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ROLE OF PRESSURE IN THE STUDY OF FULLERENES

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Although fullerenes and their compounds are very new and exhibit new phenomena, pressure has already been an important factor in the characterization and study of these materials. In order to illustrate this, we will review collaborative studies on: i) the effect of pressure on alkali and alkaline earth doped C₆₀ superconductors, ii) the effect of pressure and pressure medium on the ordering temperature of C₆₀, and iii) the role of pressure in the study of the feasibility of using C₆₀ as "lattice sieves" for separation of gases.

INTRODUCTION

Fullerenes have been available in bulk quantities for only a few years, but a rich diversity of properties from superconductivity to unusual ordering transitions and structural transitions have already been discovered. Pressure has proven to be an important parameter in the characterization and in attempts to understand these phenomena. In this paper we will briefly review the results of recent pressure studies with emphasis on our studies at Sandia in collaboration with Argonne, U. Pennsylvania and AT&T Bell Laboratories.

We will concentrate on three aspects of pressure studies of fullerenes and their compounds: i) superconductivity, which occurs when alkali or alkaline earth atoms are intercalated into the octahedral and tetrahedral interstitial sites of the fcc C₆₀ lattice. ii) The ordering that occurs when C₆₀ is cooled below about 250K resulting in a first order change from a fcc arrangement of randomly spinning C₆₀ molecules to a primitive cubic lattice of oriented molecules. iii) The concept that C₆₀ may be useful as a "lattice sieve" in separating various gases. In each of these areas, pressure studies are providing useful and unique insights.

Figure 1. Superconducting transition temperature of various alkali and alkaline earth intercalated C₆₀ compounds versus lattice constant.

SUPERCONDUCTIVITY

Our early measurements^{1,2} of the pressure dependence of T_c of K₃C₆₀ and Rb₃C₆₀ and those of Sporn et al³ coupled with measurements of the lattice constants versus pressure^{4,5} led to the realization that the superconducting transition temperature, T_c , was proportional to the lattice constant (see Fig. 1). This prompted attempts to inflate the lattice by intercalating larger alkali species. Unfortunately Cs₃C₆₀ which would be expected to have a T_c near 50K will not form in

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the fcc lattice; thus the current record high T_C compound is $\text{Rb}_2\text{CsC}_{60}$ with $T_C \sim 34\text{K}$. Its pressure derivative is large and negative⁶ consistent with the T_C proportional to lattice constant (a_0) picture. Theoretical models have been put forward which account for the T_C vs a_0 behavior.^{7,8} Kortan and coworkers⁹ have succeeded in synthesizing alkaline earth intercalated C_{60} compounds including Ca_5C_{60} which has a $T_C \sim 9\text{K}$. Ca_5C_{60} fits nicely on the universal T_C vs a_0 curve and thus might, from simple consideration, be expected to display the same large negative value for dT_C/dP as do the alkali metal C_{60} superconductors. We recently¹⁰ measured dT_C/dP for Ca_5C_{60} and obtain a positive value of $+0.1 \pm 0.05 \text{ K/kbar}$. This result is shown graphically in Fig. 2 where the onset of superconductivity is shown relative to the signature for Nb. Nb has a completely negligible pressure derivative on this scale so it is clear that the Ca_5C_{60} transition moves closer to that of Nb with higher pressure, thus dT_C/dP is positive. This result may not be so surprising in that with the donation of ten electrons from the five Ca atoms, the next higher t_{1g} band is also

Figure 2. Superconducting signatures of Nb (sharp feature) and Ca_5C_{60} (steep shoulder) at 0.7 and 5.0 kbar.

partially occupied rather than just the t_{1u} band important in the alkali C_{60} superconductors. What is clearly required is a volume dependent band structure/density of states calculation which we hope this study will prompt.

ORDERING TEMPERATURE

Our initial measurements of the pressure dependence of the orientational ordering temperature from the high temperature freely rotating fcc structure to the low temperature oriented primitive cubic lattice yielded the intuitively expected result that the transition rose with pressure.¹¹ Completely unexpected, however, was the finding that the magnitude of the effect depended dramatically on the nature of the pressure medium. With He, $dT_O/dP = 11 \text{ K/kbar}$, while with N_2 or pentane the value is 16 K/kbar (see Fig. 3). This suggests that the pressure medium is intercalating into the lattice. At high pressures the lattice can be "permanently" intercalated with pentane resulting in a different structural arrangement. We have recently observed "negative pressure" effects after application of pressures of O_2 to 1 kbar and subsequent release of the O_2 pressure. The

Figure 3. Temperature-pressure phase diagram for C_{60} using He and pentane as pressure media. Using N_2 as the pressure medium gives the same initial curve as pentane.

ordering temperature has been observed to be depressed by the order of 20 K. As the O₂ diffuses out of the C₆₀ lattice, the ordering temperature rises, slowly approaching the initial value of about 260 K. Figure 4 shows the recovery of the ordering temperature as the O₂ diffuses out of the lattice of a high pressure oxygen charged sample of C₆₀. This particular sample was charged for 48 hours at room temperature and 1 kbar. This behavior has thus far been observed only for O₂ and is still under investigation.

Figure 4. Delta (defined as the difference between the ordering temperature and in virgin C₆₀) in the oxygen charged C₆₀ vs time in hours.

We have also made preliminary measurements of the pressure dependence of ordering in C₇₀. At least two ordering temperatures have been observed presumably stemming from the hcp and fcc packing arrangements found in C₇₀. The nature of these transitions and their pressure derivatives are complicated and are not as yet understood. Clearly however pressure studies are uncovering a rich variety of phenomena as the fullerenes are intercalated with various constituents including the pressure media themselves.

LATTICE SIEVES

The unexpected results outlined above coupled with our early nmr studies of oxygen in C₆₀ led us to suggest that gas separators might

be effected with thin films of C₆₀ and other fullerenes.^{12,13} Typical filters are made from materials like polymers which have a spectrum of pore sizes. C₆₀ crystallizes in the fcc lattice and has such large interstitials that various sized molecules and/or atoms can easily penetrate and diffuse through the lattice. Figure 5 shows a face centered cubic array of spheres with the octahedral and tetrahedral sites exposed. The

Figure 5. Cutaway of a face centered cubic array of spheres which closely approximates C₆₀. The cube face or 100 plane exposes the octahedral sites, while the 111 plane exposes the tetrahedral sites.

octahedral sites will accommodate species as large as 4Å while the tetrahedral sites, the order of 2.3Å in diameter. Thus there is ample room for most elemental and many molecular species. Since here we are dealing with a lattice, there is a very precise effective pore size which may be exploited to separate quite similar gases. We have used high pressure loading of bulk C₆₀ materials with various gases and monitored the subsequent release of these gases with nmr and weight loss as a function of time. From such measurements we can derive estimates of the permeation and diffusion of these gases through C₆₀. Using these results we can infer separation factors for various pairs of gases when the

outgasing experiments are performed on the same starting C60 material. Our preliminary findings are summarized in Table I for O₂ vs N₂ and for O₂ vs H₂.

Table I. Comparison of the percentage of octahedral sites filled and characteristic release times for O₂ and N₂ from ground C60 and O₂ and H₂ from unground C60.

Gas % Filled Time (min)			Comments
O ₂	37	270	ground C60 (bulk < 20 μ) separation factor 3.0
N	19	420	
O ₂	17	2100	unground C60 (bulk 75-100 μ) separation factor 240
H ₂	27	14	

These preliminary measurements suffer from substantial uncertainties because of the sensitivity to grain size, but are clearly provocative. The successful separation of O₂ from N₂ would be of enormous importance because of the vast amounts of energy expended (0.25 Quad) each year in this process.

CONCLUSIONS

Although this is a new field of endeavor, we feel that these three examples clearly demonstrate the importance of pressure in yet another arena. Further work is called for, but new insights and even practical applications appear to be forthcoming.

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