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Recent Developments (After 2000)

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1. MgB₂

The discovery of new superconducting materials continues to surprise. One particularly interesting line of development has been the work in *s-p* element compounds. Perhaps the most unexpected finding here has been, in the late 2000s, the discovery by Nagamatsu and coworkers that MgB₂ becomes superconducting below 39 K [1].

MgB₂ is a well-known chemical compound that can be purchased commercially in powder form. Its structure is shown in Fig. 6.1 and can be viewed as a simple hexagonal stacking of graphitic boron with a Mg atom above and below the center of each boron hexagon. This is a fairly common intermetallic structure with a few low-*T_c* superconducting transition-metal borides found in a defect variant, for example, Nb₂B₅ [2]. The structural prototype is AlB₂, which is not superconducting and appears to form with substantial Al vacancies, the actual stoichiometry being close to Al_{0.7}B₂ [3]. One wonders why MgB₂ was never checked earlier for superconductivity, the probable answer being that the boiling point of Mg is lower than the melting point of B, ruling out the simple preparation via arc melting of the constituents. It turns out that the synthesis of phase pure and stoichiometric MgB₂ is difficult. The growth of single-crystalline specimens requires special

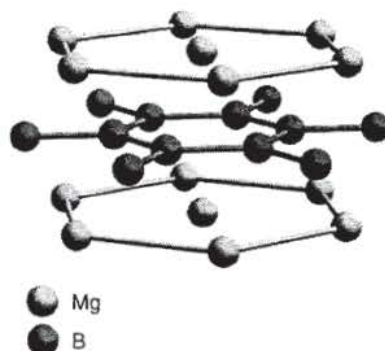


Figure 6.1 Crystal structure of MgB_2 . The upper and lower centered hexagonal sheets are Magnesium atoms which alternate with the central sheets of Boron along the hexagonal c axis [4].

techniques and a preparation process involving the Mg–B–N system under high pressure seems to be the most successful [5].

Already early studies after the discovery of superconductivity of this compound indicated that MgB_2 does not allow for large variations of the chemical composition without losing phase purity and, in most cases, without the loss of superconductivity [6]. It appears that the binary compound with the proper stoichiometry exhibits the highest T_c . Replacing boron by carbon or magnesium by aluminum at the few percent level leads to drastic reductions of the critical temperature [7]. It turns out that the value of the critical temperature also depends significantly on the purity of the boron used in the synthesis process and, in the case of single crystals, T_c can be maximized by choosing growth temperatures exceeding 2000°C . At high hydrostatic pressures, on the order of 30 kbar, MgB_2 appears to be stable up to 2200°C [8].

Considering the layered structure of the compound, shown in Fig. 6.1, it seems reasonable to expect significant anisotropies in its physical properties. Considerable anisotropies were revealed in measurements of the lattice parameters, both as a function of temperature at ambient pressure and upon varying the external pressure at room temperature [9]. In both cases the induced changes along the c axis are much more pronounced than those along the a -axis. This confirms the natural expectation that the out of plane Mg–B bonds are considerably weaker than in-plane B–B bonds. Consequently, the c/a ratio decreases with increasing pressure and with decreasing temperature. According to band-structure calculations, the in-plane B–B bonds are predominantly covalent, as expected. Band-structure calculations

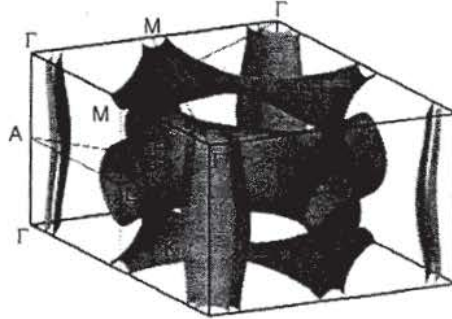


Figure 6.2 Calculated Fermi surface of MgB_2 . The two cylindrical surfaces about the Γ point are derived from σ -bonded boron, the web-tunneled one from π -bonded boron [10].

[10, 11] are also in very good agreement with experimental results probing the shape of the Fermi surface using the de Haas–van Alphen technique [12]. In this sense the electronic structure of MgB_2 and the corresponding Fermi surface, shown in Fig. 6.2, are known very well. The Fermi surface is computed to consist of four sheets, two quasi-2D σ -bonded and two π -bonded [10, 13].

The temperature dependence of the electrical resistivity $\rho(T)$ for currents in the basal plane confirms that MgB_2 is a typical metal. At room temperature ρ is on the order of $10 \mu\Omega \text{ cm}$ and $\partial\rho/\partial T > 0$ at all temperatures between 300 K and T_c . The regime of residual resistivity on the order of $1 \mu\Omega \text{ cm}$ is reached just above T_c and measured $\rho(T)$ curves may be fitted very well by using model approximations based on electron–phonon scattering [14]. Essentially the same behavior was found for $\rho(T)$ along the hexagonal c -axis albeit with, overall, somewhat enhanced values [15]. Much more anisotropic is the Hall constant R_H [15], no surprise if the shapes of the different sheets of the Fermi surface are considered. For currents parallel to the basal plane and a magnetic field oriented along the c -axis, the hole-like carriers dominate and R_H is positive. If, however, the magnetic field is parallel to the basal plane, $R_H < 0$ for currents either along or perpendicular to the c -axis. In all cases, R_H is only weakly temperature dependent. It seems interesting to note that for other isostructural metallic diboride compounds for which no superconductivity has been reported so far, R_H was found to be negative [16, 17]. Speculations on hole-like carriers favoring the formation of a superconducting state were made very early in connection with superconductivity of noble metals [18] and, more recently, in discussing superconductivity of cuprate materials [19] and also of MgB_2 [20].

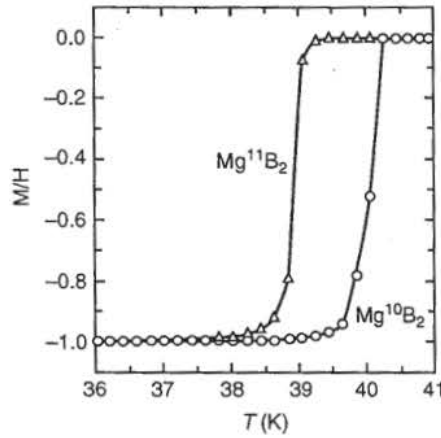


Figure 6.3 Shift of T_c upon exchanging the boron isotopes in MgB_2 (from Ref. [21]).

Because of the onset of superconductivity close to 40 K, information on the normal state value of the electronic density of states at the Fermi energy $D(E_F)$ via measurements of the specific heat $C(T)$ is not accessible straightforwardly. Several ways for solving the problem have been followed [22–24]. The reported values for the electronic specific-heat parameter γ accumulate around a value of 2.5 mJ/mol K^2 . Comparisons with results of band-structure calculations can then be used to evaluate $D(E_F)$ and the electron–phonon coupling parameter λ_{ep} . The same analyses of $C(T)$ also delivers values for the Debye temperature θ_D which is found to be on the order of 1000 K. The ^{11}B NMR response in the normal state reflects the expected overall behavior of a common metal [25, 26]. The very small Knight shift K varies little with temperature and the spin–lattice relaxation is well described by assuming a Korringa-type relaxation via conduction electrons. The numerical value indicates that orbital degrees of freedom are involved in the relaxation process [27].

In view of MgB_2 being a fairly typical metal, the obvious question is why its superconductivity already sets in just below 40 K, considerably higher than any critical temperature of other binary intermetallics. The influence of phonon excitations on T_c was checked via isotope effect measurements by exchanging isotopes on both the B and the Mg sites [21, 28]. It turns out that the boron isotope effect is particularly prominent as may be seen in Fig. 6.3, where the shift of the magnetic transition upon exchange of ^{11}B by ^{10}B is displayed. The mass exponent α_B resulting from using a simple analysis based on Eq. [4.13] in chapter 4 is approximately 0.3. The variation of T_c

upon exchanging ^{24}Mg by ^{26}Mg is much smaller and the corresponding exponent α_{Mg} is only on the order of 0.02. Detailed theoretical studies by Choi et al. [29] and by Mazin et al. [10] provided a quite complete picture of this superconductivity, which involved the dominant effect of a few special phonon modes coupling to the electronic σ -bonded boron-based conduction electron states. The surprisingly high transition temperature is the result of a rather unusual feature of the electronic structure of MgB_2 . As may be seen in Fig. 6.2, the itinerant charge carriers may be divided into two different classes, the π electrons represented by the bulkish sheets inside the Brillouin zone and the σ electrons of the quasi-2D sheets along the vertical edges of the Brillouin zone. The unusual feature here is that energy bands from covalent bonds cross the Fermi energy. The electron-phonon coupling is very different for the two groups. While two phonon branches couple unusually strongly to electrons of the σ sheets, the coupling to the π electrons is much weaker. This leads to a significant anisotropy of the coupling in k space and, at the onset of superconductivity, to the formation of two distinct large gaps in the electronic excitation spectrum. For the σ sheets, the zero-temperature gap is on the order of 6–7 meV, for the π sheets the same parameter is on the order of 1–2 meV. The computed T_c 's for these respective parts of the Fermi surface are 45 K and 15 K, the real $T_c = 39$ K resulting from their interaction.

The results of many experiments probing, for example, the specific heat [30, 31], the thermal conductivity [32], and the penetration depth [33] or involving various spectroscopic methods [34], confirm this strongly anisotropic gap formation for which the notion of two-band superconductivity

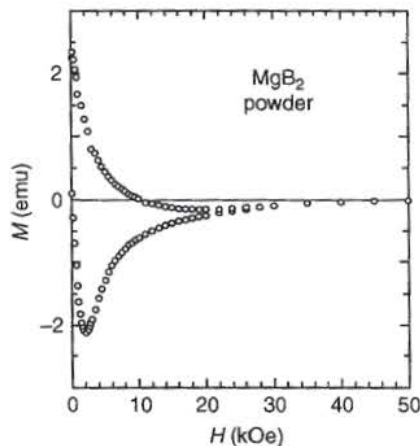


Figure 6.4 Magnetization $M(H)$ of superconducting MgB_2 at 4 K.

has been coined. The bulk of available experimental results is consistent with a nonzero gap across the entire Fermi surface, as expected for an order parameter with simple *s*-wave symmetry. Exceptions are most likely due to problems with sample quality or experimental methods.

A simple inspection of magnetization $M(H)$ curves, an example is shown in Fig. 6.4, reveals that MgB_2 is an intrinsic type II superconductor. This is also reflected in results of measurements, most of them mentioned above, allowing for the evaluation of the characteristic lengths, the penetration depth λ_L , and the coherence length ξ . In the $T = 0$ K limit and for the basal plane, λ_L is on the order of 150 nm and ξ reaches values of 6.5 nm, resulting in a rather large value of the Ginzburg-Landau parameter κ . Transport measurements allow for estimates of the electronic mean free path. Since values on the order of 50–70 nm were derived, MgB_2 can be treated as a clean-limit superconductor. As may be expected, these characteristic lengths exhibit some anisotropy for in-plane and out-of-plane conditions. This is also reflected in the anisotropy of the upper critical field $H_{c2}(T)$. It depends on temperature, and the ratio H_{c2}^{ab}/H_{c2}^c ranges between 2 and 3 close to T_c and 5–8 near 0 K [35].

Although superconductivity of MgB_2 has been discovered rather late in the game, it took only a year, at most two, to completely characterize and understand its properties. It appears that the unexpectedly high value of T_c is due to a lucky coincidence leading to some special features of the electronic and lattice excitations and their coupling which cannot easily be duplicated. Subsequent materials exploration has sought superconductivity in light *s*-*p* element containing materials, without marked success. B-doped diamond, prepared using high-pressure synthesis techniques, has been found superconducting with a $T_c = 4$ K [36].



2. Fe-BASED SUPERCONDUCTORS WITH HIGH CRITICAL TEMPERATURES

An equally surprising development has been the discovery of superconductivity, up to approximately 55 K, in a structurally related set of tetragonal layered Fe pnictides. The original observation of superconductivity related to this set of materials was contained in the thesis of B. Zimmer [37], a student of W. Jeitschko [37]. There it was found that the compound LaFeOP is superconducting with a T_c of approximately 3 K, a result they did not feel remarkable enough to merit publication. It was more than 10 years later that this fact was rediscovered and subsequently was reported

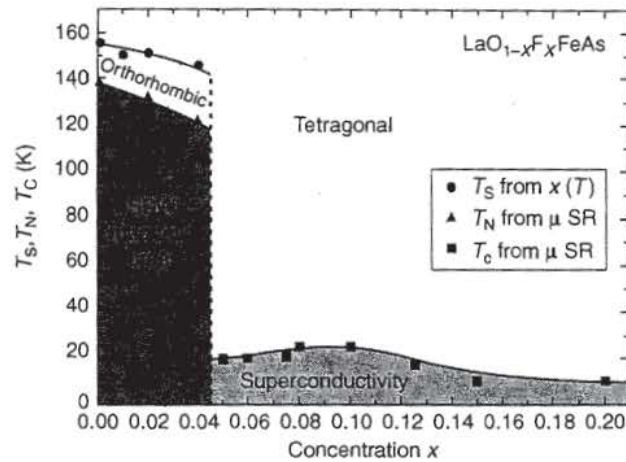


Figure 6.5 Low-temperature phase diagram of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ (from Ref. [38]).

in the literature [39]. On that occasion it was noted that by replacing small amounts of oxygen by fluorine, termed F-doping, T_c could be enhanced up to 5 K. Not much later the Ni analog was also found to be superconducting in the temperature range of liquid helium [40].

The situation changed dramatically when the isostructural compound $\text{LaFeO}_{1-x}\text{F}_x\text{As}$, with x on the order of 0.1, was found to be superconducting below $T_c = 26$ K [41]. This report touched off a storm of activity, with several hundred papers appearing on the Los Alamos archive in the next 6 months. In this sense, the reaction of the community was very much the same as those after the discoveries of superconductivity of the cuprates and, more recently, of MgB_2 . The excitement was not mainly triggered by the value of T_c , but much more by some of the features of these pnictides which, at first sight and to some extent, are reminiscent of those of the cuprates. First of all, the tetragonal parent compound LaFeOAs , although a metal is, in remarkable contrast to LaFeOP , not superconducting but exhibits a phase transition at approximately 150 K [41]. Various investigations indicate that the transition involves magnetic [38, 42–44], charge [41] and structural [42–44] degrees of freedom. As may be seen in Fig. 6.5, it is only via electron doping with F that the transitions may be quenched and superconductivity is induced, rather abruptly above a critical F concentration of a few at% [41]. By inspecting the atomic arrangement in the crystal structure, which is schematically shown in Fig. 6.6, it may be seen that FeAs sheets are embedded between spacer layers of LaO, into which the F dopants are introduced.

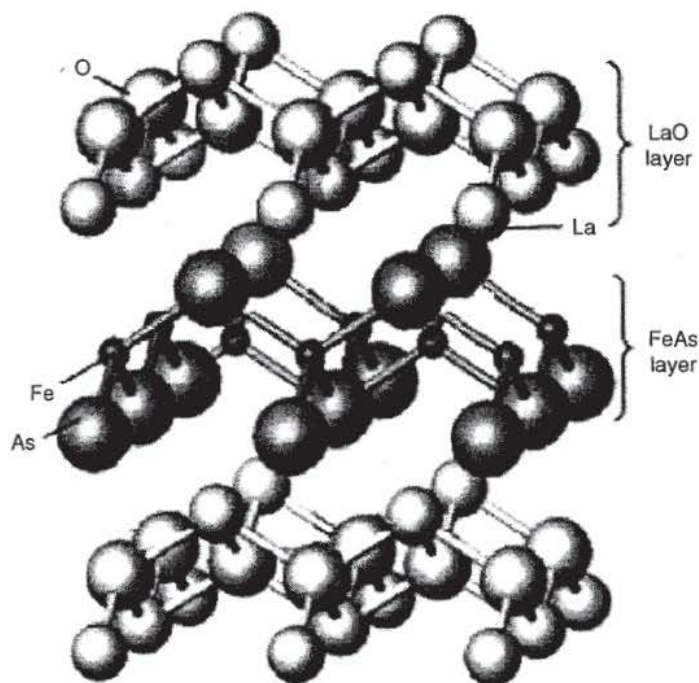


Figure 6.6 Schematic crystal structure LaOFFeAs type compounds (from Ref. [45]).

Playing with the chemical composition of these spacer layers and external pressure, T_c was more than doubled within a very short time. Results of measurements under external pressure indicated that the onset of superconductivity could be raised to temperatures above 40 K [45], but at the same time, the transition broadened significantly and the midpoint of the resistive transition reaches a maximum, at about 40 kbar external pressure, on the order of 30 K. Enhancing the pressure further, up to 300 kbar, leads to a steady decrease of T_c [45]. Nevertheless, trying to mimic external pressure by choosing to replace La by atoms of elements of the first half of the rare-earth series and distinctly smaller ionic radii were successful and at present, a compound with Sm as the trivalent cation and some oxygen deficiency instead of fluorine doping, exhibits superconductivity at approximately 55 K [46]. Doping, hole doping in this case, can be achieved by replacing part of the trivalent La with divalent Sr. So far, T_c 's on the order of 25 K have been achieved with this measure [47].

Another class of materials where Fe-As structural elements like those in LaFeOAs are found are compounds of the type $AEFe_2As_2$, with AE as an alkali-

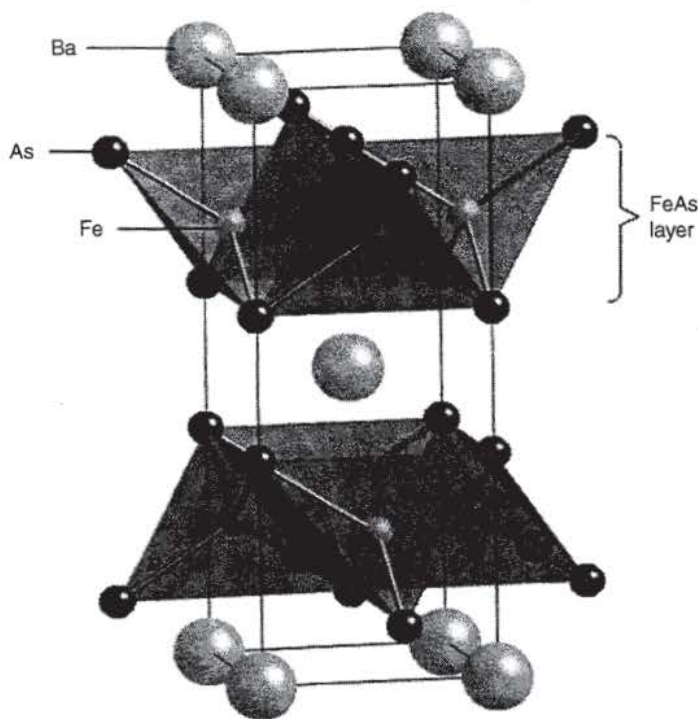


Figure 6.7 Schematic unit cell of the crystal structure of BaFe_2As_2 -type compounds (from Ref. [48]).

earth element. They adopt the tetragonal ThCr_2Si_2 structure which is notorious from superconductivity by pairing heavy electrons (see Chapter 3), but a large number of other low- T_c superconductors also crystallize with this structure. The unit cell of the crystal structure is shown in Fig. 6.7.

A typical parent compound is BaFe_2As_2 which is a poor metal and exhibits a spin-density-wave (SDW)-type transition at about 140 K [48]. Hole doping the FeAs units by replacing divalent Ba by monovalent K is poison for magnetic order but eventually leads to superconductivity with an onset at 38 K [48, 49]. The observation of superconductivity in the range of liquid-helium temperatures in AFe_2As_2 , with $A = \text{K}$ and Cs on the cation site, confirms the importance of the Fe-As subsystem for adopting a superconducting ground state [50]. The partial replacement of the alkali elements by Sr and Ca leads again to a drastic enhancement of T_c by roughly an order of magnitude [50]. The increasing concentration of A atoms, that is, the reduction of hole carriers, finally leads to the loss of superconductivity which is replaced by a SDW-type ground state. Quite remarkable is the

low-temperature $[T,p]$ phase diagram of CaFe_2As_2 . Upon increasing external pressure, the onset of the SDW state is reduced from 170 K to about 130 K [51]. A further enhancement of the pressure leads to a low-resistance phase whose onset temperature increases with pressure but gives way, at much lower temperatures, to superconductivity. The corresponding $T_c(p)$ exhibits a similar dome-like shape that is reminiscent of the $T_c(x)$ curves of the cuprates discussed in chapter 4. Here, the superconducting phase is limited to temperatures below 12 K and obviously competes with other instabilities whose nature has not fully been explored yet.

In the two types of materials mentioned above the nonplanar Fe-As subunits are embedded in adjacent layers which must, because of the observed T_c variations, be considered as charge reservoirs. It appears that they are not absolutely necessary for the onset of superconductivity in iron-based superconductors at elevated temperatures. It turns out that tetragonal FeSe is superconducting below an average critical temperature of about 8 K [52]. Here it should be recalled that FeSe may also adopt a hexagonal (NiAs) structure, in which case it has not been reported to be a superconductor. The most remarkable feature of this material is the very large variation of T_c with external pressure. The pressure derivative $\partial T_c/\partial p$ is reported to be positive and on the order of 1 K/kbar, an amazingly large value. In experiments which were limited in accessible pressures, the onset of superconductivity could be shifted from 13 K to about 27 K [53]. Various ambient-pressure data indicate that also in this case phase transitions of yet unknown character at higher temperatures precede superconductivity at low temperatures. It would seem of interest to investigate whether doping itinerant charge carriers into Fe chalcogenides is possible and, if yes, how superconductivity reacts to this external influence.

A major problem with some of these Fe-based superconductors is the often very broad transition stretching over several K, in some cases more than 10 K. This obviously calls for enhanced efforts in materials characterization, in particular checks of phase purity, an often tedious but necessary task.

Remembering the history of the cuprate superconductors, it is not surprising that a number of different experiments and theoretical model calculations were made to explore the character of the normal and the superconducting state in these Fe-based materials. Although we have to rely on the presently available and incomplete data sets, we assume that the superconductivity in all the materials mentioned in this subsection is of the same or at least similar character. From electronic band structure calculations the Fermi surface, depicted in Fig. 6.8, was predicted to consist of several

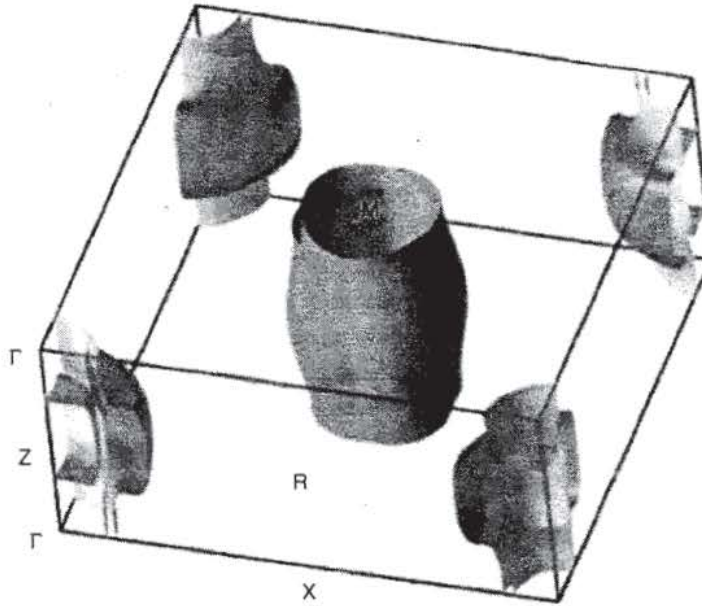


Figure 6.8 Fermi surface of LaOFeAs (from Ref. [54]).

almost cylindrical sheets at the center and in the middle of the edges of the Brillouin zone [54]. Angle-resolved photoemission spectroscopy (ARPES) experiments [55] and measurements based on observations of quantum oscillations [56] confirmed these predictions. It is therefore reasonable to postulate that the low-energy electronic excitations of these materials may be described in the Fermi-liquid approximation, as it is valid for common metals. Inelastic neutron scattering results [57] agree quite well with calculated phonon spectra [58] and thus, both the electronic and the lattice excitation spectra are well understood. The almost cylindrical shape of these surface sheets supports the so-called nesting phenomenon. This in turn may trigger Fermi surface instabilities, such as SDW formation, which are observed in the parent compounds as mentioned above.

Although it appears that the needed basic information is reasonably well under control, it is by no means clear yet why critical temperatures for superconductivity in these materials up to more than 50 K are observed. With respect to the character of the superconducting state, it seems too early to draw any definite conclusions from the available data. ARPES [59] and tunneling experiments [60] provide information on both the gap structure and its width. Comparing the measured saturated gap values ($T \ll T_c$) with $k_B T_c$ indicates that strong coupling effects have to be considered but

calculations imply that the electron–phonon interaction is rather weak [58]. Evidence for strong coupling effects has also been obtained from optical experiments [61]. It has therefore been suggested that the bosonic excitations which provide the pairing are antiferromagnetic spin–wave excitations [62], others claim that the pairing is due the high polarizability of the anions in the Fe–As subsystem and involves the formation of electronic singlet bi–polarons [63]. The available data sets from probing the gap configuration $\Delta(k)$ directly are consistent with nodeless gaps [59, 60, 64], possibly with some anisotropy across different sheets of the Fermi surface. Hence the question whether the observed superconductivity is of unconventional nature has not been answered yet. Theoretical considerations [62] suggest a gap of the so called extended s-wave symmetry which would require a phase change on the order parameter between different sheets of the Fermi surface. Direct experimental evidence for this feature has not yet been provided. Nevertheless, NMR relaxation data are claimed to be compatible with this gap configuration [65].

A convincing answer with respect to the occurrence of superconductivity in these special Fe-based materials and the characterization of the corresponding electronic condensate will require a considerable amount of work. Experiments on single-crystalline and phase pure materials will have to be done. Considering the difficulties in synthesizing these compounds with the necessary quality, this will not be an easy task. The situation is very much the same as it was for the cuprates 20 years ago.

Exactly how this superconductivity above 50 K fits into the physics of other known superconductors remains, as stated above, an open question. There is much experimental evidence that the normal-state conduction electron system may be described on the basis of the Fermi–liquid model and that the gap in the excitation spectrum in the superconducting state is nodeless. Spin–density wave-type magnetic order and structural distortions appear to compete with superconductivity in these materials. The structures contain subunits with a trend to two dimensionality, for instance, with Fe pnictide slabs alternating with La–O slabs. This rich new arena for superconducting materials invites many speculations as to how to profitably think about what is going on and inviting comparisons with other classes of superconducting materials. We discuss this below.



3. NEW PHYSICS IN LAYERED MATERIALS?

Recalling the history of superconductivity during the last two decades it can be noted that many of the new materials contradicted the folk theorem

that cubic and hence 3D materials exhibit the highest T_c 's for superconductivity. The case of the cuprates, then of MgB_2 and, more recently, of the Fe pnictides, foster the idea that layered materials or, in other words, materials whose structure may be viewed as being composed by a stacking of different layers, are able to support electronic characteristics that are quite different from those of the more common 3D-type metals and alloys.

The simple characterization of bonding in most solids, particularly those of interest here, involves the triangle of covalent, metallic, and ionic bond types. Typical metallic structures lie along the covalent/metallic line, the interesting Zintl materials whose compositions, unlike for most metallic materials, obey valence rules, along the metallic/ionic line. Historically, the Daltonide/Berthollide views in metals were resolved with the observation that the nondirectionality of the metallic bond precluded rationalizing the stoichiometries of intermetallics on the basis of valence bonds. However, the Zintl materials obey a surprising valence bond counting [66], and there are reasons to suspect that some electronic closed shell-type arguments are relevant for many other interesting metallic materials.

One can ask what are the important aspects of layering so far as the electronic properties of solids are concerned. Let us begin with cuprates (see also chapter 4 for details). The simple general picture here is a stacking of conducting CuO_2 layers and insulating oxide layers of different varieties. By simple counting, the CuO_2 layers carry a formal charge of -2 per CuO_2 -unit. This is enforced, so to speak, by the highly electropositive character of the rare-earth or alkali-earth (R) ions in the compensating oxide layers. In the cuprates, the bonding along the c -axis is quite ionic, as witnessed by the relevant elastic moduli. Why is the chemistry working this way, rather than provoking an instability in the form of a CuO_2/R_2O_3 phase segregation? Not having the clean answer, we can perhaps say that this heterogeneous layering is stabilized by, possibly dynamic, charge separation, and importantly that this charge separation provides an intralayer electronic structure of unusual character not surviving in more conventional materials.

What about the Fe pnictides? One way to think about these is based on an fcc packing of La (or equivalently As) atoms (Fig. 6.5). The fcc lattice unit cell, containing four La ions, has an equal number of octahedral sites, positioned halfway along each cube edge plus one in the cube center. Placing As onto these octahedral sites gives the rocksalt structure $LaAs$, which we can postulate as a nice ionic valence compound. Also within this nonprimitive unit cell of the fcc lattice are eight tetrahedral sites, a quarter of the way along the body diagonals. Divide these up into two sets,

the ones at $\frac{1}{4}$ and the ones at $\frac{3}{4}$ along the diagonals. Put O in one of this set of sites. This contracts the La layers above and below the introduced O. Put Fe in the other tetrahedral sites, this doing the same “contraction” of the two neighboring As layers. Again, some ionic character to the bonding appears at play, presumably leading to the 2D electronic structure.

It is interesting that this structure was originally found in the compound ZrCuSiAs, which was synthesized based on the observation that NbSiAs existed in a structure with only one of the tetrahedral sites occupied [67]. The valence bond argument here involves postulating that the pnictogen layer has considerable covalent character.

Where might one go with this sort of thinking? A first point is that the layering is “orthogonalizing” the metallic and ionic characteristics. These materials are playing things out separately, suggesting that one might be able to tune the electronics by looking for other suitable materials, even crystal structures, where similarly simple chemistry can play out. This would seem,

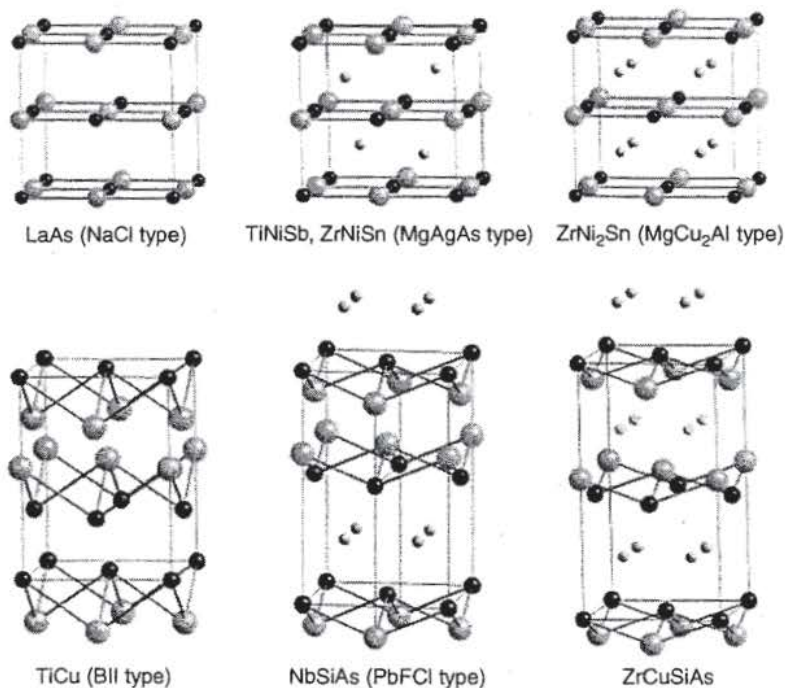


Figure 6.9 Comparison of related structures (from Ref. [67]). The oxy-pnictide superconductivity was originally discovered in the ZrCuSiAs structure as mentioned above.

without really looking closely into it, to be a large phase space of possibilities. Tuning the electronics is not to be seen as the business of doping but rather the finding of new chemical frameworks within which the layer electronics has been tuned through the compound formation. The sequence of related structures displayed in Fig. 6.9 maps a path in the search for new materials [67]. Armed with the insight that charged layer structures lead to new possibilities in the electronics of metallic materials, especially near the so-called electron precise (i.e., valence compound) boundaries, a large materials phase space awaits investigation. Electron precise materials are often congruently melting materials and as such good candidates for being synthesized as single crystals via simple methods of growth from metallic flux, but a much wider phase space of materials is accessed using the full range of synthetic techniques, such as high-pressure synthesis, for instance. It will be particularly interesting to concentrate on first row transition metal materials where the balance between the magnetic and the nonmagnetic character presents further opportunity for tuning the electronics of materials. The very electronegative p-elements are also advantageous from the above viewpoint as enhancers of charge separation.

It comes as a surprise that we have so far only found, or so it seems, competing superconducting and magnetic instabilities. Is this really all there is? It seems unlikely, and immediately comes the thought that we might not know how to recognize something really new if it is there.

What we might call the ionic/metallic hybrids can usefully be thought of as a new class of materials providing the structural framework for new electronic possibilities. In this respect and considering *layering* as an important ingredient, we recall early attempts to find superconductivity in so called intercalated compounds. The first successful attempt in this direction, by intercalating alkali atoms into graphite forming C_8A with $A = K, Rb,$ and Cs , was reported by Hannay already in 1965 [68] and later developments were reviewed in Ref. [69]. An amazingly high critical temperature of about 25 K was obtained by intercalating $HfNCl$ with Li [70]. More recently, other C-based intercalated compounds were found to be superconductors at temperatures on the order of 10 K [71], still high enough for triggering ideas about uncommon mechanisms being responsible for the transition. The onset of bulk superconductivity of the binary compound CaC_6 was established at $T_c = 11.5 K$ [72].

The same physics has also many of the possibilities that were envisioned in the finally unsuccessful pentacene experiments [73]. This area is also opening up in the study of electronic interface or states. The particular

class of materials we are discussing here has already well proven its potential, both for scientific discoveries and for technical applications [74]. In even more recent work, the idea of manipulating interface states was followed up in Cu intercalated Bi_2Se_3 [75]. Traces of superconductivity were found in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ with $0.1 < x < 0.3$. It remains to be shown, however, to what extent this superconductivity is an intrinsic property of that particular material. This case is of high current interest to theorists speculating on superconductivity at surfaces or interfaces of so called topological insulators [76, 77]. The intercalation method seems also to be successful in organic materials. In a recent work, the onset of superconductivity at $T_c = 18$ K was claimed for K_xpicene [78].

A coupled experimental/theoretical methodology holds the promise of an interesting path toward the ever present goal of understanding property/structure relations. The recent development of material-based searches for superconductors is proof enough that surprises are still out there to be discovered.

REFERENCES

- [1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y, Akimitsu J. *Nature (London)* 2001;410:63.
- [2] Cooper AS, Corenzwit E, Longinotti L, Matthias BT, Zachariasen WH. *Proc Natl Acad Sci USA* 1970;67:313.
- [3] Grin Y. private communication.
- [4] Russell V, Hirst R, Kanda FA, King AJ. *Acta Cryst* 1953; 6:870.
- [5] Lee S. *Physica C* 2003;385:31.
- [6] Buzea C, Yamashita T. *Supercond Sci Technol* 2001;14:R115.
- [7] Cava RJ, Zandbergen HW, Inumaru K. *Physica C* 2003;385:8.
- [8] Karpinski J, Kazakov SM, Jun J, Angst M, Puzniak R, Wisniewski W, et al. *Physica C* 2003;385:42.
- [9] Bordet P, Mezouar M, Nunez-Regueiro M, Monteverde M, Nunez-Regueiro MD, Rogado N, et al. *Phys Rev B* 2001;64:172502.
- [10] Mazin II, Antropov VP. *Physica C* 2003;385:49, and references therein.
- [11] An JM, Pickett WE. *Phys Rev Lett* 2001;86:4366.
- [12] Yelland EA, Cooper JR, Carrington A, Hussey NE, Meeson PJ, Lee S, et al. *Phys Rev Lett* 2002;88:217002.
- [13] Choi HJ, Roundy D, Sun H, Cohen ML, Louie SG. *Nature (London)* 2002;418:758.
- [14] Lee S, Mori H, Masui T, Eltsev Yu, Yamamoto A, Tajima S. *J Phys Soc Jpn* 2001;70:2255.
- [15] Eltsev Yu, Nakao K, Lee S, Masui T, Chikumoto N, Tajima S, et al. *Phys Rev B* 2002;66:180504(R)
- [16] Johnson RW, Daane AH. *J Chem Phys* 1963;38:425.
- [17] Juretschke HJ, Steinitz R. *J Phys Chem Solids* 1958;4:118.
- [18] Chapnik IM. *J Phys F Met Phys* 1983;13:975.
- [19] Hirsch J, Marsiglio F. *Phys Rev B* 1989;39:11515.
- [20] Hirsch J. *Phys Lett* 2001;282:392.

- [21] Bud'ko SL, Lapertot G, Petrovic C, Cunningham CE, Anderson N, Canfield PC. *Phys Rev Lett* 2001;86:1877.
- [22] Bouquet F, Fisher RA, Phillips NE, Hinks DG, Jorgensen JD. *Phys Rev Lett* 2001;87:47001.
- [23] Wang Y, Plackowski T, Junod A. *Physica C* 2001;355:179.
- [24] Ch. Wälti, E. Degen, C. Felder, C. Wigger, G. Monnier, R. Delley, B. Ott, H. R. *Phys Rev B* 2001;64:172515.
- [25] Baek SH, Suh BJ, Pavarini E, Borsa F, Barnes RG, Bud'ko SL, et al. *Phys Rev B* 2002;66:104510.
- [26] Kotegawa H, Ishida K, Kitaoka Y, Muranaka T, Nakagawa N, Takigawa H, et al. *Physica C* 2002;378:25.
- [27] Pavarini E, Mazin II. *Phys Rev B* 2001;64:R140504.
- [28] Hinks DG, Claus H, Jorgensen JD. *Nature (London)* 2001;411:457.
- [29] Choi HJ, Cohen ML, Louie S. *Physica C* 2003;385:66.
- [30] Fisher RA, Li G, Lashley JC, Bouquet F, Phillips NE, Hinks DG, et al. *Physica C* 2003;385:180.
- [31] Bouquet F, Wang Y, Sheikin I, Toulemonde P, Eisterer M, Weber HW, et al. *Physica C* 2003;385:192.
- [32] Sologubenko AV, Jun J, Kazakov SM, Karpinski J, Ott HR. *Phys Rev B* 2002;66:014504.
- [33] Carrington A, Manzano F. *Physica C* 2003;385:205.
- [34] see special chapters in *Physica C* 2003;385:215–277.
- [35] Angst M, Puzniak R, Wisniewski A, Roos J, Keller H, Miranovic P, et al. *Physica C* 2003;385:143.
- [36] Ekimov EA, Sidorov VA, Bauer ED, Mel'nik NN, Curro NJ, Thompson JD, et al. *Nature (London)* 2004;428:542.
- [37] Zimmer B, Jeitschko W, Albering JH, Glaum R, Reehuis M. *J. Alloys Compd* 1995;229:238.
- [38] Luetkens H, Klauss H-H, Kraken M, Litterst FJ, Dellmann T, Klingeler R, et al. *Nat Mater Lett* 2008;8:305.
- [39] Kamihara Y, Hiramatsu H, Hirano M, Kawamura R, Yanagi H, Kamiya T, et al. *J Am Chem Soc* 2006;128:10012.
- [40] Watanabe T, Yanagi H, Kamiya T, Kamihara Y, Hiramatsu H, Hirano M, et al. *Inorg Chem* 2007;46:7719.
- [41] Kamihara Y, Watanabe T, Hirano M, Hosono H. *J Am Chem Soc* 2008;130:3296.
- [42] de la Cruz C, Huang Q, Lynn JW, Li J, Ratcliff W, II, Zarestky JL, et al. *Nature (London)* 2008;453:899.
- [43] Dong J, Zhang HJ, Xu G, Li Z, Li G, Hu WZ, et al. *Europhys Lett* 2008;83:27006.
- [44] Nomura T, Kim SW, Kamihara Y, Hirano M, Sushko PV, Kato K, et al. *Supercond Sci Technol* 2008;21:125028.
- [45] Yildirim T. *Phys Rev Lett* 2008;101:57010.
- [46] Takahashi H, Igawa K, Arii K, Kamihara Y, Hirano M, Hosono H. *Nature(London)* 2008;453:376.
- [47] Ren ZA, Che GC, Dong XL, Yang J, Lu W, Yi W, et al. *Europhys Lett* 2008;83:17002.
- [48] Wen HH, Mu G, Fang L, Yang H, Zhu X. *Europhys Lett* 2008;82:17009.
- [49] Rotter M, Tegel M, Johrendt D, Schellenberg I, Hermes W, Pöttgen R. *Phys RevB* 2008;78:20503(R).
- [50] Rotter M, Tegel M, Johrendt D. *Phys Rev Lett* 2008;101:107006.
- [51] Sasmal K, Lv B, Lorenz B, Guloy AM, Chen F, Xue YY, et al. *Phys Rev Lett* 2008;101:107007.
- [52] Torikachvili MS, Bud'ko SL, Ni N, Canfield PC. *Phys Rev Lett* 2008;101:57006.

- [53] Hsu FC, Luo JY, The KW, Chen TK, Huang TW, Wu PM, et al. arXiv:08072369
- [54] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T, Takano Y. *Appl Phys Lett* 2008;93:152505.
- [55] Singh DJ, Du M-H. *Phys Rev Lett* 2008;100:237003.
- [56] Liu C, Kondo T, Tillman ME, Gordon R, Samolyuk GD, Lee Y, et al. arXiv:0806.2147.
- [57] Sebastian SE, Gillett J, Harrison N, Lau PHC, Singh DJ, Mielke CH, et al. *J Phys Condens Matter* 2008;20:422203.
- [58] Christiansen AD, Lumsden MD, Delaire O, Stone MB, Abernathy DL, McGuire MA, et al. *Phys Rev Lett* 2008;101:157004.
- [59] Boeri L, Dolgov OV, Golubov AA. *Phys Rev Lett* 2008;101:26403.
- [60] Kondo T, Santander-Syro AF, Copie O, Liu C, Tillman ME, Mun ED, et al. *Phys Rev Lett* 2008;101:147003.
- [61] Chen TY, Tesanovic Z, Liu RH, Chen XH, Chien CL. *Nature (London)* 2008;453:1224.
- [62] Masee F, Huang Y, Huisman R, de Jong S, Golden MS, Goedkoop JB, arXiv:0812.4539v1.
- [63] Yang J, Huevonen D, Nagel U, Room T, Ni N, Canfield PC, et al. arXiv: 0807.1040v1.
- [64] Ding H, Richard P, Nakayama K, Sugawara K, Arakane T, Sekiba Y, et al. *Europhys Lett* 2008;83:47001.
- [65] Mazin II, Singh DJ, Johannes MD, Du MH. *Phys Rev Lett* 2008;101:57003.
- [66] Berciu M, Elfimov I, Sawatzky GW, arXiv: 0811.0214v1.
- [67] Grafe HJ, Paar D, Lang G, Curro NJ, Behr G, Werner J, et al. *Phys Rev Lett* 2008;101:47003.
- [68] Parker D, Dolgov OV, Korshunov MM, Golubov AA, Mazin II. *Phys Rev B* 2008;78:134524.
- [69] Norman MR. *Physics* 2008;1:21, and references therein..
- [70] Sevon SC. In: Westbrook JH and Fleischer RL, editors. *Intermetallic compounds*. vol. 3, Chichester, England: John Wiley and Sons; 2002. p. 113.
- [71] Johnson V, Jeitschko W. *J Solid State Chem* 1974;11:161.
- [72] Hannay NB, Geballe TH, Matthias BT, Andres K, Schmidt P, MacNair D. *Phys Rev Lett* 1965;14:225.
- [73] Dresselhaus MS, Dresselhaus G. *Adv Phys* 2002;51:1.
- [74] Yamanaka S, Hotehama K, Kawaji H. *Nature* 1999;392:580.
- [75] Weller TE, Ellerby M, Saxena SS, Smith RP, Skipper NT. *Nat Phys* 2005;1:39.
- [76] Emery N, Hérold C, d'Astuto M, Garcia V, Bellin Ch, Marêche JF, et al. *Phys Rev Lett* 2005;95:87003.
- [77] J.H. Schön, S. Berg, Ch. Kloc, B. Batlogg, *Science* 287, 1022 (2000).
- [78] Reyren N, Thiel S, Caviglia AD, Fitting Kourkoutis L, Hammerl G, Richter C, et al. *Science* 2007;317:1196.
- [79] Hor YS, Williams AJ, Checkelsy JG, Roushan P, Seo J, Xu Q, et al. *Phys Rev Lett* 2010;104:57001.
- [80] Fu L, Kane CL. *Phys Rev B* 2007;76:45302.
- [81] Fu L, Kane CL. *Phys Rev Lett* 2008;100:096407.
- [82] Mitsuhashi R, Suzuki Y, Yamanari Y, Mitamura H, Kambe T, Ikeda N, et al. *Nature* 2010;464:76.