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EFFECT OF He PRESSURE ON THE SUPERCONDUCTING TRANSITION TEMPERATURES OF Na_2CsC_{60} AND $(NH_3)_4Na_2CsC_{60}$

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ABSTRACT

The Na based mixed alkali doped C_{60} superconductors show anomalous behavior with respect to the "universal" superconducting transition temperature T_c vs lattice constant a_o relation followed by most of the fcc A_3C_{60} superconductors. We have measured dT_c/dP for Na_2CsC_{60} and $(NH_3)_4Na_2CsC_{60}$ using solid He as the pressure medium to ~ 6 kbar finding dT_c/dP equal to -0.8±(0.01) K/kbar and -1.0(±0.1) K/kbar for Na_2CsC_{60} and $Na_2(NH_3)_4C_{60}$ respectively. Our value for Na_2CsC_{60} differs markedly from that obtained by Mizuki et al of about -1.3 K/kbar. However, using N_2 or Ar, we obtain values for dT_c/dP in substantial agreement with Mizuki et al who used fluorinert to generate their pressure. This work emphasizes the need for compressibility measurements with the same pressure medium in the appropriate temperature range so that meaningful comparisons can be made between various pressure measurements and models which are based on lattice spacing.

Introduction

Much has been made of the simple relation between the lattice constant and the superconducting transition temperature, T_c, of the alkali metal doped, A_3C_{60} superconductors.[1] Pressure studies as well as comparison of results for members of the A_3C_{60} family gave rise to the picture[2] shown in Figure 1. Theoretical models involving only inter and intra C_{60} interactions have been able to describe this T_c vs lattice constant behavior, essentially neglecting any details of the alkali intercolate.[3,4] We have shown[5,6] that this simple picture can break down if substantially more than the three electrons are transferred as in the alkali superconductors A_3C_{60}. For example, Ca_5C_{60} and Yb_3C_{60} have qualitatively different dependencies on lattice constant or pressure (opposite sign and nearly a factor of ten in magnitude). In retrospect this is probably not surprising because with the A_3C_{60}, three electrons are donated, half filling the first unoccupied T_{1u} band above the C_{60} gap. The Ca_5 and Yb_3 can donate sufficient electrons to completely fill the t_{1u} band and partially fill the next higher T_{1g} band. The density of states of the T_{1g} band evidently has a much different volume dependence that that of the t_{1u}.

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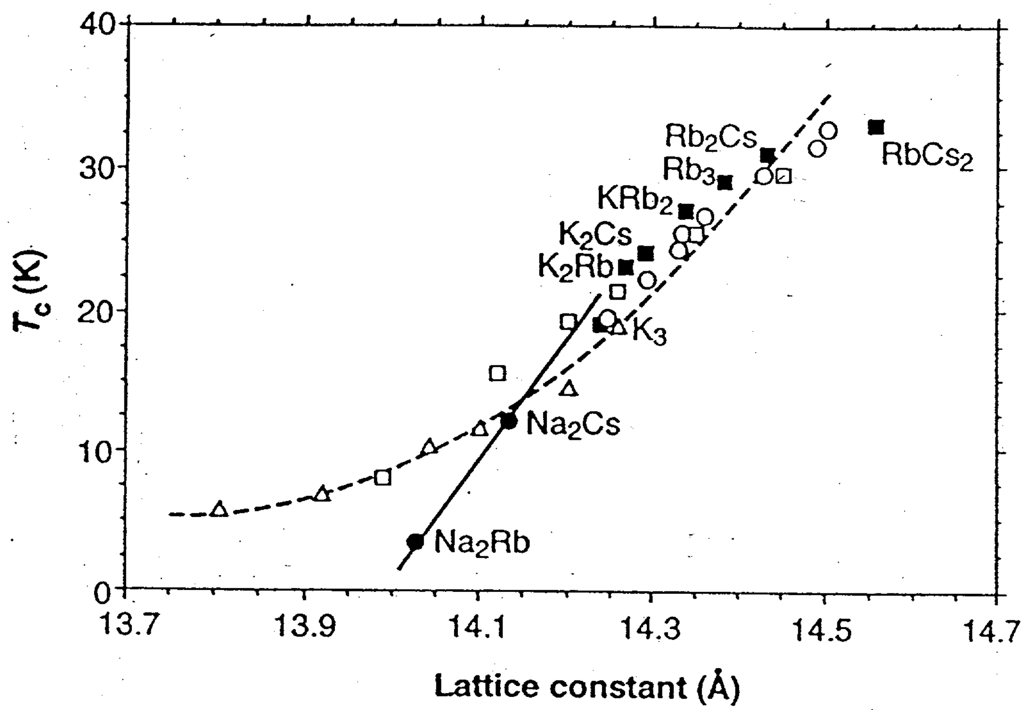

Figure 1 T_c vs lattice constant for various A_3C_{60} materials (from reference 2).

There are however further deviations from the simplest lattice constant vs T_c picture even within the A_3C_{60} case when the mixed alkali members involving Na are considered. Na_2RbC_{60} falls considerably off the curve as shown in Fig. 1 while Na_2CsC_{60} is more or less in line. This would indicate that a considerably greater negative pressure effect would be seen and indeed Mizuki et al[7] observe a 50% greater negative pressure derivative for Na_2CsC_{60} than for the nearby (in lattice parameter) A_3C_{60} superconductors. They and Yildirim et al[8] attribute this to the fact that Na_2CsC_{60} and Na_2RbC_{60} are simple cubic rather than the usual fcc structure. Our preliminary pressure measurements of T_c for Na_2CsC_{60} gave essentially the "right" value for dT_c/dP in line with the fcc A_3C_{60} materials. In this report, we present new pressure studies of $Na_2(NH_3)_4CsC_{60}$ and Na_2CsC_{60} using He and other gases as pressure media in an effort to understand these seemingly disparate results.

Experimental

Samples of $(NH_3)_4Na_2CsC_{60}$ were prepared as described earlier.[9] Briefly fcc Na_2CsC_{60} was exposed to NH_3 gas at room temperature for 1 - 2 days, sealed and annealed for 1 day at 100° C. The resultant material is fcc with a lattice constant of 14.473 A and a T_c value of 29.6 K. For the pressure measurements, an rf technique described earlier[10] in which a coil is wound around the capillary containing the superconducting powders is used. This rf technique detects the <u>onset</u> of diamagnetism and has been shown on many samples to coincide with the onset observed on the identical samples using a SQUID magnetometer. The capillary is broken under

He in the pressure cell so as to expose the material to the gaseous pressure medium. A chip Nb is affixed to the capillary to provide an internal calibration of the carbon glass thermometer which is attached to the exterior of the pressure vessel. Nb has a completely negligible pressure derivative for our purposes so is ideal for this purpose. Pressures to 5 kbar were used to determine $dT_c/dP = -1.0\pm0.15$ K/kbar for $(NH_3)_4Na_2CsC_{60}$ as shown in Fig. 2.

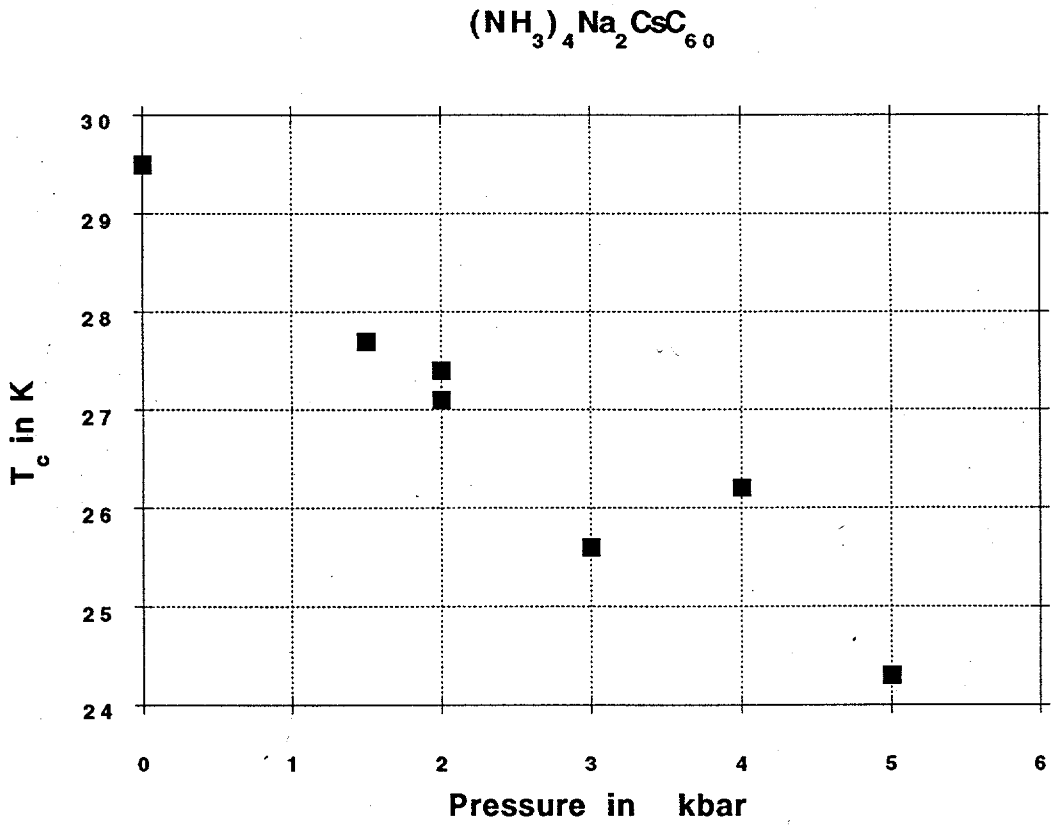

Figure 2 Effect of pressure on the superconducting transition temperature of $(NH_3)_4Na_2CsC_{60}$.

The identical techniques were employed for the study of dT_c/dP of Na_2CsC_{60}. As noted above, our initial results using He as the pressure medium gave a value of $dT_c/dP =$ -0.8(±0.1) K/kbar which is near the usual [11,12] value obtained for the fcc A_3C_{60} materials. However it is too small a derivative to be reconciled with the line connecting Na_2RbC_{60} and Na_2CsC_{60} in Fig. 1 and is much smaller than the value of -1.25 K/kbar obtained by Mizuki et al[7] using fluorinert as the pressure medium. We have observed similar differences with various pressure media in a study[13] of the pressure dependence of the orientational ordering in C_{60}. With He, the interpenetration of the lattice resulted in a 30 - 40% smaller derivative than with N_2 or pentane which presumably can penetrate much less easily.

In order to investigate our suspicion that with a small atom like Na we might have a similar penetration of the lattice with our He pressure medium, pressure measurements were made on the same sample under identical conditions except that the pressure transmitting gas was changed from He to N_2 to Ar. The situation is complicated here because the pressure media are freezing at very different temperatures which results in a loss of pressure experienced by the sample at low temperature depending upon the relative thermal expansivities of the pressure medium, the sample and the pressure vessel. At 5 kbar, He freezes at 40 K, N_2 at 130 K and Ar at 180 K. We therefore employed an internal pressure gauge consisting of a chip of high purity Sn which has a $dT_c/dP = -0.05$ K/kbar. Our results for the pressure dependence of T_c for Na_2CsC_{60} using He as the pressure medium are shown in Fig. 3 and give $dT_c/dP = -0.8(\pm 0.1)$ K/kbar. Applying a 5 kbar pressure of either Ar or N_2 room temperature results in a pressure near 3.1 kbar at liquid He temperature and gives a value of T_c of near 7 K (shown as an X in Fig. 3). The fact that 5 kbar applied pressure at roomtemperature results in the same low temperature for N_2 and Ar stems from the effect of a volume change in N_2 accompanying a solid-solid phase transition[14] compansating for the higher melting point of N_2 with respect to Ar.

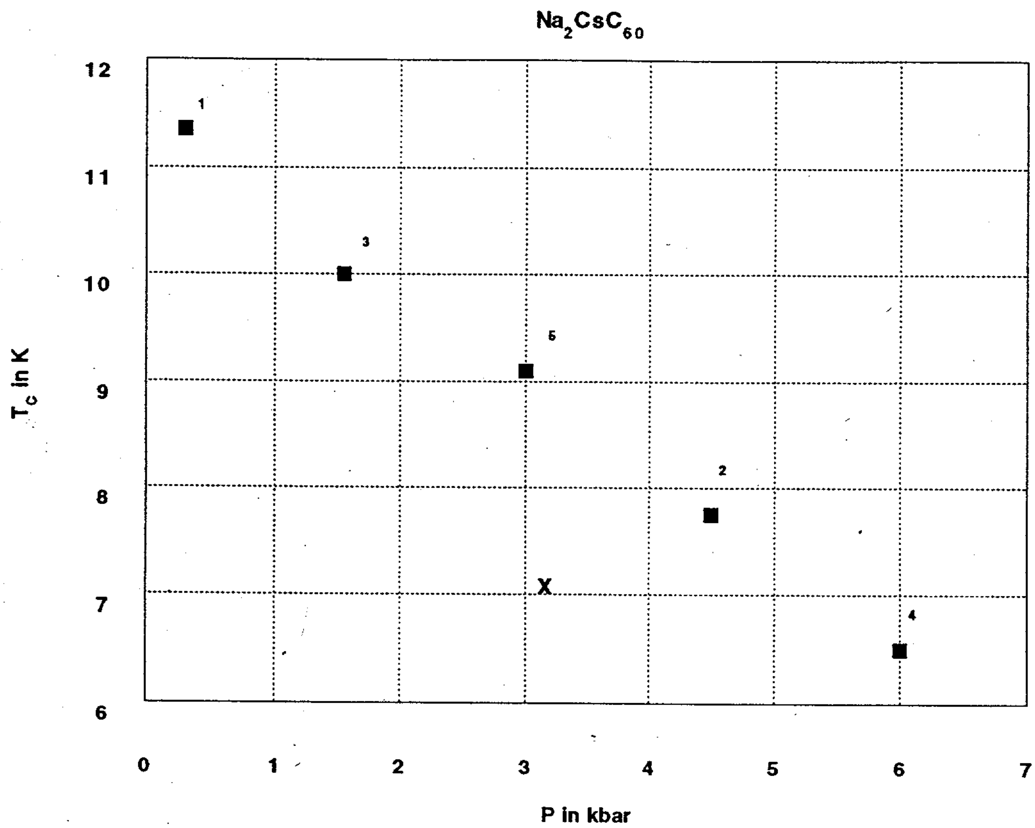

Figure 3 Effect of pressure on the superconducting transition temperature of Na_2CsC_{60}. The solid squares were obtained using He as the pressure transmitting medium and are numbered in the order in which they were taken. The point near 3 kbar and 7 K was obtained with both N_2 and Ar as the pressure medium.

Results and Discussion

We find that $(NH_3)_4Na_2CsC_{60}$ is stable under pressure cycling in the He to 5 kbar and has a pressure dependence of T_c completely in line with its position on the T_c vs lattice constant curve (see Fig. 1). Therefore, the expansion of the lattice by substitution of $(NH_3)_4Na^+$ for Na^+ in the octahedral sites expands the lattice moving T_c up to 29.5 K and pressure moves T_c back down following the simple picture quite nicely.

Our results for the pressure dependence of T_c for Na_2CsC_{60} differ markedly with pressure medium. With He, dT_c/dP = -0.8 K/kbar while with N_2 or Ar the value is -1.2 K/kbar in excellent agreement with the results of Mizuki et al[7] who used fluorinert as the medium. Quite clearly we have the situation observed earlier in pure C_{60} where the He interpenetrates the lattice so that the compressibility is reduced over that where the pressure medium is excluded as is of course the usual situation. This does not occur to a very large extent in any of the A_3C_{60} superconductors except those containing Na, presumably because K, Rb and Cs have sufficiently large atomic radii so that the He cannot penetrate the lattice.

These results then remove the apparent disagreement between our He pressure results and those of Mizuki et al[7] (and with our N_2 and Ar results). The larger pressure derivatives for the Na containing superconductors and for the apparent misplacement of Na_2RbC_{60} on the T_c vs lattice constant curve would appear to stem from the fact that the Na materials are simple cubic rather than fcc as discussed by Mizuki et al[7] and by Yildirim et al.[8] Our results emphasize the need for accurate compressibility measurements for these systems. The compressibilities must be determined using the <u>same</u> pressure medium as the particular parameter studied under pressure <u>and</u> be in the same orientational ordered structure so as to arrive at the correct volume dependence which is what can be compared with theory. This caution is now obviously valid with He for pure C_{60} and Na containing A_3C_{60} but may be true to varying degrees with other pressure media in some of these doped C_{60} materials.

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