Superconductivity in the polymeric phase of $\text{Na}_2\text{CsC}_{60}$

J. E. Schirber and B. Morosin

Sandia National Laboratories, Albuquerque, NM 87185

G. H. Kwei

Lawrence Livermore National Laboratory, Livermore, CA 94550

T. Yildirim

National Institute of Standards and Technology, Gaithersburg, MD 20899

J. E. Fischer

Matl. Sci. and Eng. Dept., University Pennsylvania, Philadelphia, PA 19104

and

J. D. Jorgensen

Argonne National Laboratory, Argonne, IL 60439

Abstract

We have studied the reversible pressure induced structural transition (primitive cubic to polymeric monoclinic) of $\text{Na}_2\text{CsC}_{60}$ and the superconductivity in both phases. We have established that the polymeric phase of $\text{Na}_2\text{CsC}_{60}$ is superconducting with an ambient pressure transition temperature about 3 K lower than that for the primitive cubic phase. We believe that an analogous lowering of the transition temperature in the corresponding phase of $\text{Na}_2\text{RbC}_{60}$ either leads to a very low transition temperature or to a total absence of superconductivity.

Keywords: Organic superconductors; $\text{Na}_2\text{CsC}_{60}$, $\text{Na}_2\text{RbC}_{60}$, pressure-induced phase

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECEIVED

OCT 16 2000

OSTI

Introduction

The discovery of superconductivity in trialkali compounds, A_3C_{60} , with superconducting transition temperature values that ranged beyond 30 K led to the discovery of an empirical curve that showed an essentially linear dependence of transition temperature, T_c , on the cubic lattice parameter [1-3]. However, this simple picture became more complex when the corresponding ternary superconductors Na_2AC_{60} (where A is K, Rb or Cs) were examined. The T_c 's for these systems either departed significantly from the universal curve, with T_c values much lower than expected, or like Na_2KC_{60} , were found to be not superconducting at all. This had been explained [4-6] by the crystal structure difference (at T_c) between the latter ternary materials which belong to the primitive cubic space group Pa3, while the former belonged to the face-centered cubic group Fm3m. Also of considerable interest and controversy was the structural transition in Na_2CsC_{60} from primitive cubic phase to the polymeric monoclinic $P2_1/a$ phase and its relationship to the existence of superconductivity in the lower symmetry phase.

In Na_2CsC_{60} , the polymeric phase can be accessed only by the application of pressure [7] while in the isomorphous Na_2RbC_{60} , slow cooling alone results in a partial transformation from the primitive cubic to the polymeric phase. Schirber and co-workers [8] reported the polymeric phase in Na_2CsC_{60} to be superconducting at a temperature several degrees lower than that of its primitive cubic phase. Prassides and co-workers [9-14] have carried out extensive studies of the structures of both Na_2CsC_{60} and Na_2RbC_{60} as a function of pressure and temperature as well as studies of the superconductivity of these compounds at ambient pressure. For Na_2RbC_{60} , rapid cooling from ambient conditions resulted in the primitive cubic phase with $T_c = 3.8$ K, but that with normal cooling or even with samples kept at 80 K for ~10 h (and then cycled back up to 180 K for an additional 10 h) in attempts to ensure complete conversion from the cubic phase to the polymeric phase, a pure polymeric phase could not be prepared. No change was observed for the onset of superconductivity on measurements to 2 K, though the superconducting fraction was markedly reduced (to ~25% of the original value) demonstrating that the two phases co-existed. For Na_2CsC_{60} , their studies showed no evidence for polymeric phase formation on cooling at ambient pressure, despite using slow cooling with prolonged standing at 200 K procedures. At ambient pressure, the T_c onset was 12 K. At ambient temperature, an onset of the polymeric phase occurred between 0.56 or 0.61 Gpa (depending on the experimental method) and 0.76 Gpa; this phase grew at the expense of

the cubic phase to 0.90 Gpa, but survived to the highest pressure (8.63 Gpa) investigated. They concluded that the polymeric state of $\text{Na}_2\text{CsC}_{60}$ is not superconducting, primarily by analogy to $\text{Na}_2\text{RbC}_{60}$, and attributed the reported superconductivity to traces of untransformed primitive phase in the pressurized samples.

In this paper we present an alternative explanation that accounts for all of their observations in both $\text{Na}_2\text{CsC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$. This explanation accounts for the occurrence of superconductivity in the polymeric phase of $\text{Na}_2\text{CsC}_{60}$ and its apparent absence in the corresponding polymeric phase of $\text{Na}_2\text{RbC}_{60}$.

Experimental

Sample preparation of $\text{Na}_2\text{CsC}_{60}$ was previously described [5,15] as was the rf impedance technique [16] for measuring T_c at pressure (T_c for our samples was 11.5 K at ambient pressure using both rf impedance measurements and SQUID magnetometer). Pressures to about 0.6 Gpa were obtained by careful isobaric freezing of the pressure medium which was He, Ne, or Ar. Earlier studies [8] showed that He interpenetrates the lattices of these compounds so Ne and Ar were employed for the bulk of the studies.

Results and discussion

As presented earlier [8], our measurements of T_c for $\text{Na}_2\text{CsC}_{60}$ resulted in different values depending upon the temperature/pressure path and history. For the primitive cubic phase, our pressure dependence of T_c agreed well with that reported by Mizuki *et al.* [9] in a study using a non penetrating pressure medium. However, in our more extensive measurements an interesting "hysteresis" is observed. For example, applying 0.5 Gpa pressure at room temperature using a non penetrating pressure medium results in a drop in T_c of about 5 K. If the pressure is then released at low temperature (<77 K), T_c does not recover to the expected value of about 11.5 K, but is found to be about 3 K lower. If the sample is then warmed above 200 K and T_c measured again, the 11.5 K transition is recovered. These results were completely reproducible on a number of samples and we assumed that this lower T_c and its smaller pressure derivative (-0.02 K/Gpa compared with -0.13 K/Gpa for the primitive cubic phase[8]) were associated with the polymeric phase described by Zhu [7].

Subsequent neutron diffraction studies discussed in detail by Morosin *et al.* [17]

verified that the identical pressure/temperature cycles resulted in the formation of the polymeric phase. On a sample initially pressurized to 0.5 Gpa at ambient temperature, the hysteresis in T_c values with pressure excursions to essentially ambient pressure were shown to result from the retention of the polymeric phase as long as the temperature was kept below ~ 200 K. Returning the sample to ambient pressure/temperature conditions allowed reversible recovery of the cubic phase. Recently, Margadonna *et al.* [14] reported in more detail the evolution of the structure of $\text{Na}_2\text{CsC}_{60}$ with pressure and temperature. These results are in general in good agreement with our earlier study [17], including the onset of the polymeric phase near 0.6 Gpa. However, the two studies differ primarily in the phase purity of the sample above the pressure induced transition. Our room temperature point at 0.6 Gpa (point 5 of Figure 1 in Reference 17) did *not* show any evidence of the primitive cubic phase. That pressure run was subsequently further cooled to 82 K in ~ 5 h, followed by release to essentially ambient pressure at ~ 82 K, then further cooled to 17 K where a longer-collection-time neutron diffraction data set was collected. Rietveld structure refinement with these 17 K data required only the addition of the cubic Ne phase[18], which of course results from the freezing of the Ne pressure medium at this temperature, but *no* primitive cubic phase. The monoclinic ($P2_1/a$) lattice parameters are $a_o = 9.375(2)\text{\AA}$, $b_o = 14.343(3)\text{\AA}$, $c_o = 9.375(2)\text{\AA}$, $\beta = 133.084(7)^\circ$, and cell volume = $1353.9(5)\text{\AA}^3$, consistent with the values reported at higher pressures [14].

Therefore, these experiments provide a clear and unambiguous demonstration that the polymeric phase in $\text{Na}_2\text{CsC}_{60}$ is a superconductor with the transition temperature about 3 K lower than that of its primitive cubic phase.

Bendele *et al.* [12] suggested that the superconductivity that we attributed to the polymeric phase is due to the untransformed primitive phase. They base this assumption on their observations of incomplete transitions to the polymeric phase, particularly in $\text{Na}_2\text{RbC}_{60}$ where the transition is induced by slow cooling and never achieves more than 70% conversion. We discount this suggestion for the following reasons: (1) We achieve *pure* polymeric phase to within the sensitivity of our measurements in both the structural and the superconducting experiments. This seems reasonable for $\text{Na}_2\text{CsC}_{60}$ because we are inducing the transition with pressure at room temperature where the kinetics are more favorable than inducing the transition by cooling the $\text{Na}_2\text{RbC}_{60}$ to 200 K. (2) If we were observing residual primitive phase superconductivity, we would expect a corresponding loss in the signal intensity due to changes in the superconducting fraction. We do *not*. Furthermore, we could not explain the 3 K lower transition temperature and the substantially lower value for pressure dependence of T_c on samples maintained in that portion of the pressure-temperature phase diagram.

Prassides and co-workers arrived at their conclusions for $\text{Na}_2\text{CsC}_{60}$ because neither they nor anyone else had detected any superconductivity in the polymeric phase of $\text{Na}_2\text{RbC}_{60}$. We believe that is what should be expected in $\text{Na}_2\text{RbC}_{60}$. On the other hand, our measurements demonstrate superconductivity in the polymeric phase of $\text{Na}_2\text{CsC}_{60}$. For the latter phase, we observe an approximately 3 K lower transition than in the primitive cubic phase. If there were a similar drop in T_c in the transition to the polymeric phase in $\text{Na}_2\text{RbC}_{60}$, either a very low T_c or no superconductivity would be observed because T_c is already at ~ 3 K in the primitive cubic phase.

Conclusion

We have demonstrated that the polymeric phase of $\text{Na}_2\text{CsC}_{60}$ may be accessed by pressurizing a sample at room temperature at a pressure of 0.5 Gpa, using a non penetrating pressure medium, followed by cooling to below 200 K. This structural transition is reversible, and the cubic phase is recovered when the sample is returned to ambient conditions. This polymeric phase has both a lower T_c and smaller pressure dependence of T_c than the corresponding values for the primitive cubic phase. On the basis of the above discussion, we have established that the polymeric phase of $\text{Na}_2\text{CsC}_{60}$ is superconducting. The corresponding phase of $\text{Na}_2\text{RbC}_{60}$ may be either non-superconducting or has a T_c below the range of experiments to date.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy (DOE) under contract DE-AC04-94AL85000 at Sandia National Laboratories, contract W-7405-ENG-48 at Lawrence Livermore National Laboratory, contract DEFG02-98ER45701 at the University of Pennsylvania, and contract W-31-109-ENG-38 at Argonne National Laboratory.

References

- [1] R. M. Fleming, A. P. Ramirez, M. J. Rosseinsky, D.W. Murphy, R.C. Haddon, S. M. Zahurak, and A. V. Makhija, *Nature* (London) 352 (1991) 787.
- [2] C.-C. Chen, S. P. Kelty, and C. Lieber, *Science* 253 (1991) 886.
- [3] J. E. Schirber, D. L. Overmyer, H. H. Wang, J. M. Williams, K. D. Carlson, A. M. Kini, U. Welp, W.-K. Kwok, *Physica C* 178 (1991) 137.
- [4] Z. K. Kniaz, J. E. Fischer, Q. Zhu, M. J. Rosseinsky, O. Zhou, and D.W. Murphy, *Solid State Comm.* 88 (1993) 47.
- [5] T. Yildirim, J. E. Fischer, R. Dinnebier, P.W. Stephens, and C.L. Lin, *Solid State Comm.* 93 (1995) 269.

- [6] K. Prassides, C. Christides, I. M. Thomas, J. Mizuki, K. Tanigaki, J. Hirosawa, and T.W. Ebbesen, *Science* 263 (1994) 950.
- [7] Q. Zhu, *Phys Rev B* 52 (1995) R723.
- [8] J. E. Schirber, L. Hansen, B. Morosin, J. E. Fischer, J. D. Jorgensen and G. H. Kwei, *Physica C* 260 (1998) 173.
- [9] J. Mizuki, M. Takai, H. Takahashi, N. Mori, K. Tanigaki, J. Hirosawa and K. Prassides, *Phys Rev B* 50 (1994) 3466.
- [10] L. Cristofolini, K. Kordatos, G. A. Lawless, K. Tanigaki, and M. P. Waugh, *Chem Commun.* (1997) 375.
- [11] K. Prassides, C. Christides, I. M. Thomas, J. Mizuki, K. Tanigaki, J. Hirosawa and T. W. Ebbesen, *J. Am. Chem. Soc.* 119 (1997) 834.
- [12] G. M. Bendele, P. W. Stephens, K. Prassides, K. Vavakis, K. Kordatos, and K. Tanigaki, *Phys. Rev. Lett.* 80 (1998) 736.
- [13] A. Lappas, C. M. Brown, K. Kordatos, E. Suard, K. Tanigaki, and K. Prassides, *J. Phys. Condens. Matter* 11 (1999) 371.
- [14] S. Margadonna, C. M. Brown, A. Lappas, K. Prassides, K. Tanigaki, K. D. Knudsen, T. Le Bihan, M. Mezouar, *J. Sol. State Chem.* 145 (1999) 471.
- [15] M. Rosseinsky, D. W. Murphy, R. M. Fleming, R. Tycko, A. P. Ramirez, T. Siegrist, G. Dabbagh and S. E. Barrett, *Nature* 356 (1992) 416.
- [16] L. R. Azevedo, J. E. Schirber, J. M. Williams, M. H. Beno and D. R. Stephens, *Phys Rev B* 30 (1984) 1370.
- [17] B. Morosin, J. E. Schirber, J. D. Jorgensen, G. H. Kwei, T. Yildirim, and J. E. Fischer, *Recent Advances in Chemistry and Physics of Fullerenes and Related Materials* 3 (1998) 446.
- [18] The Ne a_0 is = 4.4854(7) Å at our nominal 500 psi pressure and 17 K.