Polarization catastrophe at low densities of polarons: from Cuprates to Metal-Ammonia Solutions

P. Quémerais, S. Fratini
quemerai@grenoble.cnrs.fr, fratini@grenoble.cnrs.fr
Laboratoire d’Études des Propriétés Electroniques des Solides, CNRS, Grenoble
BP 166, F-38042 Grenoble cedex 9, France

Summary. — We review some results on the role played by dielectric polarons at the metal-insulator transition in polarizable materials, taking into account the long-range nature of the Coulomb interactions. The occurrence of a polarization catastrophe is examined in a model describing a Wigner crystal of polarons. The possible relevance of this scenario in the cuprates and in metal-ammonia solutions is discussed.

PACS 00.00 – .
PACS —.— – .

1. — Introduction

Many mechanisms have been proposed to understand the microscopic origin of the metal-insulator transitions (MIT) occurring in condensed matter. Since the discovery of high-Tc superconductors in 1986, the MIT occurring in the cuprates remains the focus of debates and new theoretical studies. The main idea in the original work of Müller and Bednorz [1], was to search conditions for strong electron-phonon coupling. For this reason, they focused on transition-metal oxides, a somehow heretic point of
view at that time, since such compounds belong to the category of insulators, or bad conductors. The presence of antiferromagnetism in the insulating phase made physicists focus on Hubbard and related models \cite{2}, where a magnetically ordered insulating phase occurs due to short range electronic correlations. However, the Hubbard model is able to describe "bad metals" (more precisely, metals with reduced electronic bands and with short range electronic correlations), but, strictly speaking, not insulators. The reason is that when a system of electrons is insulating, long range Coulomb interactions are not screened and must be incorporated in any model which properly describes such a state: in other words, Hubbard's model is not self-consistent through the MIT (away from half filling), as it becomes metallic already at very low doping levels.

The cuprates must be doped to finite densities of carriers to become superconducting. One can sweep out this question by invoking impurities or disorder (through Anderson localization), but up to now, there are no conclusive studies able to understand this particular and important point. Several studies have tried to incorporate long range Coulomb effects in the theoretical description of the phenomenon, but the basic mechanism of the superconducting transition, as well as the origin of the necessary finite doping density, still remain unclear. This fact is not restrained to the cuprates. In the bismuthates, where high temperature superconductivity ($T_c \approx 40K$) is observed with no trace of magnetism (which rules out the Hubbard model) the same phenomenon also occurs: $K_xBa_{1-x}BiO_3$ is insulating for $x < 0.35$ and becomes superconducting for $x > 0.35$.

Another important point is that the parent cuprates, as any insulating oxides and more generally any ionic-covalent insulating compounds, belong to the category of polar materials, as testified by the large differences between the static and high-frequency dielectric constants. For undoped La$_2$CuO$_4$ \cite{3}, for example, it is $\epsilon_s \approx 30$ in the static limit, and approaches $\epsilon_{\infty} \approx 5$ at high frequency. This takes its origin from the presence of ionized atoms in their structures, which makes the difference with other covalent insulators or semiconductors such as Si or GaAs, where the dielectric constant depends weakly on the frequency. As is well-known since the work of Fröhlich \cite{4}, when a charged particle is added to such a polar insulating compound, the system responds by screening the charge through the formation of a polaron, which is a combination of an electron (or hole) plus the associated lattice distortion carrying the low frequency polarization. In these materials, dielectric screening is at the origin of a possible strong electron-phonon coupling.

Except for the Anderson localization, which treats the effect of disorder on the single particle properties, the theoretical scenarios for the MIT generally rely on collective mechanisms, such as electron-lattice interactions (e.g. the Peierls \cite{5} instability in one-dimensional metals) or electron-electron interactions. In the above mentioned Hubbard model, the insulating behavior comes from the fact that putting two electrons (with opposite spins) on the same electronic level of a single atom costs an energy $U$, which can be larger than the kinetic energy gained in forming an electron band. Despite its simplicity, this model can be exactly solved only in one dimension using the Bethe Ansatz \cite{6}. In higher dimensions, numerical calculations or sophisticated approximations — more or less controlled — are necessary to develop a physical insight (see e.g. \cite{7,8,9}). For
example, the original proposal of Anderson [10], that a Resonating Valence Bond state should be the superconducting ground-state of a two dimensional weakly doped Hubbard model away from half filling, remains unproved up to now. Anyway, whatever the actual solution of the model is (or will be), it cannot in itself justify the existence of a finite critical doping density to get the MIT (or a superconducting transition), as we discussed above.

In what follows, we discuss in some detail two alternative scenarios, both relying on the long-range Coulomb interactions, that imply the existence of a finite critical doping density for the MIT.

1.1. The Polarization Catastrophe: Herzfeld 1927 [11]. – This is the first scenario which was proposed two years before the Bloch theorem to understand why some elements of the periodic table are metallic under normal conditions, whereas other remain insulating. One starts from the element in its gaseous phase at low density \( N \) (let us consider a metalloid such as Na as an example). The Clausius-Mossotti (Lorenz-Lorentz) theory tells us that the dielectric constant of such a gas satisfies:

\[
\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N \alpha
\]

where \( \alpha \) is the polarizability of a single isolated atom, due to the deformation of the electronic cloud around its nucleus. The original argument of Herzfeld is based on the fact that the dielectric constant diverges (and changes sign) if the right hand side of eq.(1) becomes larger than 1. A polarization catastrophe is thus expected at \( N_c = \frac{3}{4\pi \alpha} \), above which the system becomes metallic. This can be understood by taking a classical model of an electron in its atomic orbital state around the nucleus, and giving rise to a dipole moment \( p = e r \). The equation of motion is:

\[
\ddot{r} - \omega_0^2 r = \left( e/m \right) E_{\text{loc}}
\]

where \( \hbar \omega_0 \) is the electronic transition energy between two atomic levels, related to the polarizability of the atom by \( \alpha = e^2 / m \omega_0^2 \). The local electric field on the right hand side contains a Lorentz field factor \( E_{\text{loc}} = E + 4\pi e N p \) which accounts for the interactions with the other atoms in the system. As a result, the frequency of the restoring force acting on the electron under study is softened as:

\[
\omega^2 = \omega_0^2 - \omega_P^2 / 3,
\]

where \( \omega_P^2 = 4\pi Ne^2 / m \) defines the plasma frequency. For \( N > N_c \), the restoring force on the electrons vanishes, which gives a criterion for the instability of the insulating phase. For a review on recent applications of Herzfeld’s criterion to understand the metallization of some elements, the reader is referred to the papers of P. P. Edwards [12, 13]. The criterion can be recast in a different form [13], which is useful for comparison with the Mott transition (cf. next section). The polarizability of a neutral atom can be related
to the radius $a_H$ of the electronic orbital by $\alpha \approx (9/2)a_H^3$ [14]. In that case the critical density, related to $a_H$, is:

\[ N_{c_1}^{1/3}a_H \approx 0.38 \]

For $N > N_{c_1}$ the insulating phase is unstable with respect to metallization.

1.2. The Mott Transition: 1961 [15]. – Much later, a different mechanism for the MIT was proposed by Mott. He argued that in the metallic phase, the Coulomb potential of the atoms would be screened by the mobile electrons, and behave as $V(r) \approx (-e^2/r)\exp(-k_{TF} r)$, $k_{TF}$ being the inverse Thomas-Fermi screening length [14]. The potential $V(r)$ does not allow for a localized solution if $k_{TF}^{-1} \approx a_H$, where $a_H$ is the Bohr radius of the electron in the unscreened potential $\sim -e^2/r$. Consequently, the critical density for the occurrence of the insulating phase is:

\[ N_{c_2}^{1/3}a_H \approx 0.26 \]

Since it takes into account the screening of the Coulomb interaction in the metallic phase, contrary to the Herzfeld criterion, which is a condition of instability of the insulating phase, the Mott criterion is a condition of instability of the metallic phase. As we shall see, this point is of prime importance in our approach of the many-body treatment of the polaron states.

1.3. The role of polarons in the MIT mechanism. – We are left with two criteria describing respectively an instability of the insulating and of the metallic phase. There is no a priori reason for the equality $N_{c_1} = N_{c_2}$ to hold. If one looks to this problem in empty space, as we discussed above and in view of the estimates eq.(4) and (5), $N_{c_1} > N_{c_2}$, which means that there is a region of densities $N_{c_2} < N < N_{c_1}$, in which both states are stable (note that the above discussion is for $T = 0K$). The actual state is determined by the one which has the lowest energy, and it is generally the metallic state since the electrons delocalize in a Bloch band (which is half filled in our simple problem) which greatly decreases the energy with respect to localized states. In the intermediate region, the insulating phase thus appears to be metastable.

In practice, the MIT under study is observed by chemically doping a given "host" material, whose dielectric properties must be taken into account. Let us distinguish between two main classes of materials. The first class consist of non-polar (or weakly polar) materials such as conventional semiconductors (Si for example), for which the dielectric constant is almost frequency independent, $\epsilon_{\text{host}}(\omega) \approx \epsilon_{\text{host}} = \text{constant}$. In that case, the situation is analogous as in empty space, except that the Bohr radius which enters in the different criteria must be modified as $a_H^* = \epsilon_{\text{host}}a_H$. Most studies on the MIT in such compounds confirm this scenario [13]. The recent discovery of superconductivity in doped diamond close to the MIT density, could well revive the problem [16], although diamond in principle belongs to this first class of materials.
The other class corresponds to polar materials, such as metal oxide insulators (as the cuprates). In that case, complications arise from the existence of two sources of dielectric screening. One is the atomic polarization, responsible for the high frequency dielectric constant \( \epsilon_\infty \). The second is due to the displacement of the ions of the host material from their equilibrium positions, whose relevant frequency scale is \( \omega_{LO} \), the longitudinal optical frequency of the phonons. Such source of polarization acts when the particles localize, and leads (together with the atomic polarization) to the low frequency dielectric constant \( \epsilon_s \), which can be much larger than \( \epsilon_\infty \). In a metallic state at high doping levels, the electronic plasma frequency will be changed into \( \omega_P/\sqrt{\epsilon_\infty} \) and not reduced by \( \epsilon_s \). However, at low doping, the second kind of polarization acts to localize each electron (or hole) wavefunction in a bound state — a polaron — by creating a potential-well which is Coulombic at large distances. In the strong coupling limit, the localization (polaron) radius \( R_P \) is essentially that of an electron in a potential \( V(r) \approx -e^2/\tilde{\epsilon}r \), with an effective dielectric constant \( \tilde{\epsilon}^{-1} = \epsilon_\infty^{-1} - \epsilon_s^{-1} \). Polarons are formed because the gain in electronic energy due to the ionic distortion is always larger than the cost in elastic and localization energy [4].

The host material is thus able to induce the formation of polarons, and these can play a central role in the MIT. Applying the Mott criterion [17] to such bound states gives:

\[
N_{c_1}^{1/3} (\tilde{\epsilon}/\epsilon_\infty) R_P \approx 0.26,
\]

which tells us that for \( N < N_{c_2} \), some polarons must be formed out of the homogeneous electron gas.

The calculation of \( N_{c_1} \) is much more difficult because polarons are charged particles, and their mutual Coulomb interactions in the insulating phase must be taken into account to obtain reliable results. This task has been carried out through the study of the melting of a Wigner Crystal of Polarons (see next section), but the main conclusions apply more generally to any insulating polaronic state. Our main result is the following: when the electron-phonon coupling is strong, there is no possibility of getting a liquid state of polarons with metallic properties. Instead, a polarization catastrophe occurs at a density \( N_{c_1} \), above which some of the polarons must dissociate. An optical signature of this scenario has been derived: the peak in the optical conductivity due to the polaronic bound states in the insulating phase, is shifted towards lower frequency as the density increases. Secondly, owing to the polaron-polaron interactions, \( N_{c_1} < N_{c_2} \), so that a range of densities exists for which both a metallic state of free electrons and an insulating state of polarons are unstable, as is sketched on Fig.1. In between, the system could be electronically separated between a concentration \( N_{c_1} \) of localized polarons, and \( N_{free} = N - N_{c_1} \) of free electrons (or holes).

A system of crystallized polarons at density \( N_{c_1} \) has a peculiar dielectric response, with a negative dielectric constant down to zero frequency. That means that the Coulomb interactions between free electrons can be overscreened by the electrons localized in the polaronic states, and could lead to a superconducting ground state, transforming the MIT into an insulator-superconductor transition. In fact, the outcome depends crucially
Fig. 1. – A sketch of the scenario of the metal-insulator transition in nonpolar and polar materials. In usual semiconductors with frequency independent dielectric constants, the Herzfeld instability (polarization catastrophe) takes place at higher densities than the Mott instability. For polar insulators, the interactions between polarons shift the Herzfeld instability to lower densities, leaving a range of densities where polarons could coexist with free electrons (or holes). In this region the Coulomb interactions between free electrons can be overscreened by the polaronic collective excitations (see text).

on the behaviour of the counter-ionic charges (the doping ions). If these are frozen in the host structure (the case of Sr in La$_{2-x}$Sr$_x$CuO$_4$ for example), the scenario is viable. But if the counter-ions are free to move, they also respond to the negative dielectric constant of the electronic system, resulting in a true phase separation (as is the case for O in La$_2$CuO$_{4+y}$, or for metal atoms in the metal-ammonia solutions, cf. below). In the present scenario, long range interactions between polarons are responsible either for a superconducting instability, or for a macroscopic phase separation.

2. – The Wigner Crystal of Polarons

To systematically study the interactions between polarons in the insulating phase, we have carefully examined the melting of a Wigner crystal of polarons as a function of density. It was first recognized in [18] that the ground-state of polarons at low densities should be a Wigner crystal [19]. Detailed studies have been carried out on this problem.
Polarization catastrophe at low densities of polarons: from Cuprates to Metal-Ammonia Solutions

Wigner crystallization occurs at low densities because the average electron-electron interaction energy (proportional to $1/r_s^3$, where $r_s$ is the mean distance between electrons at densities $n \sim r_s^{-3}$) is much larger than the kinetic energy (proportional to $1/r_s^2$), so that the ground state is crystallized in order to minimize the potential energy. In a host polar material, a Wigner crystal of electrons is transformed into a Wigner crystal of polarons, which has two competing effects: 1) the Coulomb interactions between polarons are reduced as $\sim 1/\epsilon_s r$, which tends to destabilize the crystallized state; but 2) the effective mass of the carriers (polarons) is increased because each electron carries its own polarization cloud, and this tends to stabilize the crystallized state. In a highly polarizable material ($\epsilon_s \gg \epsilon_\infty$), the balance will essentially depend on the strength of the electron-phonon coupling. In the Fröhlich model, it is defined as $\alpha = (\hbar^2 \omega_{LO})^{1/2} e^2/\tilde{\epsilon}, m^*$ being the band mass of a free electron [24]. The strong coupling regime, where the polaron behaves essentially as a Coulombic bound state, is attained above $\alpha \approx 6 - 7$, which is not common in real materials. The cuprates seem to be an exception for two main reasons: 1) the effective electronic band mass $m^*$ is already high owing to the short range correlations, and can reach several units of the bare electron mass ($m_e$: $m^* \sim 2 - 4 m_e$ [8]; 2) coherent electron motion is constrained in two-dimensional CuO$_2$ layers, whereas the Coulomb interactions (and polarization [3]) remain three-dimensional. As demonstrated by Devreese [25], this shifts the strong electron-phonon coupling regime down to $\alpha \approx 3$. Due to the combination of these two aspects of the problem, when excess holes (or electrons) are added to the parent insulating cuprates, the formation of strong coupling Fröhlich polarons cannot be a priori avoided.

Many theoretical difficulties already arise on treating just one or two polarons. The reason is that the problem of one single polaron is already a many-body quantum problem which cannot be solved exactly. Feynman [26] provided the best solution through the use of path-integrals, replacing this many-body problem by a two body problem. In our studies of the polaron Wigner crystal, we generalized the approach of Feynman to the many-polaron system, taking advantage of the fact that the exchange between electrons can be neglected in the crystallized phase at low densities. Our basic hypothesis, that two polarons repel with long-range Coulomb interaction, is always fulfilled provided that the dielectric constant satisfies $\epsilon_\infty/\epsilon_s > 0.1$ [27] (although other ad-hoc models have been proposed to enforce the formation of bipolaronic bound states in the context of the cuprates).

Based on Feynman’s treatment of dielectric polarons, we have shown that the characteristic collective frequencies in the polaron Wigner crystal have the behaviour shown in Fig.2. A polarization catastrophe was shown to occur upon increasing the density, when the condition $\omega_{pol} \rightarrow \omega_{LO}$ is attained (the corresponding critical density $N_{c1} \approx 5 \times 10^{20}/cm^3$ obtained with the microscopic parameters of the cuprates is in good agreement with experiment). $\omega_{pol}$ is the transverse optical collective mode of the Wigner crystal of polarons, and identifies the location of an absorption peak in the optical conductivity. A simplified version for $\omega_{pol}$ is recovered in the limit $\omega_{LO} \rightarrow 0$, which reproduces
Fig. 2. – Left panel: typical behaviour of the collective excitations of a Wigner crystal of polarons in the strong electron-phonon coupling regime. “int.modes” correspond to the vibrations of the electrons localized within their potential-wells (due to both electron-electron and electron-phonon interactions), whereas “ext.modes” correspond to the low frequency vibrations of the polarons involving ionic displacements (see ref. [21] for details). $\omega_{pol}$ is the transverse collective mode observed in the optical absorption, which softens as the density increases up to the critical density for the polarization catastrophe, at which $\omega_{pol} = \omega_{LO}$. $M_p$ is the polaron mass. Right panel: Regions (in grey) in the $(k, \omega)$ plane where the dielectric constant of the Wigner crystal of polarons is negative (giving rise to overscreening) for $n = 5 \cdot 10^{19} \text{cm}^{-3}$ and $n = 1.7 \cdot 10^{20} \text{cm}^{-3}$. Such values correspond to the parameters $\epsilon_s = 30$, $\epsilon_\infty = 5$, and $m^* = 2m_e$ in the strong-electron phonon coupling regime, from ref. [21].

the original result obtained by Bagchi for a Lorentz lattice of dipoles [29]:

$$\omega^2_{pol} = \omega^2_0 - \frac{\omega^2_P}{3\epsilon_\infty},$$

where $\omega_0$ is the frequency of the electron localized in its polaron potential-well.

As was mentioned above, the dielectric constant becomes negative in large regions of $(k, \omega)$ as one reaches the critical density. This is illustrated in Fig.2 (right panel), where the sign of the dielectric constant is shown for two different densities. This result shows that, beyond the dielectric catastrophe, free electrons (or holes) can be paired by the remaining electrons localized in the polaronic states. (1)

(1) Note that the polarization catastrophe is a general phenomenon in the case of neutral dipoles (cf. section 1.1). For crystallized charged particles, on the other hand, the softening of the peak of conductivity can only occur if $\epsilon_s \neq \epsilon_\infty$, i.e. owing to the polaron formation. The reason is that if $\epsilon_s = \epsilon_\infty$, the collective frequencies in the crystallized state do not vary as the density is increased: there is no soft mode in this case.
3. – Relevance of the polarization catastrophe scenario in real compounds

The scenario described in the preceding section, which relies on very general and simple hypotheses, can in principle be observed in the insulating (or poorly metallic) phases of any strongly polarizable material, i.e. as soon as the long range Coulomb interactions are not screened. However, other ingredients are often present in the compounds of interest, that can compete with the effects evidenced above, making their clear identification difficult.

There are at least two classes of compounds where there are indeed indications of the relevance of the polarization catastrophe scenario: the superconducting cuprate materials and the metal-ammonia solutions (MAS). The former are insulating solids with a layered crystal structure, that undergo a superconducting instability above a certain critical doping level of the order of 5 – 10%. The latter are liquid solutions that exhibit phase separation and become metallic above a given critical concentration of metal ions, around 3 – 8%. Beyond the complexities specific to each class (let us mention again the ubiquitous antiferromagnetic correlations in the cuprates, and the interplay with the classical dynamics of the complex fluid in the MAS), both systems share the same two basic ingredients of the theory: they are strongly polarizable, and have unscreened interactions at low doping levels, due to the absence of mobile charges.

3'1. Cuprates. –

Polaron softening. The identification of the softening of the polaronic collective mode — the clearest precursor to the polarization catastrophe — requires systematic doping dependent measurements of the optical conductivity. Such studies have been performed in electron doped Nd$_{2-x}$Ce$_x$CuO$_4$ [30], hole doped La$_{2-x}$Sr$_x$CuO$_4$ [31] and YBa$_2$Cu$_3$O$_y$ [32], which invariably exhibit an absorption peak around $\sim 0.15\,\text{eV}$ that progressively softens and hits the frequency range of phonon excitations in correspondence with the superconducting instability (there is also a stronger broad peak at $\sim 0.5\,\text{eV}$, which softens in a parallel way but does not seem to undergo any drastic change at $x_c$). The value $\sim 0.15\,\text{eV}$ is compatible with the optical absorption of dielectric polarons in such materials.

Charge modulations. Recently, charge modulations of square symmetry and with a period of $\sim 4$ Cu-Cu lattice parameters, have been observed by scanning tunneling microscopy at the surface of Ca$_{2-x}$Na$_x$CuO$_4$Cl$_2$ [33] and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [34] and interpreted as an unusual charge ordered state, possibly related to Wigner crystallization. Although it is not clear experimentally if this is a genuine charge ordering of carriers, or if the observed modulations involve pairs of carriers, a calculation based on a phenomenological Lorentz model [35] shows that Wigner crystallization of holes is compatible with the observed periodicity, provided that an additional source of carrier localization is included. The energy scale of such additional mechanism $\sim 0.15\,\text{eV}$, deduced from the model, agrees with what is measured in optical experiments and could well be of polaronic origin. Furthermore, the square symmetry of the observed charge ordering follows naturally
from the present scenario if one accounts for the isotropic long-range repulsion between the holes, i.e. including the unscreened Coulomb interactions between different layers.

The scenario emerging from several experiments in the cuprates (including optical and photoemission experiments) points to the coexistence of localized carriers of polaronic character with free-electron like carriers. It is still unclear if these different “fluids” are spatially separated in ordered or disordered patterns, if they live at different energy scales or in different parts of the Brillouin zone.

![Graph](image)

Fig. 3. – Softening of the absorption peak in Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ vs. carrier concentration (left panel, courtesy of S. Lupi, from ref. [30]. IST indicates the insulator-to-superconductor transition) and in metal-ammonia solutions vs. concentration of metal ions, from reference [37] (right panel). Data were collected by fitting the absorption and permittivity data in refs [41,42] with a Lorentz model.

3.2. Metal-ammonia solutions. – When an excess electron is introduced in liquid ammonia, a bound state is formed which involves the long-range polarization field coming from the orientational polarizability of the ammonia molecules. Such bound state is analogous to a polaron in a ionic dielectric [36], and manifests through a broad optical absorption peak at $\sim 0.8$ eV. Upon increasing the concentration, the frequency of such absorption peak exhibits a clear softening, whose square follows a linear trend as expected from eq. (7). It extrapolates to 0 roughly at the boundary of the phase separation region [37] (see figure 3, right panel), indicating the possible relevance of the polarization catastrophe scenario in the mechanism of the metal-nonmetal transition.

An analogy between the microscopic mechanisms underlying the phase diagrams of the cuprates and the metal-ammonia solutions has been proposed in reference [38].

3.3. Other examples. – The concept of Wigner crystallization of polarons has been applied recently to other classes of compounds. In ref. [39], a lattice of ripplopolarons has been shown to arise at the surface of a multielectron bubble in liquid Helium. In ref. [40], the crystal of magnetic polarons arising as the low density solution of the double-exchange model has been discussed in the framework of the magnetic hexaborides EuB$_6$. 
REFERENCES

[1] J.G. Bednorz and K.A. Müller, Rev. Mod. Phys. 60, 585 (1988)
[2] J. Hubbard, Proc. Roy. Soc. A, 276, 238 (1963)
[3] C.Y. Chen, R.J. Birgeneau, M.A. Kastner, N.W. Preyer, T. Thio, Phys. Rev. B 43, 392 (1991)
[4] H. Fröhlich, Adv. in Phys., 3, 325 (1954)
[5] R.E. Peierls, Quantum Theory of Solids, Oxford at the Clarendon Press (1955)
[6] E.H. Lieb and F.Y. Wu, Phys. Rev. lett. 20, 1445 (1968)
[7] E. Dagotto, Rev. Mod. Phys. 66, 763 (1994)
[8] A. Georges, G. Kotliar, W. Krauth, M.J. Rozenberg, Rev. Mod. Phys 68, 13 (1996)
[9] F. Gebhard, "the Mott metal-Insulator Transition: models and methods", Springer (1997)
[10] P.W. Anderson, G. Baskaran, Z. Zou, T. Hsu, Phys. rev. Lett., 58, 2790 (1987)
[11] K.F. Herzfeld, Phys. Rev. 29, 701 (1966)
[12] P.P. Edwards and M.J. Sienko, Int. Trev. Phys. Chem., 3, 83 (1983)
[13] P.P. Edwards ad M.J. Sienko, Jour. Chem. Educ., 60, 691 (1983)
[14] N.W. Ashcroft and D. Mermin, Solid State Physics, Saunders College, Philadelphia (1976)
[15] N.F. Mott, Philos. Mag., 6, 287 (1961)
[16] E.A. Ekimov, V.A. Sidorov, E.D Bauer, N.N. Melnik, N.J. Curro, J.D. Thompson, S.M. Stishov, Nature, 428, 542 (2004)
[17] P. Quémerais and S. Fratini, Mod. Phys. Lett. B, vol.11, 30, 1303 (1997)
[18] P. Quémerais, Mod. Phys. Lett. B, vol.9, 25, 1665 (1995)
[19] E. Wigner, Phys. Rev. 46, 1002 (1934)
[20] P. Quémerais and S. Fratini, Int. Jour. of Mod. Phys. B, vol.12, 29, 3131 (1998); Physica C, 341-348, 225 (2000)
[21] S. Fratini and P. Quémerais, Mod. Phys. Lett. B, vol.12, 24, 1003 (1998); Eur. Phys. Jour. B, 14, 99 (2000); Eur. Phys. Jour. B, 29, 41 (2002)
[22] G. Rastelli, S. Fratini, P. Quémerais, Eur. Phys. Jour. B, 42, 305 (2004)
[23] G. Rastelli and S. Ciuchi, Phys. Rev. B, 71, 184403 (2005)
[24] J.T. Devreese, this volume (and references therein)
[25] F.M. Peeters and J.T. Devreese, Phys. Rev. B, 36, 4442 (1987)
[26] R.P. Feynman, Phys. Rev. 97, 660 (1955)
[27] V.L. Vinetskii and M.S. Giterman, Sov. Phys. JETP 6, 3, 560 (1958)
[28] J. Adamovski, Phys. Rev. B 39, 3469 (1989) ; G. Verbist, F.M. Peeters, J.T. Devreese, Phys. Rev. B, 43, 2712 (1991)
[29] A. Bagchi, Phys. Rev. 178, 707 (1969)
[30] S. Lupi et al., Phys. Rev. Lett. 83, 4852 (1999)
[31] A. Lucarelli et al., Phys. Rev. Lett. 90, 037002 (2003); A. Lucarelli et al., Int. Journ. Mod. Phys. B 17, 521 (2003)
[32] Y. S. Lee et al., Phys. Rev. B 72, 054529 (2005)
[33] T. Hanaguri et al., Nature 430, 1001 (2004)
[34] K. McElroy et al., Phys. Rev. Lett. 94, 197005 (2005)
[35] G. Rastelli, S. Fratini and P. Quémerais. Eur. Phys. J. B 42, 305 (2004)
[36] J. Jortner, J. Chem. Phys. 30, 839 (1959)
[37] S. Fratini and P. Quémerais, unpublished
[38] P. Quémerais, J.-L. Rainbault, S. Fratini J. Phys. IV France, Pr9-227 (2002)
[39] J. Tempere, S.N. Klimin, I.F. Silvera, and J.T. Devreese Eur. Phys. J. B 32, 329 (2003)
[40] Vitor M. Pereira, J. M. B. Lopes dos Santos, A. H. Castro Neto, cond-mat/0505741
[41] J.C. Thompson, Rev. Mod. Phys. 40, 704 (1968); J.C. Thompson and W.T. Cronenwett Adv. Phys. 16, 439 (1967); R.B. Somoano and J.C. Thompson, Phys. Rev. A 1, 376 (1970); M. Schlauf, G. Schönerr and R. Winter, Colloque Weyl VII (1991); D.W. Mahaffey and D.A. Yerde, Rev. Mod. Phys. 40, 710 (1968); W.H. Koehler and J.J. Lagowski, J. Phys. Chem. 73 2329 (1969)
[42] M. Gold and W.L. Jolly, Inorg. Chem. 1, 818 (1962)