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Pressure dependence of superconductivity in the $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ fulleride

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The pressure dependence of the superconducting transition temperature T_c of the primitive cubic quaternary fulleride $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ ($T_c = 8.4$ K at ambient pressure) is studied by the ac susceptibility technique to 2.5 kbar. The observed value of dT_c/dP is $-1.22(2)$ K/kbar. Using the compressibility data available for Na_2CsC_{60}, we find that the evolution of T_c with interfullerene spacing in $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ mimics that observed for Na_2CsC_{60} and is comparable to the fcc fulleride K_3C_{60}. However, the rate of change, dT_c/da, is about 5–6 times smaller than that reported for the quaternary fullerides $Na_2Rb_{1-x}Cs_xC_{60}$ as a function of x at ambient pressure, implying the presence of a strong alkali-metal specific effect, responsible for the differing effects of chemical and physical pressure on the superconducting properties of $Pa\overline{3}$ fullerides. [S0163-1829(99)09105-5]

I. INTRODUCTION

Alkali intercalated fullerides with stoichiometry A_3C_{60} display superconductivity with transition temperatures T_c scaling monotonically with unit cell size. This can be rationalized as arising from the modulation of the electronic density of states, $N(\epsilon_F)$, by the interfullerene spacing.[1] As the latter increases, the overlap between the $C_{60}{}^{3-}$ ions decreases, leading to a reduced bandwidth and to an increased density of states for a fixed band filling. Geometrical considerations dictate that for large alkali ions (K^+, Rb^+, and Cs^+) occupying the tetrahedral site, the crystal structure of the A_3C_{60} salts is face-centered cubic (fcc, space group $Fm\overline{3}m$).[2] The T_c is affected in essentially identical ways by both physical and chemical pressure in these systems, with only a small deviation reported for Rb_3C_{60}.[3] For smaller ions (Na^+) occupying the tetrahedral interstices, the situation is much more complicated. While the crystal structure is primitive cubic (space group $Pa\overline{3}$) (Refs. 4 and 5) just below room temperature, the close proximity of the $C_{60}{}^{3-}$ ions allows at lower temperatures low-symmetry structural transitions which are accompanied by bridging the fulleride units through single C-C bond formation.[6–8] The polymerized fulleride phases $Na_2Rb_{1-x}Cs_xC_{60}$ and Na_2KC_{60} are not superconducting,[6,9,10] and the observed superconductivity is associated with the metastable $Pa\overline{3}$ phases.

It has been of particular interest that the metastable primitive cubic family $Na_2Rb_{1-x}Cs_xC_{60}$ $(1 \leqslant x \leqslant 0)$ displays a much steeper rate of change of T_c with interfullerene spacing. The origin of this effect could be empirically ascribed to the modified structure and intermolecular potential in the $Pa\overline{3}$ structures. As the orientational state of the $C_{60}{}^{3-}$ ions changes, the electron hopping between neighbors could be affected, leading to a modified rate of change of $N(\epsilon_F)$, and hence of T_c, with interfullerene spacing. Indeed, NMR measurements[11] have confirmed that the values of $N(\epsilon_F)$ for Na_2RbC_{60} and Na_2KC_{60} are strongly suppressed. However, little difference is found in the a dependence of $N(\epsilon_F)$, as derived from temperature-dependent electron paramagnetic resonance (EPR) spectroscopy, between Na_2CsC_{60} ($Pa\overline{3}$) and K_3C_{60} and Rb_3C_{60} ($Fm\overline{3}m$),[12,13] in agreement with the finding of tight-binding calculations[14] and implying that the changed orientational state in the $Pa\overline{3}$ phases may not be the factor responsible for the depressed T_c. At the same time, magnetic susceptibility measurements at high pressure on Na_2CsC_{60} (Ref. 15) have led to the conclusion that the effects of physical[15] and chemical[16] pressure on the superconducting properties of the $Pa\overline{3}$ phases are not identical, with chemical pressure suppressing T_c much faster than physical pressure.

In order to explore the T_c-a relationship in additional Na-containing primitive cubic fullerides, we performed detailed ac susceptibility measurements on the

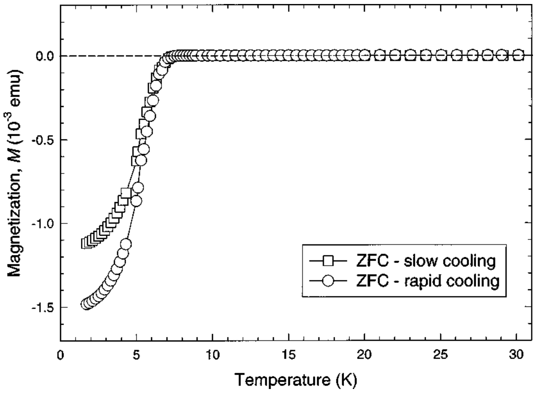

FIG. 1. Magnetization (dc) measurements on $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ under ZFC conditions at 20 Oe: (○) rapid cooling and (□) sample temperature kept at 180 K for 10 h before cooling to 1.8 K.

$Na_2Rb_{0.5}Cs_{0.5}C_{60}$ salt between ambient and 2.5 kbar applied pressure. The results show a striking similarity to those obtained earlier for the parent Na_2CsC_{60} fulleride,[15] with the rate of change of T_c with interfullerene separation, dT_c/da, being comparable to that of the fcc fullerides at similar unit cell dimensions. This contrasts sharply with the quaternary fullerides $Na_2Rb_{1-x}Cs_xC_{60}$ $(1 \leqslant x \leqslant 0)$ in which dT_c/da obtained by varying x at ambient pressure is about 5–6 times larger[16] and implies a metal-specific effect for the origin of the suppressed values of T_c.

II. EXPERIMENTAL DETAILS

The $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ sample was prepared by the reaction of stoichiometric amounts of Na, Rb, and Cs with C_{60} in a tantalum cell which was placed in a sealed glass tube filled with He gas (500 Torr). It was first heated at 207 °C for 3 h, at 297 °C for 12 h, and at 347 °C for 72 h. After grinding the sample in a glove box, it was transferred to a new glass tube and annealed at 430 °C for 20 days. Phase purity was established by high-resolution synchrotron x-ray powder diffraction measurements with the Mar Research circular image plate system on line A of the BM1 beam line at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The cubic lattice constant at 296 K was $a = 14.1137(5)$ Å. Superconducting quantum interference device (SQUID) measurements to 1.7 K at an applied magnetic field of 20 Oe were performed on a 54-mg sample loaded in a quartz tube with a thin partition in the center and introduced into a Quantum Design MPMS SQUID magnetometer. For the ac susceptibility measurements, the sample was introduced into a thin-walled glass capillary of 1.5 mm diameter inside a glove box. The sample height was ~0.5 cm, and the capillary was sealed to a length of 1 cm. The sealed capillary was introduced into uniform ac pickup (374 turns each) and field (440 turns) coils using copper wire of 0.05 mm diameter on a plastic base of 1.8 mm diameter. The coils together with a Manganin pressure gauge were loaded into a Teflon cell filled with a degassed 1:1 mixture of Fluorinert FC70 and FC77. A Swenson-type brass piston-cylinder pressure cell was used with the aid of a retaining screw to apply and maintain pressure on the sample, as described before.[17] Sample temperatures down to 2.2 K were recorded by means of a platinum-cobalt thermometer, embedded in the brass cylinder near the sample. As the piston-cylinder apparatus allows the application of pressure only at room temperature, the present system was calibrated for the pressure drop which occurs on cooling using a K_3C_{60} sample. This entailed the performance of a series of experiments in which the pressure was first being increased at room temperature, the sample cooled, and the T_c (defined as the *onset* of the appearance of diamagnetic shielding) monitored until a decrease in its value was detected. The system has proved quite

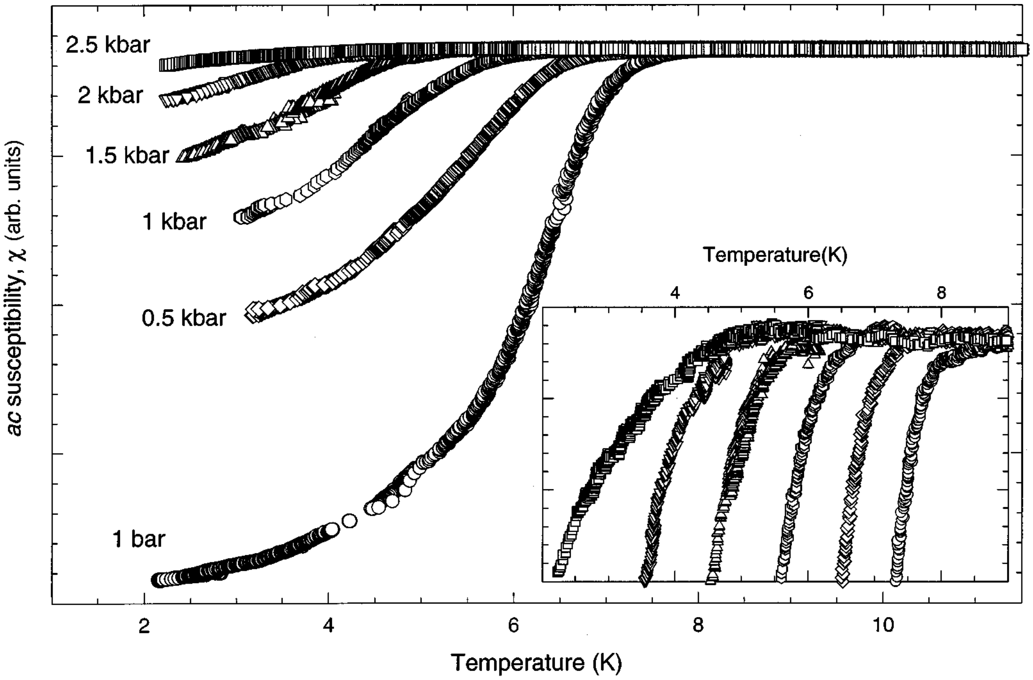

FIG. 2. Temperature dependence of the ac magnetic susceptibility χ of quenched $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ at the indicated pressures. The inset shows an expanded view of the experimental data in the vicinity of T_c.

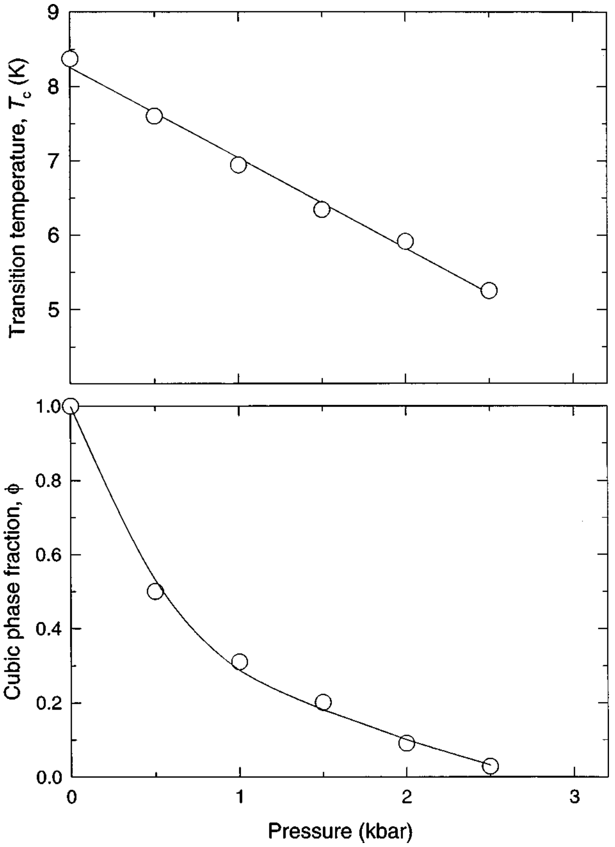

FIG. 3. Pressure dependence of the superconducting transition temperature T_c (top panel) and of the fraction of the cubic phase ϕ (bottom panel) for quenched $Na_2Rb_{0.5}Cs_{0.5}C_{60}$. The lines are guides to the eye.

robust in that an applied pressure of 3.5 kbar at room temperature was repeatedly found to be equivalent to ''ambient pressure'' at 20 K. The estimated error in pressure is of the order of ±0.2 kbar. The use of a thin-walled glass capillary is not a limitation, as it shatters well below applied pressures of 1 kbar, thus allowing the sample to mix well with the pressure medium.

III. RESULTS AND DISCUSSION

Figure 1 shows the dc magnetization of the $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ sample obtained for two different cooling protocols at 20 Oe under zero-field-cooling (ZFC) conditions. The sample was first cooled rapidly to low temperatures, and the magnetization was measured between 1.7 and 30 K. Superconductivity was observed with $T_c = 8.3$ K. The superconducting fraction, estimated from the diamagnetic shielding, was very large (~85%), implying bulk superconductivity. In a separate experiment, the sample was cooled slowly to 180 K, where it was kept for 10 h, before further cooling to 1.7 K. Following this, the dc magnetization was again measured under ZFC conditions. As Fig. 1 shows, while there is no change in T_c, a decrease of ~25% in the superconducting fraction occurs. Similar results have been reported before for the ternary fulleride Na_2RbC_{60}.[6] While upon rapid cooling the superconducting primitive cubic phase survives to low temperatures, slow-cooling protocols allow the transformation of part of the sample to the nonsuperconducting monoclinic polymer phase.[6–8] This structural transformation manifests itself in the reduced value of the superconducting fraction, and its occurrence for the present sample is consistent with the results of synchrotron x-ray powder diffraction experiments.[9] However, the fraction of the polymerized phase in $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ is smaller than that in Na_2RbC_{60}, while Na_2CsC_{60} does not polymerize at all under similar heat treatment. These results are consistent with the extreme sensitivity of the polymerization reaction on the interfullerene separation.

Detailed ac susceptibility measurements for $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ were performed as a function of temperature at pressures up to 2.5 kbar. For these experiments, the sample was heated above room temperature, and after the pressure was applied, it was rapidly quenched in liquid nitrogen. Following completion of the susceptibility measurements, the sample was rapidly heated with the aid of a heat gun before the next cycle of measurements was initiated. Figure 2 summarizes the ac susceptibility χ of $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ obtained in the pressure range 0.001–2.5 kbar. In general, the shapes of the curves are characteristic of those obtained when the particle size of the powdered samples is of the same order of magnitude as the London penetration depth. The ambient pressure ac susceptibility data show the onset of superconductivity in quenched $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ at $T_c = 8.4$ K in agreement with the dc magnetization data in Fig. 1. Increasing the pressure to 0.5 kbar leads to a decrease in both the T_c to 7.6 K and the superconducting volume fraction by ~50%. Increasing further the pressure to 2.5 kbar, in steps of 0.5 kbar, results in a smooth decrease in T_c, as is clearly evident from the inset of Fig. 2. At the same time, the superconducting fraction also gradually decreases, implying that the superconducting primitive cubic phase of $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ gradually transforms into the nonsuperconducting polymer phase with increasing pressure. The transformation is incomplete at these low pressures, and the behavior mimics what is encountered on cooling at ambient pressure. As the structural phase transition temperature T_{tr} at ambient pressure is just below room temperature (in the temperature range 250–270 K), increasing the pressure leads to a decrease in interfullerene separation, thus quickly driving T_{tr} to values above room temperature. Figure 3 displays the pressure dependence of both T_c and the superconducting fraction which we identify with the volume fraction ϕ of the primitive cubic phase of $Na_2Rb_{0.5}Cs_{0.5}C_{60}$. Here T_c varies linearly with pressure up to 2.5 kbar with a slope of $dT_c/dP = -1.22(2)$ K/kbar. This value is identical to that found before for the isostructural fulleride Na_2CsC_{60} [−1.25(2) K/kbar],[15] but considerably larger than the values of −0.78 and −0.97 K/kbar, reported for the fcc fullerides K_3C_{60} and Rb_3C_{60}, respectively.[18] At present, there is no compressibility data available for $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ and so the T_c dependence on the cubic lattice constant cannot be derived directly. However, the linear compressibility of the primitive cubic phase of Na_2CsC_{60} has been measured by both the powder neutron[12] and synchrotron x-ray[19] diffraction techniques. The measured values are $-d(\ln a)/dP = 1.8(2)\times 10^{-3}$ and $1.6(2)\times 10^{-3}\,\text{kbar}^{-1}$, respectively, somewhat larger than that of the fcc fulleride K_3C_{60} ($1.2\times 10^{-3}\,\text{kbar}^{-1}$).[20] Thus, to a good approximation, we can employ the linear compressibility value of Na_2CsC_{60} to de-

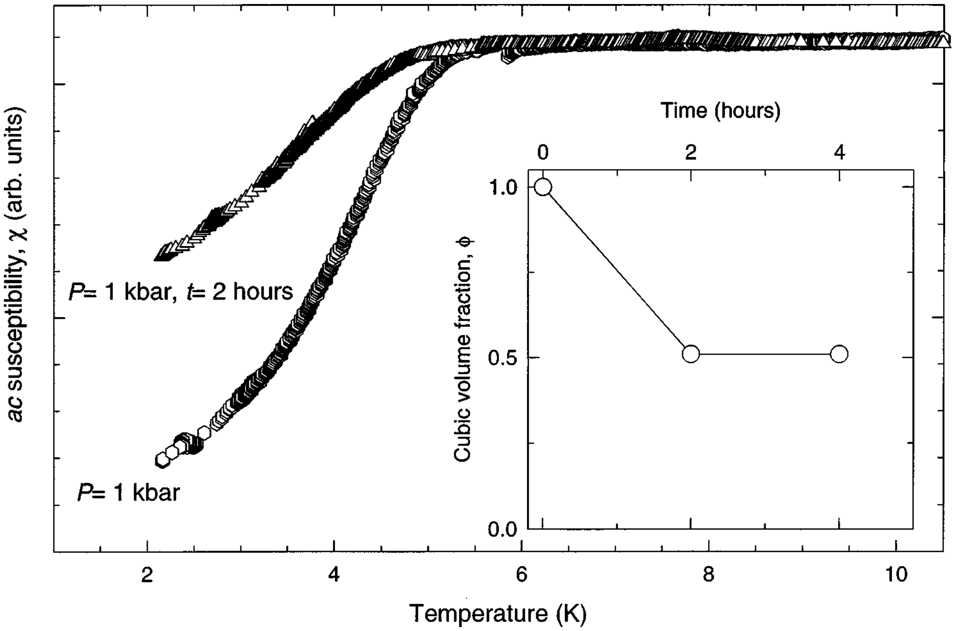

FIG. 4. Temperature evolution of the ac susceptibility χ of $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ at an applied pressure of 1 kbar. The two data sets shown correspond to equilibration times at room temperature before quenching of 0 and 2 h, as indicated. The inset displays the dependence of the superconducting fraction ϕ normalized to the value at 1 kbar with equilibration time.

termine the relationship between T_c and the cubic lattice constant a in $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ as $dT_c/d(\ln a) \approx 0.7\times 10^3$ K, a value comparable to that of K_3C_{60} ($\approx 0.65\times 10^3$ K).

We also performed measurements of the ac susceptibility χ at elevated pressures, in which the sample was first equilibrated at room temperature for various periods of time before quenching to low temperature. Some representative data of these experiments are shown in Fig. 4 for an applied pressure of 1 kbar ($T_c = 6.9$ K). Following the return of the sample to room temperature and equilibration for 2 h resulted in no detectable change in T_c. However, the superconducting fraction decreased by ~49%. Repeating the heating-cooling cycle with an additional waiting period of 2 h resulted in no further detectable changes in the ac susceptibility response. The detrimental effect on the fraction of the superconducting phase shown by extended periods of equilibration at room temperature (inset of Fig. 4) can be understood in terms of the slow kinetics exhibited by the primitive cubic→monoclinic phase transformation.[6,19]

Figure 5 depicts the relationship between T_c and lattice parameter a as adapted from Fig. 14 of Ref. 12, for a variety of fulleride salts at both ambient and elevated pressures. The present high-pressure results for the $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ salt define a new branch in this diagram with a slope identical to that found for Na_2CsC_{60} at high pressure,[15] but about 5–6 times smaller than that encountered in the quaternary fullerides $Na_2Rb_{1-x}Cs_xC_{60}$ ($1 \leqslant x \leqslant 0$) at ambient pressure.[16] Thus they reinforce the contrast in the behavior of superconducting fcc and Na-containing primitive cubic fullerides. While in the former the effects of chemical and physical pressure on the superconducting properties differ little, the latter show a clear differentiation with chemical substitution leading to a much faster suppression of T_c than application of pressure. The pressure dependence of the superconducting properties of individual members of the $Na_2Rb_{1-x}Cs_xC_{60}$ ($1 \leqslant x \leqslant 0$) family differs very little from the phenomenology established for the fcc fullerides in which the larger alkali ions K^+, Rb^+, and Cs^+ reside in the tetrahedral interstices. Thus the faster depression of T_c with interfullerene separation at ambient pressure, as x varies in $Na_2Rb_{1-x}Cs_xC_{60}$, appears to be metal specific. Its origin still poses intriguing questions and has yet to be explained unambiguously. While the conjecture that the dependence of T_c on interfullerene separation is generally much steeper in the $Pa\bar{3}$ structure than in the $Fm\bar{3}m$ one can be now discarded, a number of additional possible explanations still remain. These include (i) the existence of an as-yet-unidentified low-symmetry distortion of the primitive cubic structure; (ii) a very sensitive modulation of the degree of electron transfer between Na and C_{60} by the interfullerene separation which may lead to deviations from half filling of the conduction band and rapid suppression of superconductivity, in analogy with the situation encountered in nonsuperconducting Li_2CsC_{60};[21] and (iii) the presence of intergrowths, or coexistence at the microscopic level, of superconducting cubic and nonsuperconducting polymer domains, with the size of the latter growing as the lattice constant decreases with decreasing x in $Na_2Rb_{1-x}Cs_xC_{60}$.

IV. CONCLUSIONS

We have measured the dc magnetization of the $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ salt following rapid- and slow-cooling protocols. It is established that in this case, like in other Na^+-containing fullerides and small interfullerene separations, the superconducting phase ($T_c = 8.4$ K) is associated with the metastable $Pa\bar{3}$ structural variant which can be quenched to low temperatures. The temperature variation of the ac susceptibility was then followed to pressures as high as 2.5 kbar, establishing a rate of $-1.22(2)$ K/kbar for the decrease of T_c with increasing pressure. Combining this re-

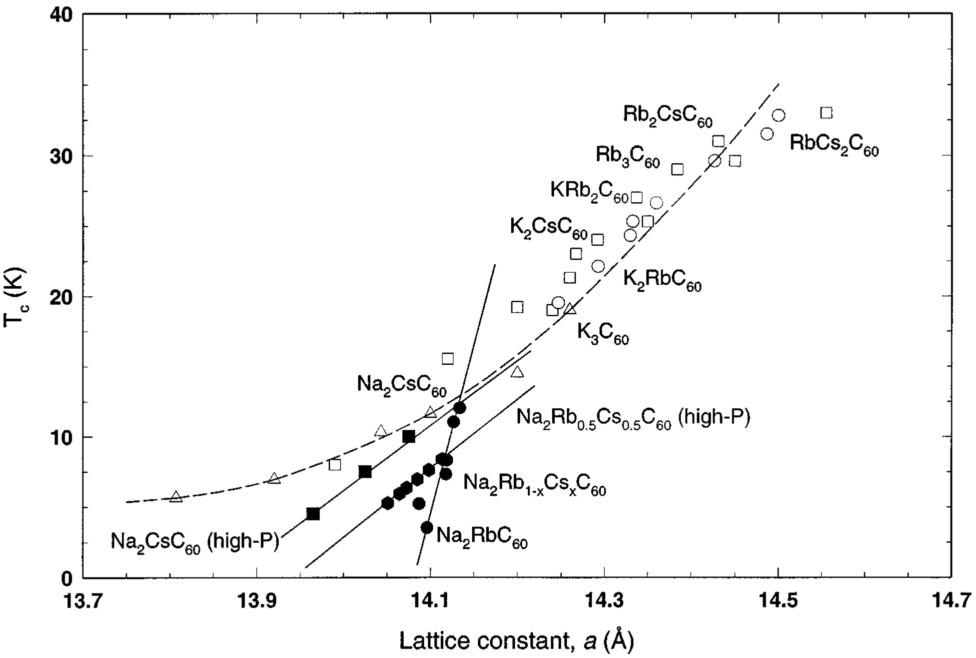

FIG. 5. Relationship between the superconducting transition temperature T_c and the cubic lattice constants a of fulleride salts over a wide range of values for a. Data indicated by open symbols are experimental measurements on fulleride salts with the $Fm\overline{3}m$ structure at both ambient and elevated pressures. Data indicated by solid symbols are experimental measurements on fulleride salts with the $Pa\overline{3}$ structure at ambient (circles) and elevated (squares for Na_2CsC_{60} and hexagons for $Na_2Rb_{0.5}Cs_{0.5}C_{60}$) pressures. The dotted line is the T_c-a relationship expected from BCS theory using $N(\epsilon_F)$ values obtained by local density approximation (LDA) calculations, while the straight lines are guides to the eye.

sult with the linear susceptibility of the isostructural Na_2CsC_{60} analog, we derived the rate of change of T_c with cubic lattice constant as $dT_c/d(\ln a) \approx 0.7 \times 10^3$ K, comparable to that of K_3C_{60}. In conclusion, the unusually steep dependence of T_c on interfullerene separation, encountered at ambient pressure for the $Na_2Rb_{1-x}Cs_xC_{60}$ family, is not apparent in the measurements on the individual members at high pressure. Rather, each reverts back to the ''normal'' T_c-a dependence, exhibited by fcc fullerides. This dichotomy in the behavior of Na-containing fullerides mitigates against early conjectures of the existence of a sensitive dependence of $N(\epsilon_F)$ on the orientational state of the fulleride ions and points towards metal-specific effects, perhaps associated with either the occurrence of polymerization or the modulation of the Na^+-$C_{60}{}^{3-}$ interaction with interfullerene spacing.

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