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ON THE PRESSURE INDUCED PHASE OF Na_2CsC_{60}

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Neutron powder diffraction at pressures to 6 kbar in gaseous Ne has been used to study the pressure-induced phase transition and compressibilities of Na_2CsC_{60}. The pressure-induced phase can be achieved by compression to ~5kbar at room temperature. If cooled this phase can be retained below ~200K upon release of the pressure. The structure is orthorhombic as previously reported (but may differ in its detailed crystal structure) with lattice constants near 80K and ambient pressure of a = 9.385Å, b = 10.06Å and c = 14.36Å. The corresponding linear compressibilities are 0.0004, 0.0014 and 0.0017 $kbar^{-1}$, respectively. Identical pressure temperature cycling results in a superconductor with an unexpectedly low pressure dependence for T_c while in this phase. Models for the superconducting behavior of this compound are discussed.

INTRODUCTION

Initial studies by Fleming et al.[1] and Chen et al.[2] on trialkali doped C_{60} showed that T_c increased linearly with their fcc lattice parameter. This relationship also held for the corresponding alloys as well as for these materials under lattice compression as additional experiments were reported[3]. However, this simple picture became more complex when the corresponding ternary superconductors Na_2AC_{60} ,where A is K, Rb or Cs, were examined. While Na_2CsC_{60} appeared to lie on the well established empirical curve of T_c vs lattice constant, Na_2RbC_{60} and $Na_2Rb_{1-x}Cs_xC_{60}$ superconductors had T_c values much lower than expected and Na_2KC_{60} was not superconducting. These differences have been explained by the demonstration[4-6] that these ternary materials belong to the cubic space group Pa3 rather than the usual Fm3m found for the majority of the trialkali doped C_{60} compounds and their alloys. Further, differences in the pressure derivatives for Na_2CsC_{60} reported by Schirber et al.[7] (using solid He as the pressure medium) and Mizuki et al.[8] (using other media) were resolved by showing that He intercalation effects occur in the Na_2AC_{60} system.[9] These effects, in which the He penetrates the lattice resulting in less compression of the material than with nonpenetrating pressure media, were first demonstrated by Samara et al.[10] in their measurement of the pressure dependence of the ordering temperature of pure C_{60}.

This paper describes our preliminary neutron structure results and details how these data contribute towards the resolution of the inconsistency in the pressure derivatives by measurements of $T_c(P)$ using a variety of pressure media. In the course of these studies we discovered that various pressure/temperature cycles yield a superconducting phase which corresponds to the pressure-induced phase reported as a "polymer" phase by Zhu[11] in his room temperature diamond anvil X-ray studies.

EXPERIMENTAL DETAILS

Samples were prepared as described elsewhere and sealed in pyrex until studied.[5,12] The large powdered sample (~250mg) was loaded using a dry box atmosphere into a thin walled vanadium tube (1cm diam x 5cm long) which was inserted into the aluminum pressure cell described in detail elsewhere.[13] Data were collected on the 90° detector banks of the Special Environment Powder Diffractometer (SEPD) at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS).[14] The pressure cell was pressurized initially at room temperature (296K), eventually cooled in order to study the stability of the high pressure phase upon pressure release, and cycled along a different path as discussed below for the available run time on the instrument. Due to shielding that is an integral part of the pressure cell, the 90° scattering angle provides data that are completely free of background scattering from the walls of the cell. The maximum working pressure of this cell is 6kbar. Typical data collection times were about 30min for lattice parameter information; however, times of about 15min were used to track the initial rapid growth or decay of the lattice parameters while the temperature or the phase changed and much longer times (as long as 12hrs) for complete data profiles to be used in the structural refinements (after the lattice parameters stopped changing). Both the structure refinement code GSAS (Generalized Structure Analysis System)[15] and the in-house IPNS code[16] were used to extract lattice parameter information and attempt structure refinements.

Samples used to determine the superconducting transition were sealed in 1mm diam. 3cm long pyrex capillaries. An rf coil was wrapped around the filled end of the capillary and mounted in Sandia's pressure system. The tip of the capillary was broken in an inert atmosphere and the pressure vessel slipped over the coil-capillary assembly. The T_c values were determined using an rf impedance technique described by Azevedo et al.[17] This technique has been used successfully on a large number of organic and high T_c materials and its signature for superconductivity has been shown to coincide with the onset of diamagnetism seen in a SQUID magnetometer on the same samples. Pressures to 6 kbar are typically achieved[18] by careful isobaric freezing of He but as will be discussed below this technique gives misleading results if improperly interpreted. In the present study, Ne, Ar, and N_2 were also used at their appropriate pressure regimes.

RESULTS AND DISCUSSION

Figure 1 summarizes our lattice parameter data for Na_2CsC_{60} obtained through pressure/temperature cycling employing Ne as the pressure medium. Cell volume for the cubic phase and two times that of the orthorhombic phase is given rather than the actual parameters for ease in the direct comparison of the pressure-induced phase. These data were obtained by least-square fitting the neutron powder diffraction profiles under various pressures and temperatures. As indicated by the sequence numbers, as pressure is increased at room temperature, 296K, the compound remains in the primitive cubic Pa3 structure to 4.61kbar (open circles), but at 5.99kbar the pattern of the profile changes to that for an orthorhombic cell (with a corresponding ~3% volume change from the extrapolated cubic value; open square). The structure transformation appears immediately (at least within the 33min time frame used for this particular run). The pressure cell was then cooled towards 82K, pressure equilibrium being achieved at 3.40kbar . (There were 15 data runs not shown between points 5 and 6 during which the lattice parameters changed slightly while both the pressure and the temperature decreased, as expected with our closed pressure system.) Pressure was then lowered towards a nominal 0.04kbar in order to retain the pressure seals (solid squares). At this point the temperature was decreased to the minimum attainable in the pressure cell, 17K, at which point a long run was collected (solid triangle). Subsequently the cell was warmed toward room

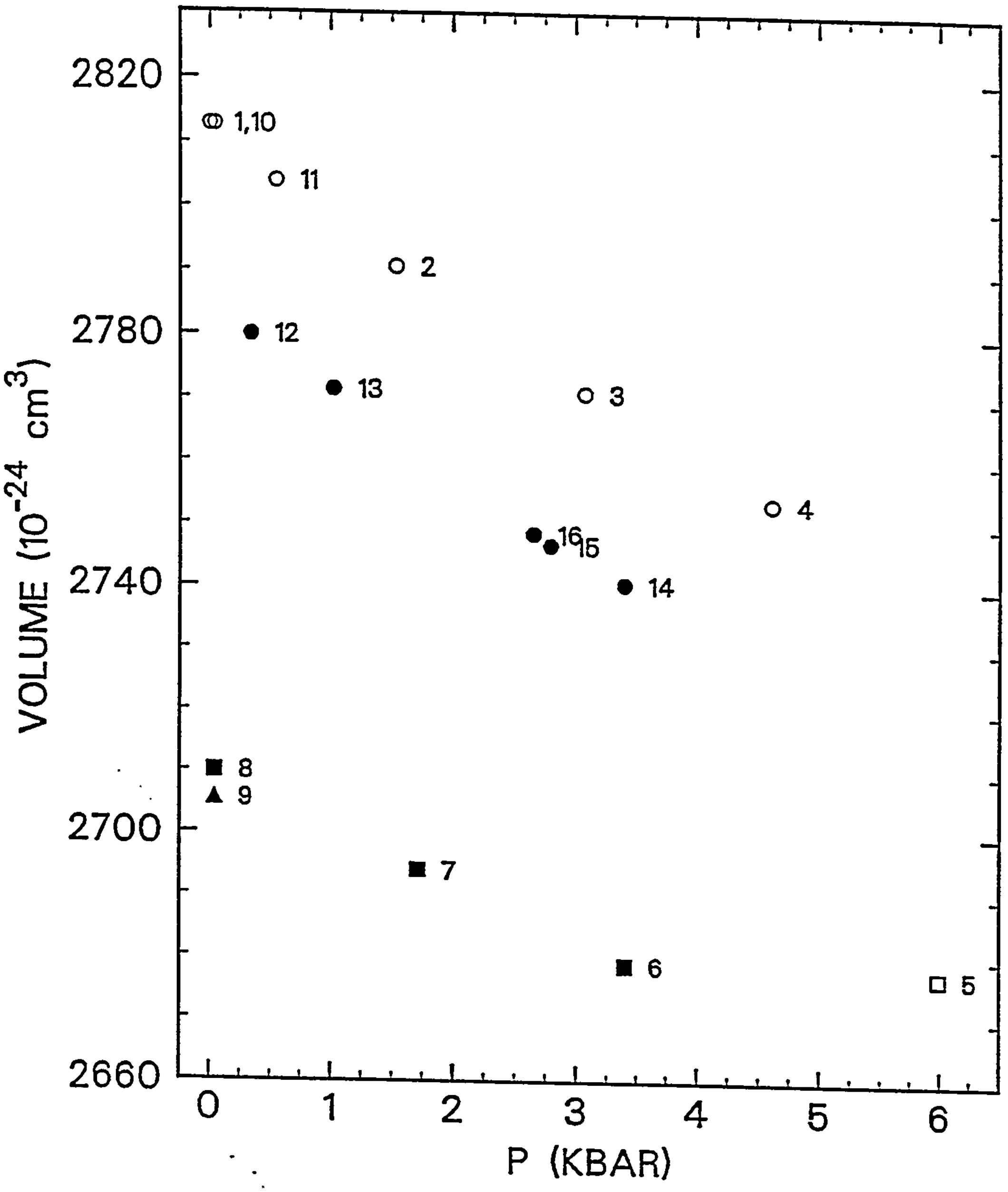

Fig. 1 Cell volume vs pressure for Na_2CsC_{60} using Ne as the pressure medium. . The volume for the lattice of the cubic phase and two times that of the orthorhombic phase is given for ease in the direct comparison of the pressure-induced phase. Numbers by the points indicate the sequence through which the sample was cycled, circles for the cubic phase, squares (and one triange, 17K run) for the orthorhombic phase, open for room temperature, and filled for low temperatures (see text).

temperature, with profiles continuously collected at 30min intervals (10 data runs between points 9 and 10 not shown). The orthorhombic phase disappeared at about 210K in one of the 30min intervals. The pressure cell was then loaded to 0.55kbar (open circle) and cooled to 83K (10 data runs between points 11 and 12 as temperature decreased while pressure drops to 0.35kbar). Subsequent pressure loading to 4.0kbar resulted in a pressure leak at values in excess of 3.47kbar; longer data runs (3hr) were collected at lower pressures in this part of the phase region (solid circles). During these latter runs, the material remained as primitive cubic.

Several bits of information can be determined from our data. The axial compressibilities of the cubic phase at room temperature and 82K are identical, 0.0016 and 0.0016 $kbar^{-1}$, respectively (values significantly smaller than the 0.0028 $kbar^{-1}$ value for pure C_{60}). In the orthorhombic phase at 83K, the linear compressibilities along the a-, b-, and c-axes are 0.0004, 0.0014 and 0.0017 $kbar^{-1}$, respectively. Thus the compressibilities values along the b- and c-axes are similar to those for the cubic phase while that along the a-axis is much smaller. One is also able to determine that the linear thermal contraction of the cubic phase at 0.55kbar is ~$8.9x10^{-6}$ deg^{-1}.

Zhu[11] reported a room temperature pressure-induced transition in Na_2CsC_{60} and in Na_2RbC_{60} at pressures near 3 kbar using diamond anvil techniques. He suggested that this reversible transition involves formation of polymer chains along the a-axis of an orthorhombic cell of Pmnn symmetry with a = 9.347Å, b = 9.898Å and c = 14.268Å. Our excellent fit with lattice parameters similar to those of Zhu shows we are looking at this phase. On the other hand, our unsuccessful attempts to obtain a good fit to Zhu's "polymer" structure or to one in which the polymer chains are essentially rotated about the a-axis (which slightly improves the fit) suggest that these structure models must be incorrect. In Figure 2 we show some of our diffraction data on the longer 17K run to illustrate the quality of our data as well as the poor fit of Zhu's model. The data include 3 peaks of Ne crystallized in cubic close packed Fm3m structure at this temperature. On our data at d-spacings larger than 2.7, the fit is somewhat better since structural details are blurred out. Such data also provide nonoverlapping orthorhombic peaks which illustrate that our Ne and orthorhombic Na_2CsC_{60} peaks have peak widths of comparable sharpness.

Figure 3 summarizes our T_c measurements of Na_2CsC_{60} for the case where the pressure is applied at room temperature and then the sample is cooled slowly at constant pressure to the freezing point of the particular gas being employed. The sample is then cooled to wherever T_c occurs. To change the pressure, the sample is warmed to room temperature and the procedure repeated. The pressure at low temperature is calculated from the known phase diagram for the particular gas. This is most accurate for He because its freezing point is the lowest. We also measure the T_c of a small chip of Sn on the rf coil. Using the known value of dT_c/dP of Sn, an independent calibration of the pressure is obtained. We find T_c varies by as much as a degree from sample to sample, presumably due to differences in doping stoichiometry. The open circles in Fig. 3 are the values of T_c

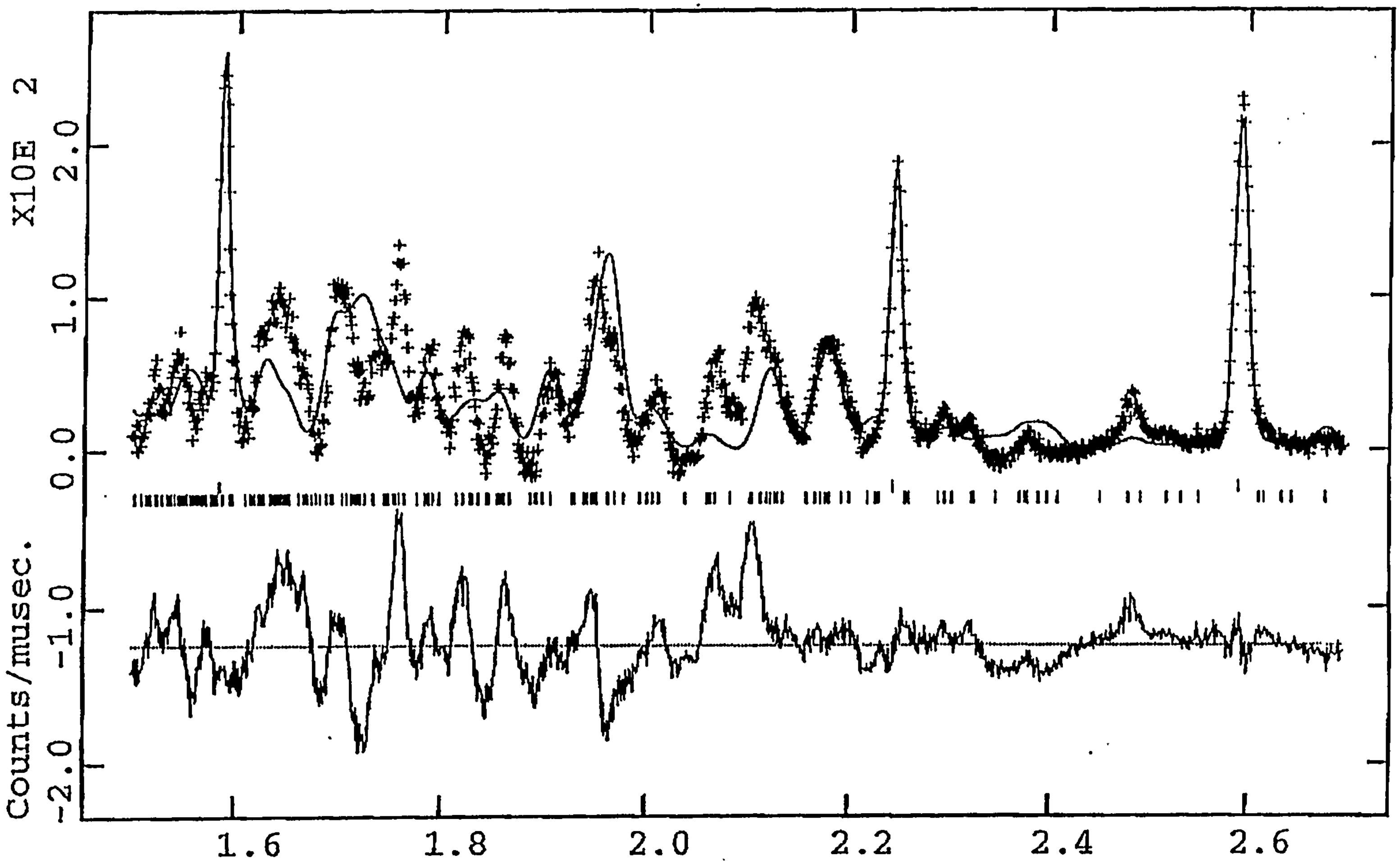

Fig. 2 Part of the neutron powder diffraction data for Na_2CsC_{60} at 17K and ~0.04kbar Ne. The points shown by plus (+) marks represent data collected using the pressure cell on SEPD at IPNS. The continuous line through the data is the calculated profile from Rietveld refinement with the "polymer" structure model illustrating the poor fit. The tick marks below the data indicate the positions for the allowed reflections for solid Ne (top) and Na_2CsC_{60} (bottom) in the orthorhombic space group. The lower curve represents the difference between the observed and calculated profiles.

obtained in He as described above and result in dT_c/dP = -0.7K/kbar. The squares correspond to points taken on a different sample using both Ar and N_2 as the pressure media. For the point near 3 kbar, 5 kbar of gas pressure was initially applied and maintained to the freezing point (190K for Ar, 135K for N_2). Fortuitously, T_c occurs at the same temperature because the larger loss in pressure upon cooling solid Ar is compensated by a phase change in N_2. The actual pressure was determined from the dT_c/dP for Sn. The slope given by the Ar and N_2 is -1.3K/kbar, which is in excellent agreement with the work of Mizuki et al.[8] who use media which do not penetrate the lattice. This result was obtained on several samples. It is consistent with data taken with Ne, which also does not penetrate the lattice at least on the time scale of these experiments. (The nonpenetration of Ne into Na_2CsC_{60} is in contrast to the case with pure C_{60} [19,20].) On a sample pressurized at 5kbar of Ne, no change in dT_c/dP was seen for 3 weeks. The diminution of effective pressure with He is consistent with that observed in the experiments of Samara et al.[10] and in recent comparisons[19] of the compressibilities of C_{60} using Ar, Ne and He.

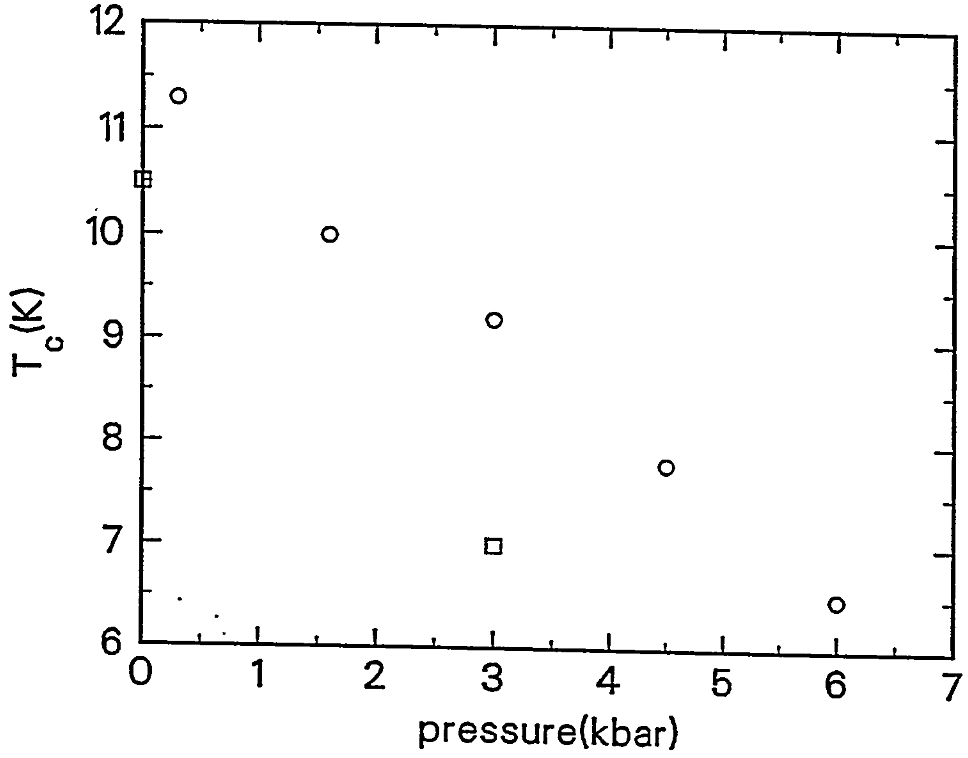

Fig. 3 Superconducting transition temperature, T_c vs pressure for Na_2CsC_{60}. The open circles were obtained with room pressure application and isobaric freezing of He. The squares were obtained using Ar and N_2 as the pressure media. The point near 3 kbar was obtained with 5 kbar of Ar and N_2 impressed at the freezing point of the particular gas (see text).

In the process of studying these effects and assessing the penetration of the various gases with respect to dT_c/dP, we discovered that with Ne as the pressure medium, unexpected changes in T_c occur depending upon the temperature/pressure path and history. For instance, if pressure to 5 kbar at room temperature is impressed on the sample in Ne and the T_c measured, the result shown in Fig. 3 for non-penetration is observed. If, however, the pressure is released at 77K (which is possible only with He, H_2 and Ne because all other media are still solid), T_c does not recover to its ambient pressure value but is about 3K lower. If we warm sequentially part way to room temperature, then check T_c , we find that the expected T_c is recovered provided the sample is warmed to ~200K. If on the other hand, we quench the sample to 77K at 1bar ("zero pressure"), then apply 5 kbar of pressure with Ne, we do not see a drop in T_c of ~ 5K as expected but instead a drop of < 2K. This striking behavior has been reproduced through many cycles on four different samples. We have also observed this effect at intermediate pressures. These results are shown schematically in Fig. 4. The solid line corresponds to changing the pressure at room temperature, the dashed lines are what is observed when the pressure is changed at 77K.

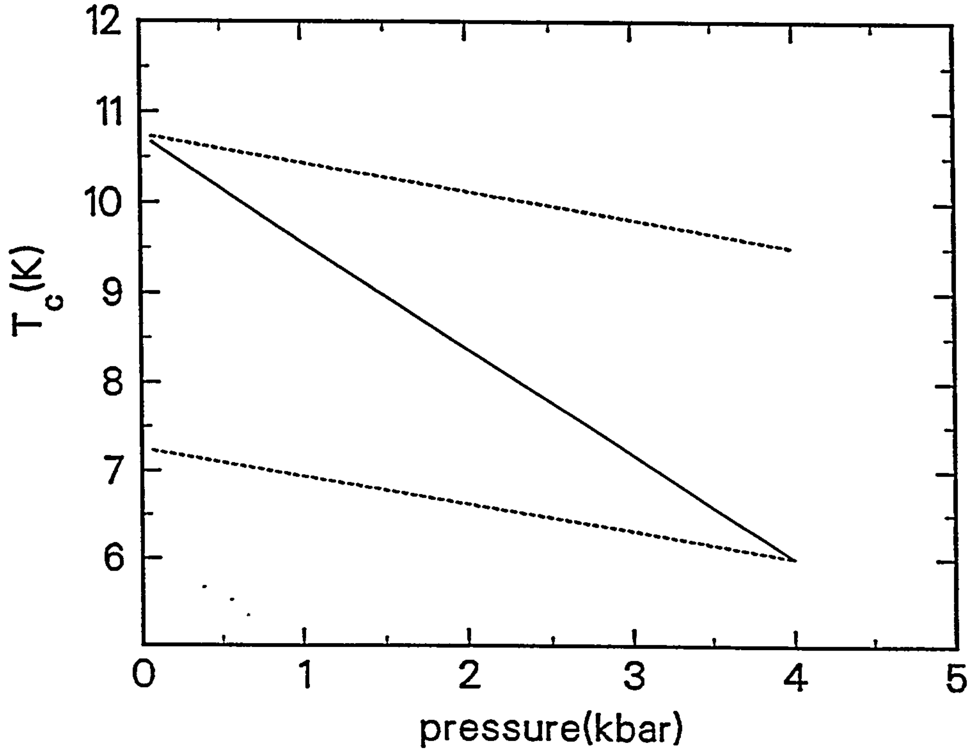

Fig. 4 Superconducting transition temperature T_c vs pressure using various pressure/temperature paths. The solid line corresponds to changing the pressure at room temperature. The dashed lines are observed when the pressure is changed at 77 K. Pressures have been corrected to correspond to actual compression of the lattice (see text).

Our high-pressure neutron diffraction studies using Ne as the pressure medium show both the formation of the high-pressure orthorhombic structure with room temperature application of pressure and its retention to ~200K following pressure release at low temperature. This suggests that as pressure is applied at room temperature (which is the case for essentially all of the published data and much of our work), the orthorhombic phase is entered either directly with pressure or upon subsequent cooling (at some as yet undefined pressure). The resulting change in T_c is then a combination of the dT_c/dP for the orthorhombic phase of about -0.2K/kbar and a loss of ~3K from the difference in volume between the primitive cubic and the orthorhombic phase.

The simplest explanation of this behavior is that a hysteretic phase change is occurring which is facile at room temperature but is sufficiently sluggish at low-temperature that the pressure can be removed at 77K without reversion to the zero pressure room temperature phase until ~ 200K.

While this picture accounts for the behavior when the pressure is applied at room temperature, cooled and the pressure removed at low temperature and subsequently warmed, it fails on the reverse path. With this model, if we were to cool at zero pressure and then apply pressure, T_c would change provided that the phase boundary is crossed and decrease at the -0.2K/kbar rate. Instead only the -0.2K/kbar contribution seems to be observed. This small value of dT_c/dP indicates we are in the polymeric phase but fail to observe the discontinuous change of ~ 3K associated with the phase change and corresponding volume change between primitive and orthorhombic.

An alternative picture would be to postulate a situation that was observed[21-23] in some of the high T_c copper oxide systems, notably $Tl_2Ba_2CuO_{6-\delta}$ and $La_2CuO_{4+\delta}$. Here it was shown that there are two contributions to dT_c/dP: 1) an intrinsic pressure dependence, probably due to the volume dependence of the band structure, which is common to all the Cu oxide based superconductors when they are optimally doped and 2) a strongly temperature dependent contribution due to oxygen mobility which results in changes in the doping and/or oxygen ordering.

One might speculate that a similar effect is operative here in that an ordering of the "dopant" Na and Cs ions by slight shifts in their positions and/or reorientation of the C_{60} takes place with increasing pressure if the temperature is high enough to permit such motion or orientation changes; this results in a drop in T_c. As in the case of the Cu oxide systems this can only be separated if pressure can be varied at both low and high temperature -- a unique feature of gas pressure techniques. With this scenario, the low temperature pressure changes measure the "intrinsic" part of dT_c/dP while the high temperature pressure changes incorporate the "ordering" effect as well. What is not so clear in this picture is the role of the high pressure transition which we know occurs abruptly and involves a small volume change. Some combination of these two models is perhaps occurring. Such a possibility would be to postulate that the volume change associated with the phase change increases linearly with pressure resulting in pressure dependent contribution to T_c (negative) which would be observed with pressure changes at high temperature. This somewhat unusual behavior would account for the entire picture shown in Fig. 4 when coupled with the intrinsic effect at low temperature, attributed to the orthorhombic phase.

CONCLUSIONS

We have confirmed the pressure-induced transition in Na_2CsC_{60} near 5kbar. The detailed crystal structure of this orthorhombic phase does not appear to be that suggested by Zhu. The effects of pressure using various gases as pressure media as well as the effect of the temperature at which the pressure is changed on the superconductivity of Na_2CsC_{60} have been examined. Both the choice of pressure medium and the temperature of pressure application have profound effects on the value of dT_c/dP. Two models are discussed: 1) a highly hysteretic phase change from primitive cubic to orthorhombic and 2) a temperature dependent ordering contribution to dT_c/dP which can be frozen out when the pressure is changed at low temperature. A combination of the effects of these models with the assumption of a pressure dependent volume change across the transition could explain the results. A detailed crystal structure remains to be determined. In addition phase boundary studies as a function of temperature, pressure, and probably cooling rate, very likely will be required to sort out these models.

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