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Physica B 296 (2001) 112–119

**PHYSICA B**

www.elsevier.com/locate/physb

# The other high-temperature superconductors

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## Abstract

Since the discovery of the high-temperature superconducting cuprates in 1986, there have been four classes of superconductors discovered that have members with critical temperature higher than the highest known in 1986. These classes are typified by (in chronological order) the representatives:  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ,  $\text{Cs}_3\text{C}_{60}$ ,  $\text{YPd}_2\text{B}_2\text{C}$ , and  $\text{Na}_x\text{HfNCl}$ , with maximum critical temperatures, respectively, of 35, 40, 23, and 25 K. These new superconductors are mostly different from the older superconductors, and certainly different from the layered cuprates. For several characteristics that are possibly important for superconductivity, two or three of the classes share similarities. There seems, however, to be almost no feature that is shared by all four classes. However, the three for which there is isotope shift data clearly qualify as phonon-coupled superconductors. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Superconductivity; Intermetallics; Quaternary compounds; Isotope effect

## 1. Motivation for this overview

From the early 1970s until 1986 when the high-temperature superconductors based on  $\text{CuO}_2$  layers were discovered, [1] the highest superconducting critical temperature  $T_c$  was 23 K in the A15 pseudobinary system  $\text{Nb}_3\text{Al}_{1-x}\text{Ge}_x$  [2,3]. Two decades of intense study had increased  $T_c$  in the A15s from  $\sim 15$  to 23 K, and the prevailing understanding of producing high-temperature superconductors at that time was encoded in a loosely formulated set of “Matthias’s rules”:

- Transition metals are better than simple metals.
- There are favorable electron/atom ratios [ $N(E_F)$  peaks].
- High symmetry is good; cubic symmetry is best.

- Stay away from oxygen.
- Stay away from magnetism.
- Stay away from insulating phases.

Here  $N(E_F)$  is the density of states at the Fermi level  $E_F$ . It has been abundantly clear that many of these “rules” have been broken by the cuprate high-temperature superconductors (HTS), which are in a class by themselves when considering superconductivity.

The purpose of this paper is to provide an overview and a comparison of four classes of materials that have been discovered since the discovery of the HTS, all of which have maximum values of  $T_c$  equal to or higher than 23 K critical temperature in the A15 superconductors. Representatives of these classes are listed in Table 1, with the year of discovery of that class, the maximum  $T_c$ , and a rough characterization of the value of  $N(E_F)$ . What will become clear is that at least three of these classes of superconductors are quite different from those that

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Table 1

Classes of superconductors, with representative member, with  $T_c > 20$  K, excluding the cuprate superconductors. The date of discovery, and rough characterization of their Fermi level density of states  $N(E_F)$  is given

Year	$T_c^{\max}$ (K)	Representative	$N(E_F)$
1973	23	Nb <sub>3</sub> Ge	Large
1988	35	Ba <sub>1-x</sub> K <sub>x</sub> BiO <sub>3</sub>	Small
1991	40	Cs <sub>3</sub> C <sub>60</sub>	Large
1994	23	YPd <sub>2</sub> B <sub>2</sub> C	Large
1997	25	Na <sub>x</sub> HfNCl	Small

Table 2

Classes of superconductors, with representative member, the Maximum  $T_c$  in the class, and indication of the measured value of the isotope shift of  $T_c$  for certain elements

$T_c^{\max}$ (K)	Representative	$\alpha_j$
23	Nb <sub>3</sub> Ge	–
35	Ba <sub>1-x</sub> K <sub>x</sub> BiO <sub>3</sub>	$\alpha_O = 0.2; 0.4$
40	Cs <sub>3</sub> C <sub>60</sub>	$\alpha_C \sim 0.3-0.4$
23	YPd <sub>2</sub> B <sub>2</sub> C	$\alpha_B \sim 0.25$
25	Na <sub>x</sub> HfNCl	?

followed Matthias's rules, and certainly different from each other.

The discussion will proceed system-by-system, in order of their discovery. Since the Cs<sub>3</sub>C<sub>60</sub> systems has been well reviewed elsewhere, the discussion here will be particularly selective. The discussion here is not focussed on the coupling mechanism per se, but since there is some isotope effect information on all but one of these systems, we will include discussion and references on this data. The isotope shift coefficient  $\alpha_j$  due to isotope replacement of element  $j$  with mass  $M_j$  in the compound is defined by

$$\alpha_j = -\frac{d \log T_c}{d \log M_j} \quad (1)$$

and a value of  $\alpha_j$  that is definitely nonzero (greater than 0.1, say) is normally regarded as clear evidence of participation of phonons in the superconducting pairing (see Carbotte's review [4]). In a harmonic phonon-coupled system, the sum of the (positive) isotope shifts from each of the elements adds to  $\frac{1}{2}$  if

Coulomb repulsion is neglected, and more generally adds to a number less than but of the order of  $\frac{1}{2}$ . The picture arising from the isotope shift data is summarized in Table 2.

## 2. The barium bismuthate system

This system is the only high  $T_c$  system whose discovery was strongly influenced by theory. Building on knowledge of the electronic structure of the Ba(Pb,Bi)O<sub>3</sub> (BPBO) system, whose  $T_c$  peaks around 13 K, Mattheiss et al. [5] reduced the carrier concentration by substituting K on the Ba site rather than Pb on the Bi site, and produced  $T_c > 20$  K in the Ba<sub>1-x</sub>K<sub>x</sub>BiO<sub>3</sub> (BKBO) system, a value which was then raised to 30 K by Cava et al. [6,7] and finally to 35 K. Doping with Rb also works [6] but that system has been studied very little.

Superconductivity in BKBO emerges from a distorted perovskite structure (space group C2/m [8], possibly P2/m at the lowest temperatures [9]) of semiconducting BaBiO<sub>3</sub>. This monoclinic structure is very low symmetry (four operations) but contains the inversion operation, hence it is not ferroelectric. Electronic structure calculations of the (unstable) cubic perovskite structure of BaBiO<sub>3</sub> indicate a metallic system – in fact, a half-filled band system – with a strongly nested Fermi surface that drives a Peierls-like, charge density wave doubling of the cell [10,11]. The Bi ions in the doubled cell become inequivalent, but the charge disproportionation has been found both experimentally and theoretically to be small. In addition, the BiO<sub>6</sub> octahedra rotate, again doubling the unit cell and complicating both the experimental characterization and the theoretical description.

Doping with K at a concentration  $x \geq 0.3$  leads to a cubic metal and  $T_c$  up to 35 K. For most purposes this system behaves in a rigid band way based on cubic BaBiO<sub>3</sub> band structure. The relevant energy range is dominated by a broad antibonding Bi 6s–O 2p band crossing the Fermi level [12].

Although there have been questions about the possible influence of residual electron–electron interactions in explaining the normal state properties

and high value of  $T_c$  in BKBO, nearly all studies have concentrated on electron–phonon (E–P) coupling, and particularly the coupling to the high-frequency oxygen modes. This view is justified by the isotope shift of  $T_c$ , where reported values are  $\alpha_O = 0.22$  [13],  $\alpha_O = 0.41$  [14], and  $\alpha_O = 0.35$  [15].

Rigid-ion-type models of the coupling indicate dominant coupling to oxygen [11,16]. A tight-binding parametrization of electronic structure and E–P matrix elements [17] also led to strong coupling, with E–P coupling strength  $\lambda \sim 1.1$  for the maximum  $T_c$ , and  $T_c$  values of over 30 K could be accounted for. Tunneling measurements [18,19] also indicate strong coupling to high-frequency phonons in BKBO, and overall features consistent with an E–P mechanism with relatively strong coupling. A very interesting loose end in this picture is the recent result of Merregalli and Savrasov [20] who have carried through the only fully first principles calculation of the phonon spectrum and E–P coupling strength for BKBO. Their results correspond only to a coupling strength of  $\lambda = 0.3$ , insufficient to account for  $T_c$  in the 30–35 K range.

Some of the basics of the BKBO system perhaps may be considered to be understood. But why it so much better a superconductor than, say, the oxide  $\text{LiTi}_2\text{O}_4$ , or more to the point, the very similar compound BPBO? It is dangerous to make a serious comparison to  $\text{LiTi}_2\text{O}_4$  ( $T_c = 13$  K), as it is one of only two out of many oxide spinels that is metallic and thus may be curious itself. (The other conducting spinel is  $\text{LiV}_2\text{O}_4$ , an even more curious heavy fermion compound.) At present, there may be no better information on the strong difference between BKBO and BPBO than that which guided Mattheiss et al. [5]: altering the Fermi level toward half filling (and strongest coupling to the oxygen bond stretch vibrations) by  $\text{Bi} \rightarrow \text{Pb}$  induced charge ordering waves on the  $\text{Pb}$ – $\text{Bi}$  sublattice; varying the electron count by  $\text{Ba} \rightarrow \text{K}$  leaves the  $\text{Bi}$  sublattice intact. As a result the system retains structural stability further into the strong coupling regime.

### 3. The fullerides

The fullerene ( $\text{C}_{60}$ )-based solids have been studied so heavily and reviewed so thoroughly

[21–26] that there is little to add here except to put them into the context of these classes of superconductors. Gunnarsson has given a detailed review [22] of the various theoretical considerations that enter into the superconductivity of the fullerides. Superconductivity was discovered first in the tri-alkali-fullerides such as  $\text{K}_3\text{C}_{60}$  [27,28] in the area of  $T_c \sim 20$  K, but there are now several combinations of alkali or alkaline earth metal atoms that can produce superconductivity when placed in interstitial sites in the fullerene lattice. The highest value reported is 40 K for  $\text{Cs}_3\text{C}_{60}$  under pressure [29].

These fullerides are simply unique, not only in the world of superconductivity but in crystalline solids in general. Structurally, the solids consist of a lattice determined mostly by the highly symmetrical, closed shell  $\text{C}_{60}$  molecules. Electronically, the fullerene molecule can be viewed almost as a nearly spherical ‘superatom’, supplying superatom orbitals that have a more angular structure than a transition metal’s  $d$  suborbitals have, but otherwise are orbitals with small overlap with neighboring orbitals [30–32].

The alkali (or alkaline earth) ions go into the interstitial sites in the solid, and change the structure somewhat, but the primary effect is to donate their valence electrons to the narrow ( $< 1$  eV wide)  $\text{C}_{60}$ -derived bands. The hopping is however large enough compared to the intra-molecular Coulomb repulsion that metallic behavior results, and in many cases superconductivity arises. Superconductivity was discovered [27] around 20 K in  $\text{K}_3\text{C}_{60}$  almost as soon as metallicity was obtained.

The many considerations that arise in evaluating whether superconductivity in fullerides arises for E–P coupling has been reviewed by Gunnarsson [22]. A similarity to BKBO is that the coupling results mainly from the high frequency phonons. In the fullerides these modes are those that modulate the C–C bonds most strongly, which are primarily those in which the C atoms move tangentially to the surface of a  $\text{C}_{60}$  molecule.

Several isotope shift experiments have been reported, and are referenced and discussed in previous reviews [21,22]. The accepted value is around  $\alpha_C \sim 0.35$ , which is a normal value for a conventional superconductor. (Much larger

values have been reported in two cases but apparently do not represent intrinsic shifts.) An experiment by Chen and Lieber [33] is particularly noteworthy. They realized that a (say, 50%) mixture of  $^{12}\text{C}$  and  $^{13}\text{C}$  can be achieved in a fulleride in two distinctly different ways: each buckyball can contain half of each (statistically, of course), with the solid made of these similar buckyballs, or, buckyballs can be made separately of each isotope, and the solid made of a 50% mixture of each type. Optical measurements on the solids confirmed that substitution occurred as expected – in the first case the infrared-active phonons were mass-averaged, while in the second case the phonons were mass-differentiated. In the first case,  $\alpha_c \approx 0.3$  was obtained, consistent with the value quoted above (this is the standard way of doing the isotope replacement). In the second case, the anomalously large value of  $\alpha_c \sim 1.3$  was obtained. This result still has no satisfactory explanation. Since the change of mass is 8%, it is possible – but not likely – that the linear approximation assumed in Eq. (1) breaks down. Another possibility is a large anharmonicity of strongly coupled phonon modes. The most strongly coupled are the  $H_g$  symmetry modes of the buckyball, but anharmonicity is not apparent in other data on these modes.

It was emphasized by Schlüter et al. [34] that there is a monotonic relationship between the value of  $T_c$  and the shortest distance  $d$  between two C atoms on neighboring  $\text{C}_{60}$  molecules, with  $T_c$  increasing with  $d$ . This effect is generally explained (see Ref. [22]) as resulting from the expression

$$\lambda = N(E_F)\langle V \rangle. \quad (2)$$

The Fermi surface averaged pairing potential  $\langle V \rangle$  is insensitive to spacing, being largely a molecular property. The bandwidth decreases, however, as the intermolecular spacing – and hence hopping – decreases, and  $N(E_F)$  increases. This trend will finally be halted by correlation effects; however, it seems to hold for all fullerides superconductors fabricated so far.

#### 4. The rare earth–transition metal–borocarbides

The first discoveries in this system were reported in 1994. Superconductivity in this system was

discovered by Mazumdar, Hagarajan, and collaborators in the Y–Ni–B ternary system [35] and in the Y–Ni–B–C quaternary system [36] at 12 K. Cava et al. [37] obtained superconductivity in the  $\text{LnNi}_2\text{B}_2\text{C}$  system for  $\text{Ln} = \text{Y}$  and for the lanthanides  $\text{Ln} = \text{Tm}, \text{Er}, \text{Ho},$  and  $\text{Lu}$ . For the Lu compound  $T_c$  was above 16 K. The phase was identified as a layered structure of the modified  $\text{ThCr}_2\text{Si}_2$  type [38]. This system can be made with most of the lanthanides, and after the initial excitement over the relatively high  $T_c$  in this system, the strong subsequent activity has centered largely on the competing and sometimes coexisting magnetic and superconducting order parameters [39]. Some overviews are available [40,41], but an extensive review is yet to be undertaken.

Rather early on,  $T_c \approx 23$  K was reported in the Y–Pd–B–C system [42,43] and was naturally suspected to be  $\text{YPd}_2\text{B}_2\text{C}$  with the same crystal structure, but it has proven to be very difficult to isolate a large enough fraction of the phase to determine the structure unambiguously. There have been disagreements in the literature about whether the 23 K superconducting phase has the same structure as the other borocarbides [44–46], but the majority of the evidence seems to indicate so. Very recently, Dezaneti et al. [47] claimed to have made the direct identification.

The layered crystal structure of  $\text{YNi}_2\text{B}_2\text{C}$  suggested that this was another quasi-two-dimensional system, as the cuprates had been found to be. Electronic structure studies indicated this should *not* be the case [48–50] but that the electronic structure should be only weakly anisotropic. This prediction has been substantiated by the extensive experimental data that has appeared due to the availability of clean, large single crystals [39].

There is nothing so remarkable in the band structure, of either  $\text{LuNi}_2\text{B}_2\text{C}$  ( $T_c = 16.6$  K) or the isostructural, isovalent  $\text{YPd}_2\text{B}_2\text{C}$  (apparently the  $T_c = 23$  K compound) to indicate that it should be an unusually good superconductor. In a general sense it might be said that it is an intermetallic (or -metalloid) compound that is comparable to  $\text{Nb}_3\text{Ge}$ , but there are other such intermetallic compounds with a rather high value of  $N(E_F)$  that are not good superconductors.

One obvious and suggestive feature is a band that is quite flat near the  $(\pi/a, \pi/a, 0)$  part of the Brillouin zone. This band has not had any simple interpretation in terms of a tight-binding picture. It has a majority of Ni d character, but is split off from the main Ni d band region and is hybridized with both B and C, and interactions with the rare earth atom also seem to have some importance for this band [51]. It is this band that produces the peak in the density of states very close to  $E_F$ , a peak that is clearly central to the high value of  $T_c$ . A simpler guess, however, based on the band structure and the strong Ni character, would be that magnetism, not superconductivity, would arise.

An estimate of the relative coupling strength of the four atoms in  $\text{LuNi}_2\text{B}_2\text{C}$  [52] gave the ratios B:C:Ni = 50%:30%:20%, i.e. these atoms may have contributions that are comparable in magnitude. Mattheiss et al. pointed out [53] a strong dependence of the position of the flat band to the position  $z_B$  of the B atom, translating into strong coupling to the B atom. Laurie and Franck [54] reported an isotope shift of  $\alpha_B = 0.27$ , indicating that B motion is very strongly involved in enhancing  $T_c$ .

On the experimental side, strong coupling effects have been seen through neutron spectroscopy of the phonons of these compounds by Kawano et al. [55], by Stassis et al. [56], and by Gompf et al. [57], leaving no doubt of the strong d–p coupling in this system. The overview by Drechsler et al. [58] should be consulted for further information and references.

## 5. The transition metal chloronitrides

The layered compounds  $\text{ZrNCl}$  and  $\text{HfNCl}$  have been known for some time, [59,60] but it was reported only in 1996 that they could be doped – intercalated – with Li or Na to become metallic and superconducting [61–64]. An impressive value of  $T_c = 25$  K was reached by Yamanaka et al. [62] in  $\text{Na}_x\text{HfNCl}$  with an estimated value of  $x \sim 0.3$ .

The structure of this system is shown in Fig. 1.  $(\text{HfN})_2$  (or  $(\text{ZrN})_2$ , but we take the Hf compound for definiteness) bilayers are cladded on either side

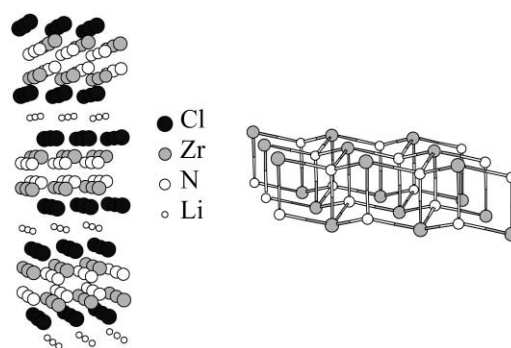


Fig. 1. Structure of the Na-doped  $\text{HfNCl}$  structure. Left: arrangement of the Na, Cl, and HfN layers. A full monolayer of Na is pictured. Right: bonding configuration of the  $(\text{HfN})_2$  bilayer. Note that Hf and N are bonded to each other across the bilayer as well as within it.

by Cl ions, and in the undoped compounds this six layer slab is van der Waals bonded to neighboring slabs. Electronic structure studies [65–67] obtain a gap of 1.5–2 eV, similar to the experimental value. The system is consistent with a formal ionic description  $\text{Hf}^{4+}\text{N}^{3-}\text{Cl}^-$ , with the Hf d shell empty. Further study indicates however that an ionic picture is limited, because there is a strong covalent component to the bonding involving N p and Hf d states that shows up in the band character and in the valence charge distribution.

Virtual crystal calculations indicate [65,66] that the doped-in Na atom gives up its valence electron to a Hf d–N p band within the layer, in line with expectations. This band is comprised of in-plane orbitals ( $d_{xy}$ ,  $d_{x^2-y^2}$  and  $p_x$ ,  $p_y$ ), which being above the filled N p bands and at the bottom of the Hf d bands, is probably best characterized as non-bonding. Since there are two such layers, a bonding combination and an antibonding combination forms, split by  $\sim 1.5$  eV. It is the layer-symmetric d–p band that the additional electrons occupy. This situation can be seen in the left panel of Fig. 2.

It is not easy to ascertain accurately the fraction  $x$  of Na, and hence conduction electrons, in the superconducting parts of the samples, although  $x \sim 0.3$  has been quoted as the likely value. At this doping level, the Fermi energy still lies within the lowest conduction band, which is a surprisingly low

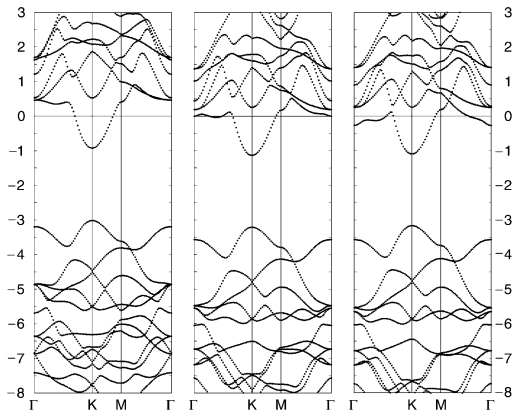


Fig. 2. Virtual crystal band structure in symmetry direction of  $\text{Na}_x\text{HfNCl}$ , for (left)  $x = 0.25$ , (center)  $x = 0.35$ , and (right)  $x = 0.45$ . The band structure becomes notably non-rigid-band-like for  $x = 0.45$ , and there are even important differences (besides band filling) between the  $x = 0.25$  and the  $x = 0.35$  bands. Note that it is right around  $x = 0.35$  where the flat bands (strongly Hf  $d_{z^2}$ -like) begin to become occupied.

mass ( $m^* = 0.6 m_e$ ) band that leads to a small value of  $N(E_F)$  and seems unlikely to encourage either strong E–P coupling or large electron correlation effects. This state of affairs has presented a conundrum in trying to account for the pairing mechanism. No isotope shift data have been reported.

Recent analysis of the condition of samples, and the middle and right panels of Fig. 2 suggests a possible resolution of this puzzle. Oró-Solé et al. [68] have shown that samples are likely to more inhomogeneous than previously thought, and therefore the value of  $x$  in the superconducting regions may be different than supposed. Fig. 2 indicates that around  $x \sim 0.35$ , the second conduction band begins to become occupied. This band is quite flat over some regions of the Brillouin zone, due to its strong  $d_{z^2}$  character that couples primarily to N  $p_z$  orbitals with a  $dp\pi$  overlap, which is typically much smaller than the  $dp\sigma$  overlap that leads to the low mass band. This flat band leads to a high value of  $N(E_F)$ , and possibly to correlation effects as well. One should note in this regard that the electronic structure around the Fermi level is very strongly two dimensional, a feature that may also play a part in the pairing mechanism.

## 6. Comparisons and contrasts

There seems to be little mystery why the fullerenes, and the borocarbides are superconducting at roughly the observed temperature. The transition metal chloronitride system is newer and much less effort has been expended on it. Even the chemical composition of the superconducting phases are uncertain, and there is reason to believe this value may be crucial. The first three systems are E–P coupled systems, and there is simply no clear information yet on the fourth system.

The first three systems are also comprised of type II superconductors, and estimates of materials parameters [65] indicate the chloronitrides are type II as well. This feature is of central interest in the borocarbides, since many of the materials have competition between magnetic ordering and superconductivity.

As noted in the introduction, Matthias' rules are profoundly violated by these new classes of superconductors with  $T_c > 20$  K and by the HTS. One can observe that there are characteristics that are common to some of all of these newer classes:

1. must be multicomponent – more than a binary;
2. at least one site should have variable occupancy (“dopant”);
3. large electronegativity difference between constituents;
4. proximity to a magnetic or insulating phase;
5. mixed antibonding bands at the Fermi level;
6. there are favorable electron/ion ratios.

Regarding new rule 1,  $\text{A}_3\text{C}_{60}$  is binary in the strict sense, but it is a much richer system than standard binary compounds. The other systems have four elements. As for new rule 2, the borocarbides must be considered as stoichiometric. They can be alloyed on certain sites, but that flexibility is not central to their superconductivity. The fullerenes also tend strongly toward stoichiometry, where  $T_c$  is highest. For the other two systems, BKBO and  $\text{Na}_x\text{HfNCl}$ , a variable concentration is crucial, as it is in many HTS systems. The electronegativity difference (3) is large in at least three of the systems. In the borocarbides, there may be some ionic character but it is difficult to identify and quantify. In

fact, the borocarbides in many ways seem to be more complicated intermetallics in the mold of the A15 compounds such as Nb<sub>3</sub>Ge.

Only the borocarbides are not near (in some rough sense) an insulating phase (4). Unlike the HTS, none of these phases are intrinsically magnetic (magnetic ions can be put into the borocarbides, and the systems display very interesting phenomena). The suggestion of 5 is difficult to assess. The band character at  $E_F$  may be important, but no strong regularities are apparent. Three of the systems might be said to show favorable electron/atom ratios (6): C<sub>60</sub>, BKBO, and the doped chloronitrides. Only one of the four classes deviates from three dimensionality, so reduced dimensionality does not seem to be a strong factor.

### Acknowledgements

I acknowledge D.J. Singh, R. Weht, and A. Filippetti for their collaboration on some of the work discussed in this paper. This research was supported by the Office of Naval Research grant N00014-97-1-0956.

### References

- [1] G. Bednorz, K.A. Müller, *Physica B* 64 (1986) 189.
- [2] J. Gavaller et al., *IEEE Trans. on Magnetism* MAG-11 (1975) 192.
- [3] J.R. Gavaler, M.A. Janocko, C.K. Jones, *J. Appl. Phys.* 45 (1974) 3009.
- [4] J.P. Carbotte, *Rev. Mod. Phys.* 62 (1990) 1027.
- [5] L.F. Mattheiss, E.M. Gyorgy, D.W. Johnson Jr., *Phys. Rev. B* 37 (1988) 3745.
- [6] R.J. Cava et al., *Nature* 332 (1988) 814.
- [7] R.J. Cava, B. Batlogg, *MRS Bulletin* 14 (1989) 49.
- [8] D.E. Cox, A.W. Sleight, *Solid State Commun.* 19 (1976) 969.
- [9] S. Pei et al., *Phys. Rev. B* 41 (1990) 4126.
- [10] L.F. Mattheiss, D.R. Hamann, *Phys. Rev. B* 28 (1983) 4227.
- [11] N. Hamada et al., *Phys. Rev. B* 40 (1989) 4442.
- [12] L.F. Mattheiss, D.R. Hamann, *Phys. Rev. Lett.* 60 (1988) 2681.
- [13] B. Batlogg et al., *Phys. Rev. Lett.* 61 (1988) 1670.
- [14] D.G. Hinks et al., *Nature* 335 (1988) 419.
- [15] S. Kondoh et al., *Physica C* 157 (1989) 469.
- [16] D.A. Papaconstantopoulos et al., *Phys. Rev. B* 40 (1989) 8844.
- [17] M. Shirai, N. Suzuki, K. Motizuki, *J. Phys.: Condens. Matter* 2 (1990) 3553.
- [18] Q. Huang et al., *Nature* 347 (1990) 369.
- [19] N. Tralshawala et al., *Phys. Rev. B* 51 (1995) 3812.
- [20] V. Mereghalli, S.Y. Savrasov, *Phys. Rev. B* 57 (1998) 14453.
- [21] W.E. Pickett, in: H. Ehrenreich, F. Spaepen (Eds.), *Solid State Physics*, Vol. 48, Academic Press, New York, 1994, pp. 225–347.
- [22] O. Gunnarsson, *Rev. Mod. Phys.* 69 (1997) 575.
- [23] V. Buntar, F.M. Sauerzopf, H.W. Weber, *Australian J. Phys.* 50 (1997) 329.
- [24] T. Yildirim, *Proc. Symp. on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Vol. 6, Electrochemical Soc., Pennington NJ, 1998, p. 360.
- [25] L. Degiorgi, *Adv. Phys.* 47 (1998) 207.
- [26] H. Ehrenreich, F. Spaepen (Eds.), *Solid State Physics*, Vol. 48, Academic, New York, 1994 (The entire volume is devoted to reviews of properties of fullerene solids).
- [27] A. Hebard et al., *Nature* 350 (1991) 600.
- [28] R.M. Fleming et al., *Nature* 352 (1991) 787.
- [29] T.T.M. Palstra et al., *Solid St. Commun.* 93 (1995) 327.
- [30] S.C. Erwin, W.E. Pickett, *Science* 254 (1991) 842.
- [31] S. Saito, A. Oshiyama, *Phys. Rev. Lett.* 66 (1991) 2637.
- [32] N. Troullier, J.L. Martins, *Phys. Rev. B* 46 (1992) 1754.
- [33] C.-C. Chen, C.M. Lieber, *Science* 259 (1993) 655.
- [34] M. Schlüter et al., *J. Phys. Chem. Solids* 53 (1992) 1473.
- [35] C. Majumdar et al., *Solid State Commun.* 87 (1993) 413.
- [36] R. Nagarajan et al., *Phys. Rev. Lett.* 72 (1994) 274.
- [37] R.J. Cava et al., *Nature* 367 (1994) 252.
- [38] T. Siegrist et al., *Nature* 367 (1994) 254.
- [39] P.C. Canfield, P.L. Gammel, D.J. Bishop, *Physics Today* 51 (1998) 40.
- [40] L.C. Gupta, *Phil. Mag. B* 77 (1998) 717.
- [41] H. Takagi, M. Nohara, R.J. Cava, *Physics B* 237–238 (1997) 292.
- [42] R.J. Cava et al., *Nature* 367 (1994) 146.
- [43] Z. Hossain et al., *Solid State Commun.* 92 (1994) 341.
- [44] V. Strom et al., *J. Mat. Res.* 11 (1996) 572.
- [45] E. Tominez et al., *J. Alloys Compounds* 275–277 (1998) 123.
- [46] Y.Y. Sun et al., *Physica C* 230 (1994) 435.
- [47] L.M. Dezaneti et al., *Physica C* 334 (2000) 123.
- [48] W.E. Pickett, D.J. Singh, *Phys. Rev. Lett.* 72 (1994) 3702.
- [49] L.F. Mattheiss, *Phys. Rev. B* 49 (1994) 13 279.
- [50] J.Y. Rhee, X. Wang, B.N. Harmon, *Phys. Rev B* 51 (1995) 15 585.
- [51] W.E. Pickett, D.J. Singh, unpublished.
- [52] W.E. Pickett, D.J. Singh, *J. Supercond.* 8 (1995) 425.
- [53] L.F. Mattheiss, T. Siegrist, R.J. Cava, *Solid State Commun.* 91 (1994) 587.
- [54] D.D. Lawrie, J.P. Franck, *Physica C* 245 (1995) 159.
- [55] H. Kawano et al., *Phys. Rev. Lett.* 77 (1996) 4628.
- [56] C. Stassis et al., *Phys. Rev. B* 55 (1997) R8678.
- [57] F. Gompf et al., *Phys. Rev. B* 55 (1997) 9058.
- [58] S.-L. Drechsler et al., *Physics C* 317–318 (1999) 117.

- [59] V.R. Juza, J. Heners, *Z. Anorg. Allg. Chem.* 332 (1964) 159.
- [60] V.R. Juza, H. Friedrichsen, *Z. Anorg. Allg. Chem.* 332 (1964) 173.
- [61] S. Yamanaka, H. Kawaji, K. Hotehama, M. Ohashi, *Adv. Mater.* 9 (1996) 771.
- [62] S. Yamanaka, K. Hotehama, H. Kawaji, *Nature* 392 (1998) 580.
- [63] S. Shamoto, T. Kato, Y. Ono, Y. Miyazaki, K. Ohoyama, M. Ohashi, Y. Yamaguchi, T. Kajitani, *Physica C* 306 (1998) 7.
- [64] S. Shamoto, T. Kato, Y. Ono, Y. Miyazaki, K. Ohoyama, M. Ohashi, Y. Yamaguchi, T. Kajitani, *J. Phys. Chem. Solids* 60 (1998) 1431.
- [65] R. Weht, A. Filippetti, W.E. Pickett, *Europhys. Lett.* 48 (1999) 320.
- [66] R. Weht, A. Filippetti, W.E. Pickett, *High Temperature Superconductivity*, in: S.E. Barnes, et al., (Eds.), *Proceedings of the Miami HTS99*, AIP, New York, 1999, p. 141.
- [67] C. Felser, R. Seshadri, *J. Mater. Chem.* 9 (1999) 459.
- [68] J. Oró-Solé et al., *Solid State Sci.* 2 (2000) 77.