_2\text{RbC}_{60}$. Thus, even though the presence of different orientational ordering should have undoubtedly modified the $N(E_F)$, and as a consequence, the T_c , no such effect was apparent. Does not the T_c depend on the $N(E_F)$ value? At this point there has been no simple explanation for not only the "anomalous" T_c of the $\text{Na}_2\text{RbC}_{60}$ solid, but also the "normal" T_c of $\text{Na}_2\text{CsC}_{60}$. We believe that it is impor-

tant to understand such an anomalous feature for elucidating the superconductivity in C_{60} -based superconductors.

These considerations motivated the present work in which we address the relation between T_c and lattice constant for simple-cubic fullerenes by measuring the evolution with pressure of the superconducting properties of Na_2CsC_{60} .

In this paper we will explain the apparent paradox of the anomalous T_c for the Rb and normal T_c of the Cs isostructural samples, that is, there exist *two* universal curves, describing the dependence of T_c on the interfullerene spacing: one for fcc and another much steeper for simple cubic fullerenes, with the differences arising through the changed orientational state of the fulleride ions.

The Na_2CsC_{60} sample was prepared by reaction of stoichiometric quantities of C_{60} , Na, and Cs, contained in a tantalum cell inside a sealed glass tube filled with He to 600 Torr, at 200°C for 12 h and at 430°C for three weeks with intermittent shaking. Phase purity was confirmed by x-ray-diffraction measurements. The sample was superconducting with a T_c of 12 K and a superconducting volume fraction of more than 59% measured with a superconducting-quantum-interference-device (SQUID) magnetometer. A Rb_3C_{60} superconductor with a T_c of 29.5 K was also prepared as a reference sample for comparisons with published high-pressure data. For the pressure work, the technique using a Swenson-type piston-cylinder apparatus was employed. The T_c under pressure was determined with an ac susceptibility method using the primary and secondary coils wound around the sample. The frequency of the magnetic field was 923 Hz. The data were collected as output signal of a lock-in amplifier. Nearly hydrostatic pressure was retained in a Teflon cell filled with a fluid pressure transmitting medium (mixture of Fluorinert FC70 and FC77). The force applied to the high-pressure apparatus was controlled not to change during the measurements on cooling and heating, that is, these measurements were performed always at constant pressure. The reproducibility of the present ac susceptibility data was checked by repeating the measurements at each pressure three times.

Figure 1 shows the ac magnetic susceptibility, χ , of the present Na_2CsC_{60} sample as a function of temperature in a pressure range from 0.2 to 0.6 GPa. No transition to a superconducting state was observed at 0.8 GPa down to 2 K. The pressure dependence of T_c is presented in Fig. 2. The error bars in the temperature in Figs. 2 and 3 represent the scatter of the data for triply-performed measurements. As it can be seen, T_c varies linearly up to 0.6 GPa with a slope of $dT_c/dP = -12.5 \pm 0.2$ K/GPa. This value is considerably larger than the values of -7.8 and -9.7 K/GPa,⁷ reported for K_3C_{60} and Rb_3C_{60} , respectively. Figure 2 shows unequivocally the larger dT_c/dP in Na_2CsC_{60} than the counterpart on the fcc fullerenes. At present, the compressibility of Na_2CsC_{60} is not known, and thus we cannot derive the relation between the T_c and the lattice constant at the various applied pressures directly from the present experimental re-

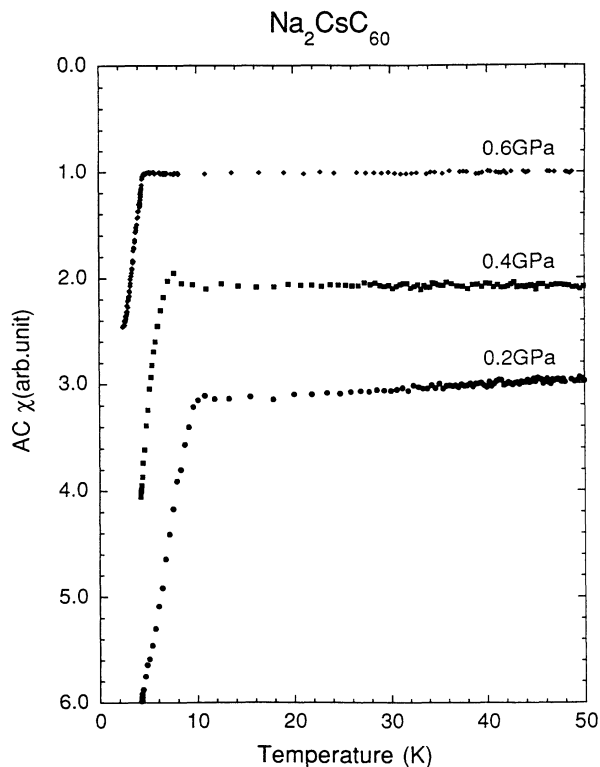


FIG. 1. Temperature dependence of ac magnetic susceptibility curve $\chi(T;P)$ of Na_2CsC_{60} obtained under the indicated pressures.

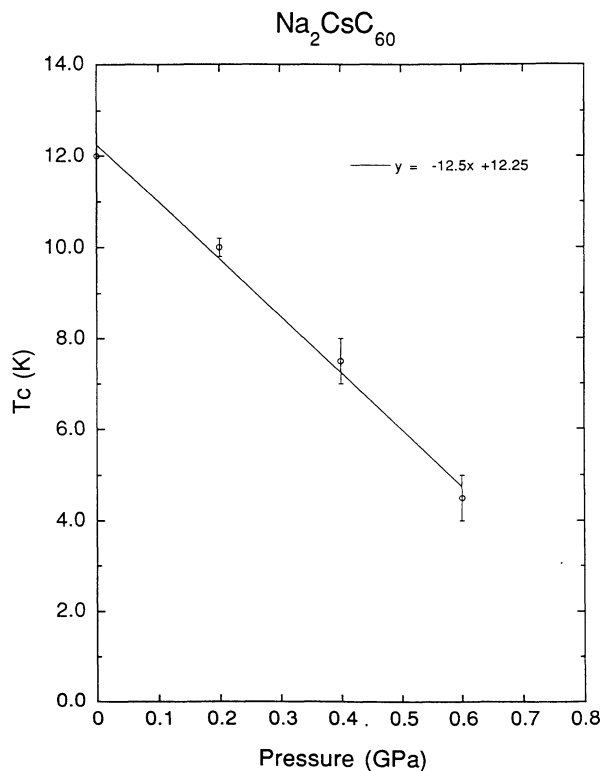


FIG. 2. Evolution of the superconducting transition temperature T_c determined from $\chi(T)$ curves with pressures. The error bars in the temperature axis represent the scatter of the data for three measurements.

sults. However, to a first approximation, we can obtain an estimate of the lattice constant of $\text{Na}_2\text{CsC}_{60}$ at elevated pressures by using the linear compressibility value, $-d \ln a / P$ (a = lattice constant), of $1.2 \times 10^{-2} \text{ GPa}^{-1}$, measured for K_3C_{60} .⁸ In this way, the lattice constants at each pressure can be derived. In Fig. 3, the T_c 's observed at each pressure are plotted against the lattice constant values, together with the present high-pressure results on Rb_3C_{60} and earlier values on various superconducting $M_3\text{C}_{60}$ (or $M_{3-x}M'_x\text{C}_{60}$) fullerides.^{8,10} It is clearly seen that the relation between T_c and the lattice constant in $\text{Na}_2\text{CsC}_{60}$ is markedly different from the one established in merohedral fcc fullerides. Yet it coincides exactly with the line obtained at ambient pressure for simple-cubic $\text{Na}_2\text{CsC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$ (shown by a solid line in Fig. 3).

We believe that this agreement is not fortuitous, although the exact value of the $\text{Na}_2\text{CsC}_{60}$ compressibility is currently unknown. We do not expect it to be substantially different from the value assumed in the present study, as can be inferred from several high-pressure studies of fullerene solids.¹⁵⁻¹⁸ High-pressure work on pristine C_{60} established¹⁷ that the compressibility of $-d \ln V / dP = 5.5 \times 10^{-2} \text{ GPa}^{-1}$ reported earlier^{15,16} was for the simple cubic phase of the materials. Moreover, Samara *et al.*¹⁷ concluded that the compressibility of the fcc and sc were not too different. More detailed measure-

ments¹⁹ later established that the compressibility of the fcc is roughly 30% larger than that of the sc phase. As a result, we can conclude that the compressibility of the fullerene solids is only weakly dependent on the orientation of the C_{60} molecules in the solid. Thus, we can conclude that our approximation that the compressibility of $\text{Na}_2\text{CsC}_{60}$ is of the same order of magnitude as that of K_3C_{60} is reasonable. As fcc phases appear to be somewhat softer than sc ones,¹⁹ agreement of the present high-pressure data with the ambient pressure ones could be even better. Thus the transition temperatures of the fcc fullerides and the sc fullerides follow their own relations different to each other but common in the fullerides having the same structures.

Originally $\text{Na}_2\text{RbC}_{60}$ was assumed to be an "anomalous" fullerene superconductor, and much effort was spent in an attempt to understand its behavior, which was thought to provide an important clue for the mechanism of superconductivity in these systems. The question arises about whether or not the density of state at the Fermi surface is an important controlling factor for T_c . Our present experiments clearly establish the existence of simple "universal" relation between T_c and interfullerene spacings for *all* alkali-metal intercalated C_{60} superconductors; the different structural families characterized by the different orientational states of the C_{60}^{3-} ions only give rise to different dT_c/da (a = lattice constant) gradients. Thus the unexpectedly low T_c of $\text{Na}_2\text{RbC}_{60}$ should result from the much steeper dependence of $N(E_F)$ (and/or electron-phonon coupling V) on the intermolecular separation in sc than in fcc fullerides. Recent theoretical calculations by Hamada²⁰ within the framework of the tight-binding approximation have shown that indeed $N(E_F)$ for a sc structure is more sensitive to lattice constant variations than for a fcc structure, entirely consistent with the results of the present experiments. In addition, the position of $\text{Na}_2\text{CsC}_{60}$ on the universal curve of the fcc fullerides is wholly fortuitous. By taking into account the tight-binding calculations,^{20,21} which indicate that $N(E_F)$ is higher for a sc structure than for a fcc one, a strong possibility is then that the fortuitous position of $\text{Na}_2\text{CsC}_{60}$ arises from the compensating effects of a slightly reduced electron-phonon coupling constant V , originating through the stronger influence of the Na^+ ions on the C_{60} geometry.¹⁴ Recent neutron-inelastic-measurements on $\text{Na}_2\text{RbC}_{60}$ and $\text{Na}_2\text{CsC}_{60}$ (Ref. 22) seem to give support for such a hypothesis, but additional accurate experimental and theoretical studies of $N(E_F)$ and V are certainly needed.

In conclusion, we have unraveled a relationship between the superconducting transition temperature T_c and the lattice constant in alkali-metal intercalated C_{60} compounds by applying pressure on the $\text{Na}_2\text{CsC}_{60}$ superconductor having a simple cubic structure (space group $Pa\bar{3}$) at ambient pressure. T_c is found to have a substantially steeper dependence on the lattice constant in a simple cubic structure when compared with the face centered cubic structure (space group $Fm\bar{3}m$) fulleride superconductors. The present results provide us with two important insights. First, the intuitive expectation based on a BCS

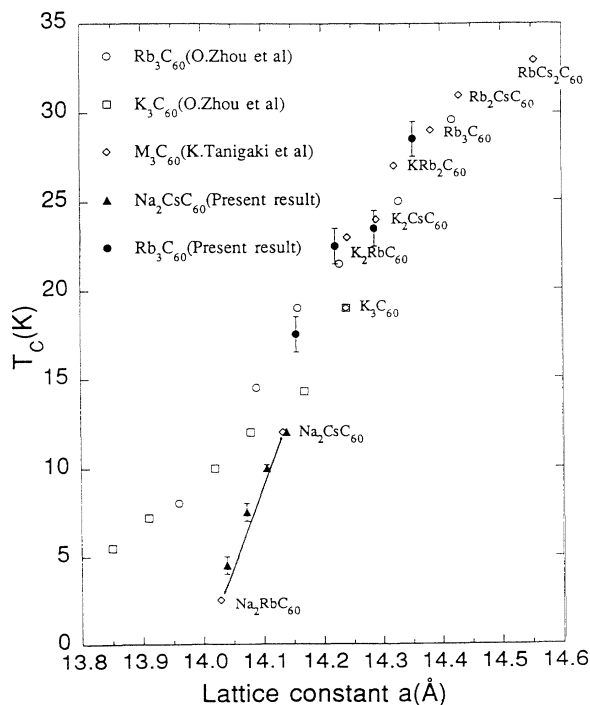


FIG. 3. Evolution of the superconducting transition temperature T_c with the lattice constant of various $M_3\text{C}_{60}$ compounds, including points provided by pressure works. Filled symbols (● and ▲ for Rb_3C_{60} and $\text{Na}_2\text{CsC}_{60}$, respectively) are the present pressure data. Open symbols (○ and □ for R_3C_{60} and $\text{Na}_2\text{CsC}_{60}$, respectively) are the pressure data from Ref. 8, and symbols ◇ are the data on various compounds from Ref. 10. The solid line is obtained by connecting the data points at ambient pressure for $\text{Na}_2\text{RbC}_{60}$ and $\text{Na}_2\text{CsC}_{60}$.

theory that an increased $N(E_F)$ leads to higher T_c 's still holds for all alkali-metal intercalated C_{60} superconducting materials, including Na_2RbC_{60} , which was wrongly thought to be an "anomalous" compound. We believe that this result will act as an important ingredient in all models of superconductivity in C_{60} -based materials. Second, it has been shown unambiguously that the relative orientation of C_{60} molecules in the solid does affect sensitively the details of the electronic structure, as revealed by the existence of the second "universal" line. This requires explicit consideration of an additional "new parameter," namely molecular orientation. Simply

speaking, we may view the C_{60} molecule not just like a "large atom," but like a large atom with "spin." Then, the C_{60} -based solids should lead to a variety of physical properties, just by tuning the "spin" orientation.

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