Superconductivity

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Pnictide Oxides: A New Class of High-T_C Superconductors

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Current reports on superconductivity at temperatures up to 55 K in pnictide oxides with the ZrCuSiAs structure have sparked tremendous interest in the scientific community. In these systems, LaFePO and LaNiPO had been known to show superconductivity, although only at low temperatures (4–7 K).[1–3] After the publication of a superconducting transition at 26 K in the fluoride-doped iron arsenide $LaFeAsO_{1-x}F_x$[4] in March 2008, reports on higher and higher critical temperatures (T_C) have emerged quickly. New results were posted almost daily on the e-print server of the Cornell University Library (arXiv.org). By exchanging lanthanum with rare earth ions of smaller atomic radii, the critical temperatures increased from 26 K in $LaFeAsO_{1-x}F_x$ to 55 K in $SmFeAsO_{1-x}F_x$[5] within a couple of days. Besides fluoride, either divalent strontium ($La_{1-x}Sr_xFeAsO$, $T_C = 25$ K) or a lower oxygen content ($SmFeAsO_{1-x}$, $T_C = 55$ K) can be used to dope the parent compounds.[6] The upper critical fields (B_{c2}) reach values as high as 65 T.[7] Since the discovery of the cuprate superconductors in 1986,[8] no other material has reached superconducting transition temperatures as high as 55 K. Thus, a completely new class of high temperature superconductors has been discovered.

LaFeAsO and the other new superconductors crystallize in the tetragonal ZrCuSiAs structure (space group *P*4/*nmm*).[9] In this filled variant of the PbFCl type, two-dimensional layers of edge-sharing $FeAs_{4/4}$ tetrahedra alternate with sheets of edge-sharing $OLa_{4/4}$ tetrahedra (Figure 1). Because of the differences between the ionic nature of the Ln–O bonds and the more covalent Fe–As bonds, a distinctive two-dimensional structure forms, where ionic layers of lanthanum oxide alternate with metallic layers of iron arsenide. The metallic and the superconducting properties of LaFeAsO emerge from the FeAs layers.

These compounds resemble the topology of the cuprate superconductors with their two-dimensional copper oxide planes. However, there is an important difference: in the cuprate superconductors, there is no direct interaction between two copper atoms, whereas in LaFeAsO, there is an overlap of the iron 3d orbitals because of the relatively short Fe–Fe distances (about 285 pm). Because of this, the new pnictide oxide superconductors are electric conductors at room temperature.

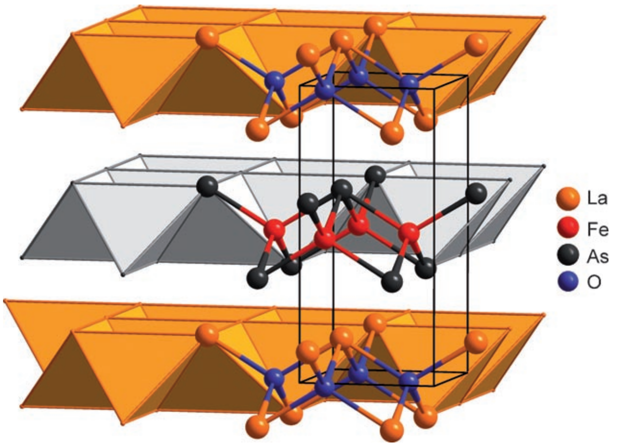

Figure 1. The crystal structure of LaFeAsO.

According to the Bardeen–Cooper–Schrieffer (BCS) theory, superconductivity in metals arises from the coupling of conduction-band electrons into Cooper pairs, and is mediated by vibrations of the crystal lattice (phonons). In its original form, the BCS theory restricts superconductivity to temperatures below about 30 K. In fact, there used to be no known metallic compounds with critical temperatures above 30 K for a long time. Among the most important metallic superconductors are the A15 compounds (Nb_3Ge, $T_C = 23$ K), the Chevrel phases ($PbMo_6Se_8$, $T_C = 18$ K), and the rare-earth borocarbides (YPd_2B_2C, $T_C = 23$ K), which have been known since 1994.[10] The highest critical temperature for metallic compounds before the advent of the new iron arsenide superconductors was 39 K for the metallic boride MgB_2, whose superconducting properties were discovered in 2001. This temperature is clearly above the limit of classical BCS superconductors. Today, it is generally accepted that the formation of Cooper pairs in MgB_2 is also mediated by phonons, and can be well explained with expanded BCS theory (two band superconductivity).[11]

Besides these selected examples, there is a vast variety of metallic superconductors with transition temperatures well below 10 K. Thus, it is not surprising that little attention was

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paid to early reports on the metallic quaternary phosphide oxides LaFePO ($T_C \approx 7$ K) and LaNiPO ($T_C = 4.5$ K), but today it is clear that these systems hold enormous potential. $SmFeAsO_{1-x}F_x$ has the highest transition temperature of all metallic superconductors so far. Only the ceramic cuprates reach even higher critical temperatures of more than 130 K ($HgBa_2CaCu_2O_{6+x}$, $T_C = 133$ K).[12] Shortly after their discovery, it became evident that this kind of superconductivity cannot be explained by the BCS theory alone. The central and still highly disputed question is about the pairing mechanism of the electrons, and it is still discussed from both physical and chemical points of view. However, after two decades of vigorous research, there are actually more than twenty new theories about high-temperature superconductivity in cuprates, which are more or less related to the conventional BCS theory.[13] Currently, there is no prospect of a conclusive concept, but novel systems, such as MgB_2 and the recent discovery of pnictide oxide superconductors, have always given a fresh impetus to theoretical work.

Latest results indicate that pnictide oxides are unconventional superconductors like the cuprates. The calculated electron–phonon coupling constant (λ) is 0.21, and therefore too small for such high critical temperatures. This value is comparable to that of cuprate superconductors ($\lambda \approx 0.3$), which suggests a primarily non-phonon-mediated mechanism.[14] If undoped, LaFeAsO is a poor metal at the verge of a magnetic instability. The latter effect manifests itself in certain anomalies of the electrical conductivity and magnetic susceptibility at about 150 K. These anomalies are caused by an unstable spin density wave (SDW), which leads to a distortion of the structure below this temperature. The magnetic moments show antiferromagnetic order below 134 K. Both the structural distortion and the magnetic order vanish in F-doped, superconducting $LaFeAsO_{1-x}F_x$, because the ordering of the antiferromagnetic SDW is suppressed in this case. This strongly hints at a fundamental role of magnetic fluctuations within the iron layers, which possibly cause the pairing of conduction-band electrons.[15] A further analogy to the cuprate superconductors is thus represented, where superconductivity arises by hole doping of the antiferromagnetic parent compound. In pnictide oxides, superconductivity can either be induced by doping the FeAs layers with electrons ($LaFeAsO_{1-x}F_x$, $T_C = 26$ K) or with holes ($La_{1-x}Sr_xFeAsO$, $T_C = 25$ K). Whether or not the mechanism is the same as in the cuprates has to be shown by future experiments on the isotope effect, the symmetry of the BCS wave function, and the superconducting energy gap. From a chemical point of view, the most significant difference is that the magnetic and superconducting properties of LaFeAsO are affected by direct contact between the 3d metal atoms, which is not the case in the cuprates.

Jeitschko's group was the first to prepare rare earth pnictide oxides several years ago.[16] Initially, the amount of oxygen in these compounds could not be exactly determined, and some of these compounds were described as ternary phosphides. More than 100 of these quaternary $RETPnO$ compounds with ZrCuSiAs-type structure have been subsequently prepared by the research group from the University of Münster (RE = rare earth element, T = transition metal, Pn = P, As, Sb).[17] This class of substances has an outstanding variability in feasible combinations of different elements. Many series exist for most of the trivalent rare earth elements and species, with Mn, Fe, Co, Ni, Zn, Ru, and Os as the transition metal known to exist. More compounds with phosphorus and arsenic as pnictogen rather than antimony have been published; compounds with the latter pnictogen are only known in combination with manganese or zinc as the transition metal.[18] Generally, this class of compounds could also allow different stacking variants, but only the $RE_3Cu_4P_4O_2$-type structure with RE = La, Ce, Pr, and Nd[19] as well as some species with actinides as electropositive component are known.[17,20] In this context, also the many known compounds with manganese and a divalent alkaline earth metal and $EA_2Mn_3Pn_2O_2$-type structure (EA = Sr, Ba; Pn = P, As, Sb, Bi) have to be mentioned. The research groups of Schäfer and of Kauzlarich have studied the structural and magnetic properties of these compounds.[21]

The synthesis of pnictide oxides can follow different routes. Single-phase polycrystalline samples can be obtained by a ceramic route. As a first step, the rare earth element is reacted with the pnictogen to a binary rare earth monopnictide ($RE + Pn \rightarrow REPn$) in a sealed silica tube.[1] The monopnictide is subsequently mixed with the transition metal oxide TO and pressed into pellets, which are heated at 970–1520 K. Temperature and reaction time vary with different starting materials. Either tantalum crucibles or silica tubes can be used as reaction containers. In some cases, high-pressure sintering can also be utilized to support the reaction. Single crystals (up to millimeters in size) can be grown from salt fluxes. In a typical experiment, $RE + Pn + T$O is reacted with an excess of a NaCl/KCl flux, and the flux can simply be dissolved in deionized water after reaction. In some cases, also tin fluxes can be used, as in the synthesis of ternary phosphides.[22] Besides the transition metal oxides, RE_2O_3 or CeO_2 can also provide oxygen. Fluorine doping of the $RETPnO_{1-x}F_x$ compounds is possible either by using the rare earth trifluorides or FeF_3 as fluorine donors.[1,2]

Of course, the main attention is currently directed to the superconducting properties of the doped phases. However, initial investigations of compounds with the paramagnetic rare earth metals also show interesting magnetic phenomena. CeRuPO is a rare example of a ferromagnetic Kondo lattice; CeOsPO shows antiferromagnetic ordering,[23] along with β-CeZnPO and β-PrZnPO,[24] whereas the corresponding antimonide compounds CeZnSbO and PrZnSbO are paramagnetic down to low temperatures.[25] Preliminary ^{121}Sb Mössbauer examinations show transferred hyperfine fields at low temperatures.[18]

Electron-precise pnictide oxides of the kind $RE^{3+}T^{2+}P^{3-}O^{2-}$ are often transparent to the visible spectrum and are yellow to dark red in color, depending on their thickness.[24,26] Accordingly, these $REZnPnO$ compounds are semiconductors.[25] Absorption spectra of $REZnPO$ single crystals (RE = Y, La, Pr, Nd, Sm, Dy) in the NIR/Vis region show an interesting variability of their optical band gaps and f–f transitions with high resolution ligand-field splittings.[24]

The new pnictide oxide superconductors will generate enormous interest in the near future. Even at this early stage, their high critical temperatures and magnetic fields provide interesting perspectives for applications, which are currently dominated by A15 superconductors. If the critical temperatures of the new compounds reach the boiling point of liquid nitrogen (77.13 K), which is not beyond the bounds of possibility, they could even replace the ceramic cuprate superconductors. Their advantage would be a good conductivity over the non-superconducting temperature range.

Apart from the range of applications, this new class of high temperature superconductors will provide new impetus to this research topic; also, but not only, with regard to better understanding of high-temperature superconductivity. Furthermore, there is an abundance of possibilities to chemically modify these systems and study their physical properties. After MgB_2, another seemingly simple and well-known class of compounds is in the center of interest. In the face of an enormous number of further "simple" solid-state compounds which have been characterized structurally, but not with regard to their properties, one can look forward to similar surprises in the future.

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