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Heavy-anion solvation of polarity fluctuations in pnictides

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Abstract – Once again the world of condensed matter has been surprised by the discovery of yet another class of high-temperature superconductors. The first reactions would of course be that these iron-pnictide- and iron-chalcogenide-based materials must in some way be related to the copper-oxide-based superconductors for which a large number of theories exist although a general consensus regarding the correct theory has not yet been reached. Here, we point out that the basic physical paradigm of the new iron-based superconductors is entirely different from the cuprates. Their fundamental properties, structural and electronic, are dominated by the exceptionally large pnictide electronic polarizabilities.

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Cuprate essentials. – There is little doubt that the electronic properties of copper-oxide parent compounds are determined by the strong Cu 3*d* on-site Coulomb repulsions and moderate O 2*p* to Cu 3*d* charge transfer energies, leading to energy gaps for charge fluctuations of 2 eV or greater, localized spin-(1/2) magnetic moments on Cu, extremely strong superexchange driven antiferromagnetic coupling of these localized spins and magnetic excitation energy scales for single magnons extending up to 0.5 eV.

Another often quoted important property of the cuprates is the two-dimensional character of the magnetic interactions and the electrical transport properties. This two-dimensional behavior strongly enhances the importance of magnetic quantum fluctuations as evidenced by the strong zero-point spin deviations and suppression of the long-range magnetic ordering temperature (T_N) from the one expected from mean field theory. Another undisputed fact is the strong degree of covalent mixing of the O 2*p* orbitals and the Cu 3*d* states in the cuprates. This drives the very strong superexchange interactions and the reduction of the local moments. This quite naturally leads to the conclusion that the electron lattice interactions can be very strong leading, according to some, to the importance of electron-phonon coupling in describing the transport properties of these materials.

Comparing cuprates and pnictides: Local picture.

– So what are really the similarities and differences between the cuprate high T_c 's and the iron-pnictide (FeAs) and iron-chalcogenide (FeSe) based compounds [1–10]? First of course both Cu²⁺ and Fe²⁺ have strong tendencies to form a high-spin state with local magnetic moments. In both cases, band theory predicts a rather two-dimensional behavior at low-energy scales [11–17]. For Cu²⁺ in a square planar coordination of oxygens the local spin is 1/2. For Fe²⁺ in a tetrahedral coordination of As (or Se), the e_g and t_{2g} orbitals are inverted and the high-spin state would be $S = 2$. A comparison, however, in terms of local electronic properties implicitly assumes that in both systems the on-site d - d Hubbard U is much larger than the d bandwidth and in the case of Fe, Hund's rule coupling is larger than crystal and ligand field splitting of the Fe d levels resulting in a high-spin case. It also assumes that the charge transfer energy in the ZSA scheme [18] is positive in both cases resulting in a charge excitation gap.

It is clear that in the FeAs the case for Fe being in a local moment high-spin state is much less convincing than it is for Cu. First of all, we are dealing with arsenides and generally we would expect the effects of covalency on the ligand field splitting to be so large that Hund's rule would be overruled and a low-spin state with spin 1 would result.

For the cuprates, it is generally accepted that the gap is of a charge transfer type because the Cu d - d interaction

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(Hubbard U) is much larger than the charge transfer energy and the charge transfer energy for transition from O $2p$ to a Cu $3d^{10}$ state is positive. Also, this is a much less likely scenario for the arsenides. First, the electron negativity of As^{3-} is much smaller than that for O^{2-} hence in this ionic picture we would again expect it to be in the charge transfer regime of ZSA [18] but the charge transfer gap should be very small and probably negative, resulting in a p -type metal.

Also experimentally, the magnetic properties of LaFeAsO, although somewhat anomalous, are not at all suggestive of a local moment $S = 2$ state, but rather suggest at most a small local moment [19,20] and a transition to an antiferromagnetic spin density wave (SDW) phase below about 150 K [19]. Recent systematic studies as a function of F doping exhibit an increasing susceptibility with temperature indicating a temperature activated magnetic moment for temperatures above the SDW or superconducting transition [21]. Of course, provided that U is large, a low-spin state can only be achieved if Hund's rule coupling $J_H = (1/14)(F^2 + F^4)$, where F^2 and F^4 are Slater-type integrals, is strongly reduced to a fraction of its atomic value and becomes comparable to the small crystal field splitting predicted by band theory [22–25]. This, however, is hard to realize because as discussed in the past [26] the higher-order Slater integrals are not reduced by a polarizable surrounding to lowest order because they do not involve charge. On the other hand, the monopole integral F^0 , which basically determines the Hubbard U will be strongly influenced by the surroundings because it dictates the energies involved in charge fluctuations involving only $3d$ electrons.

FeAs band structure effects. – In the comparison between cuprates and FeAs so far we have concentrated on a local approach neglecting the translational symmetry and band structure effects. Even if local approaches are very successful in discussing the basic aspects of the electronic structure of many $3d$ transition metal oxides, band structure effects and translational symmetry are another important part of the problem. In a translational invariant solid, the tendency to form local moments is first of all dictated not by Hund's rule coupling, but rather by the competition between the Hubbard U , which suppresses on-site polarity fluctuations and the one-particle band dispersion which lives off polarity fluctuations. Hence, the first condition for the formation of a local moment is that $U > W$, where W is the one electron $3d$ bandwidth. Recent LDA calculations, however, indicate a d band dispersion width of at most about 2 eV, hence we need to find a way of reducing the Hubbard U to about 2 eV in order to suppress local moment formation [22,23].

Arsenic bandwidth and its spread-out charge distribution. – This brings us to the heart of the discussion of the large differences between oxides and arsenides. In oxides, the O $2p$ states form rather large bandwidths of about 6 eV in the cubic oxides and are lowered somewhat to 4 eV in the two-dimensional cuprates. The LaFeAsO

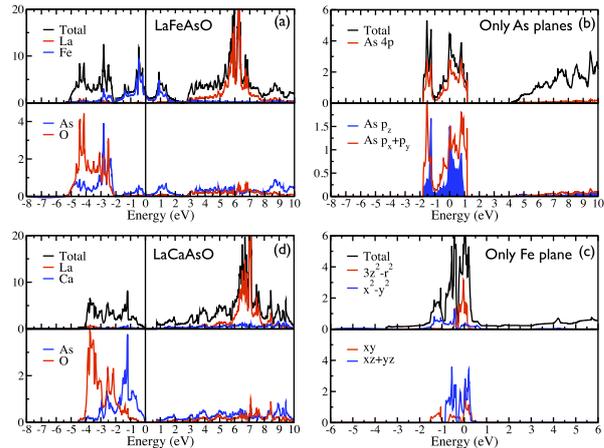


Fig. 1: (Colour on-line) LDA density of states for (a) LaFeAsO; (b) As and (c) Fe planes calculated leaving out all the other atoms; (d) LaCaAsO (see footnote ¹). The zero of energy is at the Fermi energy, E_f .

layer structure is, however, very different from the closed packed O lattices in most oxides. In fact the As-As bond length of almost 4 Å is extremely large. Hence, in spite of the large orbital radii of the $4p$ electron states, the As-As hopping integrals are quite small. This is nicely demonstrated by a band structure calculation of the As lattice in the LaFeAsO structure, while leaving out all the other atoms, see fig. 1(b). The total arsenic bandwidth is only about 3 eV so that As in this system behaves like a narrower bandwidth system than O does in oxides.

Having concluded on the rather atomic-like nature of the role played by As, we also observe that the As charge density is in fact strongly spatially spread out. We will come back to this later. We first focus on the role of the Fe-As hybridization. The total and atom projected density of states are shown in fig. 1(a). As also others have shown [14–17,25] the only bands prominently present close to the chemical potential are Fe $3d$ based bands. In fact, looking at the partial projected density of states the amount of As character in this energy region is rather small. Of course, this observation is qualitative since the partial density of states refers to states inside the muffin tin region and since, as mentioned above, the As $4p$ states are rather extended we may not be capturing their full contribution. Nonetheless comparing the Fe $3d$ density of states close to E_f with the total, which involves all the states also outside the muffin tin radii, we see that these states are very strongly Fe $3d$ dominated. To demonstrate this rather modest Fe-As hybridization in this energy region, we show in fig. 1(c) the Fe density of states that we get if we remove all the other atoms from the structure. This is the band structure that would result from only Fe-Fe hopping integrals. We see that this

¹The LaFeAsO band structure is calculated with the FPLAPW DFT code WIEN2K [27]. The exchange and correlation effects are treated within the generalized gradient approximation (GGA), after Perdew *et al.* [28]. The calculations were performed using crystal structure reported by de la Cruz *et al.* [19].

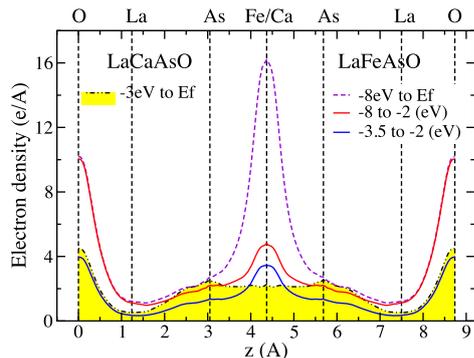


Fig. 2: (Colour on-line) Electron charge distribution in the unit cell of (right) LaFeAsO and (left) LaCaAsO as a function of the distance z perpendicular to the Fe-As layers, calculated with various energy integration limits and integrated over the ab -plane. The atomic planes are depicted with vertical dashed lines.

density of states and total bandwidth are comparable to that of the compound itself.

All this leads us to a rather surprising picture of basically an Fe $3d$ band structure with little hybridization with As and a dispersional width of about 2 eV plus modest crystal and ligand field effects resulting in additional $3d$ band splittings. But at the same time the electrons in this Fe d band are propagating in the close proximity of a rather extended charge distributions around the As centers. It is this extended charge distribution about the As in which the Fe $3d$ electrons have to move that interests us most at this time. To demonstrate the spatial extent of the As charge distribution further we show the occupied charge density integrated over the ab -plane and integrated over energy between the limits as indicated in fig. 2(right) as a function of z , the distance along the c direction. Indicated also in the figure are the positions of the As, Fe, La, and O planes. Integrating over the energy from -8 eV to E_f we see a strong peak at the Fe plane due to the Fe $3d$ electron states being on a rather broad distribution of electron density extending far past the As plane but dropping to almost zero at the La plane position. This broad distribution is a result of the As-based electrons that have a very broad rather constant density extending far away from the As nuclear position toward the Fe and La planes. The charge density in the region -3.5 to -2 eV is again this broad distribution in the As plane region. This demonstrates again the highly peaked density caused by the Fe d states positioned in and close to a rather broad density resulting mostly from As $4s$ -, $4p$ -, and $5s$ -like states.

To demonstrate the spread-out character of the As states even further, we computed the band structure of the fictitious compound LaCaAsO in which the $3d$ states below the Fermi energy are absent. The same lattice parameters as for the Fe compound were used and the density of states is shown in fig. 1(d). The region close to E_f is again dominated by As states now hybridized with the Ca $4s$ and $4p$ states that are mainly above E_f . Important for our discussion is the charge density

calculated as above as a function of the distance along the c -axis which for the energy range -3 to E_f clearly demonstrates this broad charge distribution resulting from the As valence states hybridized with the Ca $4s$ and $4p$ bands.

Hence, the picture that emerges is that of d electrons moving in a broad distribution of charge density that is rather loosely bound to but resulting from As $5s$, $4p$ states hybridized with Fe $4s$, $4p$ states. This is the kind of charge distribution one would get from a sparse lattice of large negative As ions with spatially extended $4p$ orbitals strongly penetrating into the interstitial region between Fe and As and also between La and As. The large As-As bond length results in a small As $4p$ band dispersion. The large spatial extent of these $4p$ orbitals is to a large extent caused by the fact that a $4p$ orbital has two radial nodes. Also, the tail region is much less strongly angularly directed than the O $2p$ orbitals. Hence, in spite of the large radial extent, the hybridization with the strongly directed Fe $3d$ orbitals is rather limited.

We conclude that the model that presents itself is the one of tightly bound Fe $3d$ electrons propagating in a lattice of rather isolated As negative ions. Similar conclusions with regard to the Fe-As hybridization are also reached from a tight binding fit to the band structure [29]. This brings us to the next level of important basic questions, namely: i) What stabilizes this strange structure in the first place? ii) Why is there not a large local Fe moment in spite of the rather narrow d bands and the rather atomic nature of the $3d$ states? iii) What could possibly be the origin of effective attractive interactions between the d electrons resulting in a superconducting state?

What stabilizes the layered pnictide structure?.

– According to conventional wisdom, the Madelung potential plays the most important role in the cohesive energy of ionic compounds like the transition metal oxides. The Madelung potential stabilizes cubic structures in which the positive cations are surrounded by negative anions and *vice versa*. Layered structures break this rule because they make use of the large polarizability of one of the ions, either the anion or the cation. The most common, of course, are the sulfides, selenides, and tellurides, such as TiS₂, MoS₂, and TiTe₂, but there are also numerous examples in halides like the bromides and iodides. As discussed in detail by Haas [30] and by Wilson and coworkers [31], these layered structures make use of the strong polarizability of usually the anion which in these structures is placed in a very asymmetric surrounding of cations, resulting in a large electric field at the anion site. This field polarizes the anion and the induced dipoles interact with neighboring dipoles and the monopoles of the positive central layer to lower the energy. If the polarizability is large enough this induced dipole-monopole interaction can be larger than the point charge interactions in a cubic lattice.

A prototypical example is the layering of a Ti⁴⁺ central layer that is sandwiched between two S²⁻ layers, which provides the conditions just described. These sandwiches

are then repeated. A very important aspect of these kinds of layer structures is that the surface consisting of charged S^{2-} ions is in spite of the charge *not* polar since the charge is exactly $-1/2$ of the charge of the central layer underneath which is the condition for a non-polar surface. Polar surfaces will reduce their large energy due to internal electric fields by reconstructing and one way is to electronically reconstruct by moving electrons so that the surface layer has $-1/2$ the charge of the layer underneath [32,33]. In the definition of a truly layered compound we should include the condition of a non-polar surface when cleaving parallel to the layers. With this definition, materials like YBCO, for example, are not really layered since such surfaces would always be polar [34]. Also LaFeAsO is not really layered in this sense and one would expect it will not be easily cleavable without introducing some sort of electronic or lattice reconstruction. The reason is that the Fe^{2+} is surrounded by $1/2$ layers of As^{3-} yielding a net charge of -1 for this sandwich, which in the c -axis direction then alternates with a charge of $+1$ for the LaO sandwich. The way to stabilize this layered structure is to make use of the extremely large electronic polarizability of As, the reason for the half-layers is simply a matter of ionic size. The large As^{3-} ions could not possibly be accommodated in a full layer.

In light of these structural observations, it is important to recall that the electronic polarizability α of ions is roughly equal to their volume. Hence, the polarizability of O^{2-} is between 0.5 and 3.2 \AA^3 [35–37] and obviously that of S^{2-} (4.8 – 5.9 \AA^3), Se^{2-} (6 – 7.5 \AA^3), and Te^{2-} (8.3 – 10.2 \AA^3) are progressively larger. This is why oxides mostly form cubic structures and the heavier chalcogenides form layered structures [30]. Similarly, fluorides form cubic structure and chlorides, bromides and iodides often form layered ones. The electronic polarizability of As^{3-} can easily be derived from the ones of the chalcogenides. The radius of As^{3-} (222 pm) is comparable but larger than that of Te^{2-} (211 pm) and Se^{2-} (191 pm), and according to the volume ratios, As^{3-} has an electronic polarizability of 9 – 12 \AA^3 . This large polarizability stabilizes the As-Fe-As sandwich structure, to which the La-O-La sandwich is slaved.

Screening of Hubbard U . – What about the small or non-existent local moment in spite of the relative narrow Fe $3d$ bandwidths? Also here the very large high-frequency electronic polarizability of As plays a prominent role. As described in our studies of the oxides in the mid-1980s [38], the reduction of the Hubbard U from its atomic value of about 20 eV to less than 10 eV in oxides is to a large extent due to the electronic polarizability of O^{2-} . The Hubbard U is formally defined as the additional energy it costs to place two electrons (or holes) on the same site relative to having them on far removed sites, which is equivalent to the ionization potential minus the electron affinity of an atom with a given number of d electrons (six in the present case). Note that this involves a change of two particles. Now the ionization potential in a polarizable medium is lowered

not by conventional screening effects described by a dielectric constant but by the polarization of the surroundings and the subsequent potential produced by these induced dipoles at the position of the ionized site. This is the same effect that stabilizes ions in a polar solvent —the solvation effect. In a solid of course one is dealing with propagating charges so that the polarizability of interest is the dynamic electronic polarizability involving an energy scale larger than the typical one particle bandwidth of 2 eV , the so-called optical electronic polarizability.

Neglecting first the dipole-dipole interactions and assuming linear response, we have $U = U_0 - 2E_p$ with polarization energy $E_p \sim \frac{1}{2} \sum_i \alpha_i E_i^2$, where U_0 is the bare free ion value and E_i is the electric field at the i -th site due to a charge of ± 1 at the origin. If we neglect the dipole-dipole interactions and take the field $E_i = \pm e/R_i^2$ from the point charge and consider only the nearest neighbors we get $U = U_0 - 2(\frac{Z\alpha}{2} e^2/R^4)$, where Z is equal to the number of nearest polarizable neighbors. Using $\alpha = 10 \text{ \AA}^3$ for the As^{3-} polarizability, the Fe-As distance $R = 2.4 \text{ \AA}$ and $Z = 4$ we obtain $U = U_0 - 17.3 \text{ eV}$! The extremely large induced dipole moments cause this enormous polarization energy. The size of these moments implies at the same time that dipole-dipole interactions cannot be neglected, and we find that in this case they reduce the E_p of the four neighbors by about a factor three. As the Coulomb interaction is long range, we also take the effects of further neighbors into account, which in the end leads to a total polarization of $2E_p = 10.0 \text{ eV}$ calculated for a plane of $4 \cdot 10^4$ polarizable As ions. In other words U is strongly “solvated”, especially if in addition also the Fe-As bond polarizability is taken into account. Hence, it is not so surprising that indeed U is smaller than W , leading to a quenching of the local moment due to polarity fluctuations in the band theory.

This large electronic polarization reduction of the single particle ionization energy will result in the dressing of a particle much like that with phonons but now with virtual electron-hole excitations describing the polarizability of As. These “electronic polarons” would have an increased effective mass. This has been addressed in a recent quantum mechanical approach to the problem and we find a modest mass enhancement of a factor of two [39].

Longer-range effects of large pnictide polarizability. – What about an attractive interaction that could be responsible for superconductivity? The on-site Coulomb interaction will most likely not be reduced to zero or become attractive. However, there is something very special about this particular pnictide crystal structure that can strongly reduce the nearest-neighbor interaction. The point is that two neighboring Fe ions have two common As ions as neighbors (fig. 3). Hence, let us go back to our original derivation of the polarization reduction of U and do this for the nearest-neighbor interaction V . One now obtains $V = V_0 - \frac{1}{2} \sum_{\text{common}} \alpha [(\mathbf{E}_1 + \mathbf{E}_2)^2 - E_1^2 - E_2^2]$, which reduces to $V = V_0 - 2\alpha \mathbf{E}_1 \cdot \mathbf{E}_2$, where 2 refers to

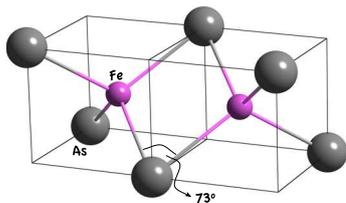


Fig. 3: (Colour on-line) FeAs tetrahedral sub-lattice in the crystal structure of LaFeAsO formed by the edge-sharing FeAs₄ tetrahedra.

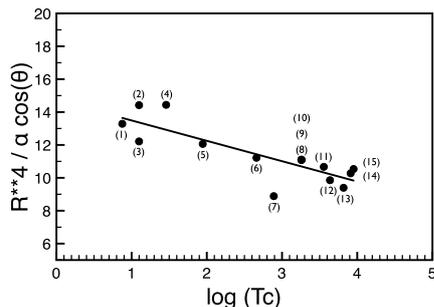


Fig. 4: The superconducting transition temperature T_c of various iron and nickel-pnictide superconductors *vs.* the computed inverse screening energy $E_{\text{scr}} = \alpha e^2 (\cos \Theta) / R^4$ of the nearest-neighbor Coulomb interaction, suggesting the presence of superconductivity with a higher T_c in materials with larger electronic screening energy E_{scr} . R is Fe-As bond length, α the electronic polarizability ($\alpha_{\text{As}} = 10 \text{ \AA}^3$, $\alpha_{\text{P}} = 9 \text{ \AA}^3$), and Θ is the Fe-As-Fe bond angle. The solid line is a guide to the eye. The data points represent the following materials: (1) LaONiAs [40]; (2) LaONiP [41]; (3) BaNi₂P₂ [42]; (4) LaONiP [43]; (5) LaOFeP [44]; (6) LaOFe_{0.89}Co_{0.11}As [45]; (7) LiFeAs [46]; (8) LaO_{0.92}F_{0.08}FeAs [47]; (9) LaO_{0.92}F_{0.08}FeAs [19]; (10) LaO_{0.87}F_{0.13}FeAs [48]; (11) CeO_{0.84}F_{0.16}FeAs [49]; (12) Ba_{0.6}K_{0.4}Fe₂As₂ [9]; (13) TbO_{0.9}F_{0.1}FeAs [50]; (14) NdO_{0.8}F_{0.2}FeAs [51]; (15) PrO_{0.85}F_{0.15}FeAs [52].

the number of common As neighbors and E_1 (E_2) are the electric fields of Fe₁ and Fe₂ with common As neighbors. This leads to $V = V_0 - 2\alpha e^2 (\cos \Theta) / R^4 = V_0 - 2E_{\text{scr}}$, where Θ is the Fe-As-Fe bond angle. For $\Theta = 180^\circ$, the screening-induced interaction is repulsive ($E_{\text{scr}} < 0$), as we showed in previous papers explicitly dealing with polarizability [53,54]. However, for an angle of less than 90° , this interaction is attractive and reduces the nearest-neighbor Coulomb repulsion. Taking the polarization of the As ions in the plane into account and including the effect of dipole-dipole interactions (see for instance eqs. (11)–(13) in ref. [38]), we obtain $V = V_0 - 3.83 \text{ eV}$. Now V could easily become attractive since the bare repulsion between the Fe sites at a separation of 2.8 \AA is only 5.1 eV and 10 \AA^3 is a lower end estimate for the polarizability of As^{3-} . We find that for $\alpha = 12 \text{ \AA}^3$ due to the local field effects the nearest-neighbor Coulomb interaction becomes overscreened and V becomes effectively attractive.

These estimates demonstrate that it is quite possible that because of the curious structure of the rather

isolated As ions with a huge polarizability and the less than 90° Fe-As-Fe bond angle that the nearest-neighbor d - d Coulomb interaction becomes attractive, while longer-range interactions are still repulsive. If superconductivity is indeed driven by this mechanism, one expects to have a direct relation between T_c and the nearest-neighbor screening energy $E_{\text{scr}} = \alpha e^2 (\cos \Theta) / R^4$, which determines the effective attractive interaction in this oversimplified approach. In fig. 4, the inverse of this polarization energy is plotted as a function of T_c , for 15 different superconducting iron and nickel pnictides. It is encouraging that empirically these two quantities are apparently related, even if a further elaboration of the detailed microscopic theory is required for a definite assessment of this relation. Both the details of the band structure close to E_F and the fact that a central Fe ion and two of its nearest neighbors share one As neighbor dictate the pairing symmetry of the superconductor. The particular structure of the Fe-As lattice will reduce the effective mass for a motion in the plaquette around the central Fe ion and influence the energy of such a s , p , d wave pair [39].

This mechanism of superconductivity reminds us clearly of the Little model put forward for organics [55]. In this model, the phonons are basically replaced by virtual excitons on side chains to the chain carrying the free carriers. The role of the excitons is then the same as that of the phonons except now with a very large “phonon” energy which enters as a pre-factor in the BCS theory of T_c . The problem noted concerning this is that these effects are supposed to produce an attractive on-site interaction which would require a very large retardation effect that however is not consistent with the large excitation energy. In our case, the polarizability of As can be modeled with an electric field mixing the As p and s orbitals which one can think of as a virtual excitation of a p - s exciton in the As “side” slab now, rather than a chain. In previous work, we have, in fact, modeled the polarizability of O^{2-} in terms of p - s virtual excitations on oxygen [38,53,54]. The most important difference with the Little model is that we suggest an attractive nearest-neighbor interaction which requires little if any retardation and also provides for possible non- s -wave symmetries. This mechanism also reminds us of the one introduced by Allender, Bray, and Bardeen at the interface between a semiconductor and a metal [56]. Also here the virtual excitations in the semiconductor across the band gap —excitons— could mediate an effective attractive interaction between the metal electrons. In our case, the semiconductor is formed by As $4p$ bands as the valence bands and As $5s$ hybridized with Fe $4s$, $4p$ as conduction bands. The metal is formed by the Fe $3d$ bands. Ginzburg was perhaps the first to actually discuss this type of mechanism [57].

Conclusions. – A model for superconductivity in the arsenides emerges, which is a result of the strong dynamic high-frequency polarizability of the large As^{3-} ions. It leads to the Fe $3d$ electrons propagating like electronic polarons, attaining a nearest-neighbor attractive

interaction. The peculiar pnictide lattice structure makes this excitonic interaction attractive because of the less than 90° Fe-As-Fe bond angle. *Nota bene*, it was recently discovered that FeSe forms a pnictide structure while it superconducts [58], vividly illustrating the case that if one is able to reduce the chalcogen bandwidth in going from the common dichalcogen structure to the pnictide structure, isolating the polarizable chalcogen anion, a superconducting state can arise.

In the history of excitonic superconductivity, the discovery of the pnictides might make a real difference. We argued that the pnictide-type structures are the naturally occurring crystal structures that optimize the conditions for excitonic superconductivity. This in turn gives guidance in the search for superconductors with a higher T_c , suggesting a substantial increase for materials with large electronic polarization energies. Prime candidates will be materials with heavy, highly polarizable anions provided that they are dilute enough not to form very wide bands and that the bond angles meet the criteria described above. This actually leaves open a very wide range of possible new high-temperature superconductors. We also note that the proposed mechanism is driven by inter-site off-diagonal Coulomb matrix elements, and hence also reminds us of Varma's mechanism for the cuprates although it is quite different in the details [59].

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