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Iron-based superconductors / Supraconducteurs à base de fer

Foreword

This thematic issue is focused on the so-called iron-based superconductors that, since the discovery of superconductivity in F-doped LaFeAsO by Hosono's group in 2008, have become one of the latest hot topics in the field of condensed matter. The idea is to give an up-to-date overview of the fundamental properties of this novel family of high-T_c superconductors. The contributors have been selected from among EU groups and researchers with close EU collaborations who can best address these properties and give a global perspective onto the (many) different subtopics. We have tried to make an objective selection useful for the reader, but we apologize for the unavoidable (and not always intentional) shortcomings of our choice.

Before detailing the specific aspects of iron-based superconductors, we shall recall briefly first the context of the scientific work on superconductivity and its relationship to magnetism in metallic compounds.

BCS electron-phonon superconductivity

Since its discovery in 1911, the phenomenon of superconductivity (SC) has been a conceptual challenge and the inspiration of intense research investigations. At that time, quantum solid-state physics was still in its infancy, and the emergence of a new state of matter exhibiting the Meissner effect and zero electrical resistance was a total puzzle.

The Ginzburg–Landau theory, developed on the conceptual basis of the Landau theory of phase transitions and the related phenomenon of superfluidity, elegantly explained the phenomenology of superconductivity. At this level, the milestone was the identification of the superconducting order parameter with a "macroscopic" wave function. Almost in parallel, it was microscopically clarified that i) the electron–phonon coupling in solids can lead to an attractive interaction between electrons, ii) for even an arbitrarily small attraction, the Fermi surface is unstable with respect to the formation of electron pairs (Cooper pairs), and iii) the emergence of a coherent state of Cooper pairs due to this instability yields superconductivity. The later breakthrough came in 1957 with the BCS (from Bardeen, Cooper and Schrieffer) theory of superconductivity, establishing that the superconducting instability implies the opening of a gap in the electronic structure at the superconducting transition temperature T_c. Subsequently, Gor'kov demonstrated the tight link between the BCS theory and the more universal Ginzburg–Landau theory. Furthermore, the Migdal–Eliashberg formalism generalized the BCS theory to the strong coupling limit, thus enabling quantitative estimates of T_c in metallic Fermi gases with weak electronic correlations.

Up to the 1970s, superconductivity was mainly observed in simple metals and metallic alloys for which the above BCS framework applied. The malleability of these alloys is interesting for applications, as this enables the fabrication of wires and of more or less complicated cables. However, quantitative estimates indicated that T_c can hardly be much higher than $\sim$25 K in such BCS superconductors.

More recently, new BCS superconductors have been discovered in which T_c exceeds this upper limit: MgB_2 ($T_c = 39$ K) in 2001, and H_2S in December 2014 ($T_c \sim 200$ K under an applied pressure of $\sim$2 Mbar). The novelty of MgB_2 is in its layered structure composed of alternating Mg and B planes. This generates two metallic bands cutting the Fermi surface, which, in the superconducting state, develop two different SC gaps. This feature, together with the lightness of the involved atoms (which implies higher Debye frequencies compared to metallic alloys), is behind the increased T_c. In H_2S, high pressure is required to solidify the gas and transform a part of it into H_3S, in which SC apparently sets in.

Regardless of possible applications, these remarkable new compounds give us the chance of gaining additional knowledge about the subtleties and limitations of the BCS picture. They show us, in particular, that T_c can be in fact very high even within BCS and is mostly limited by the actual lightness of the atomic states involved. This revitalizes the idea that, if the molecular bonds of H_2 can be broken at high pressures, then a crystal of hydrogen atoms displaying BCS superconductivity with the highest T_c could be realized. In any case, the recently reported case of H_2S is still under scrutiny.

Unconventional superconductivity and electron–electron correlations

During the last decades, SC has also been discovered in various other materials displaying strong electron–electron correlations and hence anomalous electronic properties already in their normal metallic state. In chronological order, this category includes heavy fermions (1978), 1D organic molecular compounds (1980) and layered CuO_2 planar structures (cuprates) (1986). The latter display T_cs above 77 K at ambient pressure (i.e. above the boiling point of liquefied nitrogen), thus giving some hopes for large-scale industrial use of SC.

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The case of the cuprates is special for various reasons. The undoped (parent) phases of these materials are Mott magnetic insulators. However, by playing with chemical substitutions, the carrier concentration can be modified at will and thus metallicity and SC can be promoted. Thus, these systems opened a fantastic route for the study of the long-standing issue of the interplay between magnetism and SC. At first glance, the strong electron–electron repulsive interactions responsible for the Mott behaviour and for the magnetism in these systems can be expected to be totally detrimental to SC. However, it is now understood that they can promote an electronic pairing mechanism if the interacting electrons are localized on orbitals with little overlap. In the 2D structure of the cuprates, the resulting pair states yield a **k**-dependent SC gap, with nodes along the 2D Brillouin zone diagonals and maxima in the $(0,\pi)$ and $(\pi,0)$ directions. This corresponds to a d-wave symmetry of the SC gap that is of the order parameter, and has indeed been observed in the case of cuprates.

In the Mott insulator phase, the holes occupy a single empty $3d_{x^2-y^2}$ Cu orbital. By doping with extra holes, the orbitals obtained from the hybridization between these $3d_{x^2-y^2}$ Cu orbitals and the $2p_x$ (or $2p_y$) ones of the O atoms are gradually populated. As a result, a single d orbital is involved in the conduction band of these materials. The resulting phase diagram switches progressively with increasing doping between a Mott insulator and a single band metal and superconductor until SC disappears beyond a maximal doping of about 0.3. Between the Mott phase and the optimally doped superconductor, there appear "strange metallic" and "pseudogap" phases. Those phases remain among the most mysterious ones of these compounds, and continue to be investigated intensively.

Most other superconductors exhibiting electron–electron correlations apparently display exotic SC often with regard to their order parameter symmetries. In the heavy-fermion and organic superconductors, the pairing mechanism may be mediated by an exchange of spin fluctuations rather than by a phonon exchange. One remarkable case is that of the layered ruthenate compound Sr_2RuO_4, in which pair states are believed to exhibit $S=1$ triplet SC states with p-wave symmetry.

Novel aspects of the Fe pnictides or chalcogenides

In the Fe-based SCs, the Fe can be expected to be in a $3d^6$ configuration (ionic state with formal valence $\sim 2^+$) according to the chemical formulas of these compounds. Therefore, in contrast to the cuprates, many d electronic levels are involved in their electronic structures. Indeed the multiband character of the Fe-based compounds will be seen to be an important difference with the other classes of unconventional superconductors. The other characteristic property of these compounds is that they often remain metallic, even in conditions favouring magnetic states. This is detailed hereafter in the presentation of the contributions to this special issue.

Structures and phase diagrams

The typical phase diagrams displayed by the Fe-based superconductors are reviewed in this issue by **Martinelli et al.** [1]. Most of the systems undergo a structural transition closely followed by antiferromagnetic ordering. These transitions are suppressed by (electron- or hole-) doping or pressure, which eventually enables the emergence of SC. In view of this recurrent pattern, spin degrees of freedom are believed to drive both structural and superconducting transitions. Specifically, the structural distortion is generally seen as a by-product of the postulated spin-nematic order,[1] while SC is linked to $(\pi,0)$ AFM fluctuations. The latter phenomenon is also strongly supported by the characteristic band structure of the Fe-SC, and argues in favour of the so-called $s+-$ superconductivity[2] as detailed by **Hirschfeld** [2]. Thus, in some sense, structural and superconducting transitions in Fe-SCs are commonly believed to be two sides of the same coin (and hence the "need" to study these phenomena altogether). The "generic" phase diagram has many specific details depending on the system under consideration. This is thoroughly detailed by Martinelli et al. for the most extensively studied cases of the (11) Fe(Te, Se), (122) XFe_2As_2 (X = Ca, Sr, Ba, Eu), (1111) LnFeAsO (Ln = lanthanide) and (111) XFeAs, and briefly compared to heavy-fermion systems, organic superconductors and cuprates.

Magnetism

The theoretical frameworks describing the main magnetic properties of the Fe-based superconductors are reviewed by **Bascones et al.** [3]. In this respect, Density Functional Theory (DFT), introduced by **van Roekeghem et al.** [4] in more detail, plays an important role thanks to the moderate character of the electronic correlations in these systems. Thus, DFT calculations can be used to extract the parameters of effective models and descriptions of Fe-SC magnetism in terms of itinerant or localized spins that can be seen as complementary. Bascones et al. review the success and limitations of these approaches in explaining the most common $(\pi,0)$ stripe-AFM order found in Fe-SC, with an emphasis on the important role of the so-called Hund coupling.[3] In addition, they discuss how the transport anisotropies observed in the AF state of Fe-SC can be interpreted in terms of the Drude-weight anisotropy induced by the magnetic order. Finally, they address the question of the Fe-SC "magnetic softness" that favours the emergence of a remarkably large number of different magnetic orders in these systems.

The neutron scattering studies of the magnetic excitations in Fe-SC, reviewed by **Inosov** [5], are crucial investigations that require large single crystals of high quality. The review focuses on the subgroup of "classical" Fe-SC materials best

[1] The term "nematic" is borrowed from the terminology used in liquid crystals to denote an emerging order that breaks some elements of rotational symmetry (typically a four-fold rotation axis: $C_4 \to C_2$, in the case of the Fe-based SCs).

[2] The term $s+-$ denotes an s-wave superconducting gap with a π-phase difference (i.e. sign reversal) on different Fermi surface sheets.

[3] The Hund's coupling is the energy scale associated with intra-atomic exchange, reducing the Coulomb repulsion of two electrons in different orbitals with parallel spins compared to two electrons in the same orbital.

suited for neutron studies and on recent discoveries incorporating Fe–Pt–As compounds to this subgroup. With regard to the non-superconducting parent compounds, Inosov discusses open questions related to the scaling between the anisotropy gap that opens below the Néel temperature, the ordered magnetic moment value and the corresponding polarization of the spin waves. He also points the challenge of detecting the transfer of spectral weight between (initially) equivalent wave-vectors related to different magnetic domains, as well as the influence of both magnetic and non-magnetic impurities. When it comes to superconducting compounds, Inosov highlights the most recent findings related to the so-called resonant mode[4] and its unusual behaviour. Finally, the author critically addresses the attempts of probing spin-nematicity by means of neutron scattering experiments.

Nematicity

This question of spin or, more generally, electronic nematicity that appears prior to magnetic ordering is addressed specifically in the contributions of **Böhmer & Meingast** [6] and **Gallais & Paul** [7] to this dossier. The first authors discuss how shear-modulus measurements can be used as a probe of electronic nematicity. They describe a novel technique based on a three-point bending setup in a capacitance dilatometer, which can be used for both static and dynamic measurements, and discuss in detail the measurements carried out for well-chosen cases. $Ba(Fe, Co)_2As_2$ display the "canonical" behaviour of a tetragonal-to-orthorhombic transition in close proximity to the $(\pi, 0)$ stripe-AFM order. $(Ba, K)Fe_2As_2$ in contrast, can display AFM order in a non-distorted tetragonal phase, while FeSe provides the reciprocal case of structural distortion in the absence of magnetic order.

The contribution of Gallais and Paul nicely combines theory and experiments on Raman spectroscopy as tools to probe electronic nematicity. In the theoretical part, a simple model for describing the charge nematic instability is introduced and a detailed analysis of its Raman response is presented. It is shown, in particular, that the sharpening of a low-frequency quasi-elastic peak in the Raman spectrum is a clear signature of an instability of purely electronic origin (as this feature is decoupled from acoustic phonons). This theoretical analysis provides the basis for the interpretation of the careful experiments presented on $Ba(Fe, Co)_2As_2$. They reveal that the sharpening of the quasi-elastic peak can in fact be associated with a purely electronic transition temperature that is lower than the "thermodynamic" transition temperature in which acoustic phonons are also involved (and at which the sharpening is cut-off).

The shear modulus results are compared by Bohmer and Meingast to alternative probes of electronic nematicity, namely strain-dependent resistivity measurements and Raman experiments. This leads to intriguing conclusions. First, these probes turn out to be not completely equivalent, with shear-modulus and Raman measurements revealing different behaviours as compared to strain-dependent resistivity. Second, the shear-modulus softening can be interpreted as entirely due to spin degrees of freedom in both $Ba(Fe, Co)_2As_2$ and $(Ba, K)Fe_2As_2$, while it seems to require an important contribution from orbital degrees of freedom in FeSe. This calls for future studies to clarify the situation.

Electronic structure and transport properties

The electronic and magnetic properties are highly influenced by the multiband character of the electronic structure. The latter is evident already in simple DFT calculations of the band structure that do reveal that the five bands derived from the 3d electronic orbitals are partially filled and thus do cut the Fermi energy. The resulting Fermi surfaces are not so different from those seen by ARPES experiments as detailed by van Roekeghem et al. However, one needs to scale the energies to map out quantitatively the DFT and ARPES data. This implies the occurrence of a mass enhancement that reflects the magnitude of the electron–electron correlations, somewhat dependent on the material. The comparison of ARPES data to DFT calculations in the large variety of families of Fe-based materials allows us to study in great detail the incidence of tiny structural effects on the magnitude of the correlations, so that correlation effects can be investigated much better here than for any other existing family of correlated compounds.

Furthermore it is demonstrated that the magnitude of the Hund coupling is playing a large role, as it suppresses orbital fluctuations and determines the correlation strength, possibly in an orbital-differentiated manner. To reproduce this situation theoretically one needs then to use more relevant approximation schemes such as GW and DMFT, which are detailed by van Roekeghem et al. and which will be essential in future improvements of the band structure calculations.

Therefore, an analysis of the experimental macroscopic properties requires some care in order to disentangle the contributions of the various bands as highlighted by **Rullier-Albenque** [8] in the case of transport properties. There, it is demonstrated that the phase diagram can be fully mapped out from the evolution of the resistivity or Hall effect data versus temperature. This has been done for various substitutions in the 122 families of compounds. In such measurements, both electronic structure and scattering effects intervene, and even in undoped compounds one evidences that the electron bands dominate both the resistivity and the Hall effect, so that scattering of electrons is less efficient than hole scattering.

Rullier-Albenque could evidence that the electron number required to explain the transport data is in good agreement with that obtained by ARPES Fermi surface measurements. At high T a change of the number of carriers suggested by the transport data could even be recently associated with a shift of chemical potential seen in ARPES. As for the low-T scattering rates they were found to follow quite generally a Fermi liquid T^2 behaviour, with a residual resistivity contribution which gives some insight into the incidence of impurities, substitutions, and intrinsic defect content.

[4] The resonant mode is a sharp low-energy feature observed in the spin-excitation spectrum of unconventional superconductors below the superconducting T_c.

In LiFeAs, a detailed analysis requiring up to three bands with distinct relaxation times could be done, using magnetoresistance data. It has been shown as well that the AF fluctuations are not seen in the in-plane resistivity but can be detected in magnetoresistance data.

Taking into account the multiband characteristics is apparently also the best way to analyse the complex frequency dependence of the optical infrared spectra detected in 122 compounds. In the $Eu(As_{1-x}P_x)_2Fe_2$ family studied by **Zapf et al.** [9], a two-component Drude model can be used to describe the carriers' contributions together with high-frequency features associated with inter-band transitions. This has been performed both in the SDW compound and in the metallic phase of the P-substituted compounds. In the SDW pure compound, the relaxation rate of the Drude peaks has been found to decrease markedly below T_{SDW}, which shows the strong influence of magnetic ordering. In P-substituted compounds, the two Drude features evidence a differentiation between electrons and hole mobilities, with shorter relaxation times for the latter. This is in good qualitative agreement with the two-component analysis of the transport experiments done in the Ba-122 compounds.

Superconductivity

The multiband character dominates as well the SC state properties and the order parameter symmetry than can differ upon details of the Fermi surface, as reported by Hirschfeld. The usual paradigm is that the 2D holes and electron pockets can be easily nested, which can lead the magnetic instabilities and altogether might favour superconducting states with opposite order parameter signs on the two pocket, hence the $s+-$ state. The latter is usually assumed to be due to an exchange of AF spin fluctuations. But as we have seen, the Fermi surface can be easily modified by external control parameters, which allows us to study the robustness of the SC state to such perturbations and could give pertinent information on the pairing mechanism, which might depend on the Fe-SC family.

After a presentation of the experiments that suggest $s+-$ pairing or probe the gap anisotropy and/or nodal character, Hirschfeld reviews the theoretical approaches that permit to determine the behaviour and sign of the gap on the various Fermi surface pockets. Though most of those implying spin fluctuation exchange fit the $s+-$ scenario, a great variability is detected depending on the way in which the electron correlations are taken into account. He also pays some attention to the possible role of orbital ordering, for which one might expect orbital fluctuation scenarios for SC with $s++$ order parameter symmetry.

While the discussion of this standard $s+-$ paradigm is still running, one should highlight the discovery of fascinating new families of high-T_c Fe-SC, namely FeSe and its intercalated varieties, in which electron or hole pockets are missing. Those are presently intensely investigated, as they apparently display larger correlations and as one might expect there a large contribution of d-wave order parameter symmetry and distinct origins for SC. Hirschfeld discusses in depth the possible theoretical scenarios and the experiments that might help to probe the actual physics prevailing in those systems, which are at the heart of the investigations to be pursued.

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Henri Alloul
Laboratoire de physique des solides,
UMR CNRS 8502, Université Paris-Sud,
91405 Orsay, France

Andres Cano
Institut de chimie de la matière condensée de Bordeaux,
UPR CNRS 9048,
33608 Pessac cedex, France

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