Mixed valence and superconductivity

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Mixed-valence (MV) systems are referred to here as MV-2 and MV-3 depending on whether two or three consecutive valence states are involved. MV-3 systems range from systems with Hubbard $U > 0$, corresponding to a single stable, intermediate valence state, and $U < 0$, corresponding to stable alternating valences differing by two units. Experiments using inelastic neutron scattering or inelastic X-ray scattering show softening of breathing phonon modes in MV systems compared with related systems with a single valence. It is hypothesized that softening is due to coupling between potential energy surfaces, corresponding to differing localizations of the electron. As predicted, softening is larger in the delocalized case. A mechanism for superconductivity is suggested.

Keywords: superconductivity; phonon softening; inelastic neutron scattering; potential energy surface; electron pair

1. Introduction

Since valence is a property of a single metal ion, mixed-valence (MV) systems, finite or infinite, are understood by most people as systems with localized valences. However, the nature of MV is such that delocalization appears in certain ranges of the parameter values ($2H_{12} > \lambda$; Brown 1980; Prassides 1991). Therefore, delocalization is an obvious part of MV theory and has been so for 40 years (Hush 1967; Robin & Day 1967). In infinite crystalline systems, delocalization leads to a metallic spectrum and metallic conductivity.

MV systems with valences differing by one or two units will be referred to here as MV-2 and MV-3 systems, respectively. In a localized MV-2 system, two adjacent valence states are important. There are two diabatic potential energy surfaces (PESs) at equal energy, corresponding to $M^+M$ and $MM^+$. In MV-3 systems, three consecutive valence states appear with the three diabatic PESs corresponding to $M^+M^-$, $M^-M^+$ and $MM$ (Prassides & Day 1984, 1985; Prassides et al. 1986; Prassides 1991). The two with MV are equal in energy, while MM, corresponding to a single valence state, is higher in energy by the Mott–Hubbard parameter $U$, equal to the free energy of the disproportionation reaction

$$2M \rightarrow M^+ + M^- \quad (\Delta G^0 = U).$$

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Mott, who did not himself use the term disproportionation, suggested that \( U \) is a few electronvolts in NiO, CuO and other ‘Mott insulators’. A band gap equal to \( U \) was thereby introduced artificially in the Hubbard model. The localization condition used by Mott is that \( U > 0 \) in equation (1.1) (Mott 1990).

Delocalization, in the sense of the MV-2 model, is achieved if \( 2H_{12} > \lambda \), where \( \lambda \) is the reorganization energy. The latter is a measure of structural changes when an electron is donated to or accepted at a site, and simultaneously a measure of how strongly the electron is bound to the lattice. In view of the fact that the rates of self-exchange reactions span more than 10 orders of magnitude, it appears necessary to include \( \lambda \) in theories of electron conductivity. The band model for electrons should be used only if \( 2H_{12} > \lambda \). If this is not the case, the system is best described if the nuclei are assumed to be distinguishable for the moment and the local corrections to the electronic wave function accounted for before the proper translation-invariant state is projected out.

In the MV-3 case, there are really two conditions for delocalization: the Mott–Hubbard condition \( U \approx 0 \) and a condition of a similar type to \( 2H_{12} > \lambda \) in MV-2 systems. If \( U \geq 0 \) (Mott insulators, antiferromagnetic ‘spin density wave’ (SDW) systems) or if \( U < 0 \) (‘negative-U’ compounds, charge density wave (CDW) systems) the compound is insulating. If \( U \approx 0 \) and \( H_{12}/\lambda \) large, electron pair transfer may occur without activation energy. Since MV-3 systems involve two electrons, a reasonable hypothesis is that MV-3 systems, fulfilling both delocalization conditions, become superconducting at low \( T \) (David 1987; Larsson 1989, 1998). MV-2 systems, involving a single electron, delocalize to ordinary metals (Larsson 2006).

Electron–phonon interaction plays the key role in conventional BCS theory of superconductivity, where it is supposed to be the source of pair formation. Phonon softening has been found by inelastic neutron scattering (INS) and inelastic X-ray scattering (IXS) in several high-\( T_c \) superconductors such as cuprates (Braden et al. 2002, 2005; Reznik et al. 2006) and bismuthates (Braden et al. 2002), demonstrating that phonons are important in the latter superconductors as well. Thereby, a widely held opinion among theoretical solid-state physicists during the last 20 years is contradicted. On the other hand, systems that are non-superconducting, for example manganites (Reichardt & Braden 1999) and nickelates (Yoshizawa et al. 2000; Tranquada et al. 2002), also show softening of breathing modes. In the absence of a ‘least common denominator’ for softening, one has turned to ‘strong correlation effects’ as an explanation; however, the physical content of the latter term is unclear. In the present paper, it is suggested that the primary common property for systems that show softening is MV.

In MV-3 theory, nuclear–electron coupling is due to reorganization energy, i.e. to the \textit{motion} of a pair, but is unnecessary for the \textit{formation} of a pair, as is generally the case for electron pairs in chemistry. In a crystal, the phonon spectrum is perturbed because the electron pair perturbs the structure around itself. This is described in terms of the PESs of standard MV-3 theory. Delocalization and softening thus have the same source, namely modification of the PESs of the breathing modes. In both cases, the electronic wave functions are formed at low energy from valence states, which are coupled to the breathing phonon modes.

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2. Softening of vibrational modes

In the standard harmonic adiabatic treatment, the second derivative of the total energy is calculated (Born & Huang 1954)

\[
\frac{\partial^2 E}{\partial u_{\alpha,l,k} \partial u_{\beta,l',k'}} = \Phi(\alpha, \beta, l-l', k, k'),
\]

where \( \alpha \) and \( \beta \) are \( x, y \) or \( z \), coordinates of nuclei \( l \) and \( k \) (\( l', k' \)). The frequencies are determined from a secular equation. There is no general way to treat anharmonicities and non-adiabaticities of the type of a double-well potential, although the problem has been discussed (Zacher 1987; Hardy & Flocken 1988) not least in connection with MV-3 theory (Prassides et al. 1986). Non-adiabaticity has been included in the MV-2 case (Klimkäns & Larsson 2000).

Softening is determined experimentally with reference to some standard system, for example an undoped system such as \( \text{La}_2\text{NiO}_4 \) or \( \text{La}_2\text{CuO}_4 \), where the doped system is \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) or \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), with \( x \geq 0 \). In a localized picture, sites are introduced where the oxidation state of Ni and Cu, respectively, is raised from +2 to +3. Great changes in the phonon spectrum have thus been associated with double-well potentials as well as with superconductivity.

To derive an expression for \( E \) along breathing modes or half-breathing modes, we use MV theory and use \( X \) as the independent variable. The origin is set so that the equilibrium geometries are \( X_0 \) and \( -X_0 \).

In the MV-2 case, the diabatic states PESs (\( \text{M}^+\text{M} \) and \( \text{MM}^+ \)) may be described by the following equations:

\[
H_{11} = \frac{1}{2}k(Q + Q_0)^2 \quad \text{and} \quad H_{22} = \frac{1}{2}k(Q - Q_0)^2.
\]

The reorganization energy is \( \lambda = 2kQ_0^2 \). The interacted PESs (\( E \)) are determined from the following secular equation:

\[
\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0. \tag{2.3}
\]

The interaction matrix element \( H_{12} \) may be chosen to fit the actual energy difference between the PES when \( R_1 = R_2 \). This energy difference can be calculated in a quantum chemical calculation, where \( Q = 0 \). If the calculated energy difference is \( \Delta \), we choose \( H_{12} = \Delta/2 \). The solution of equation (2.3) is given by

\[
E_{\pm}(Q) = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2} = \frac{k}{2} (Q^2 + Q_0^2) \pm \sqrt{k^2 Q_0^2 Q^2 + H_{12}^2}. \tag{2.4}
\]

The lower curve has a maximum for \( Q = 0 \), if \( 2H_{12} \leq 2kQ_0^2 = \lambda \). For \( 2H_{12} > \lambda \), there is no maximum and hence a delocalized valence. Figures 1 and 2 show a localized and an almost delocalized case, respectively.
In the MV-3 case, the interacting diabatic states, $M^+M^-, M^-M^+$ and $MM$, may be described by the following equations:

$$H_{11} = \frac{1}{2} k(Q + Q_0)^2, \quad H_{22} = \frac{1}{2} k(Q - Q_0)^2 \quad \text{and} \quad H_{33} = \frac{1}{2} k Q^2 - U. \quad (2.5)$$

The eigenvalues corresponding to the PESs are determined from the following secular equation (Prassides et al. 1986):

$$\begin{vmatrix}
H_{11} - E & 0 & H_{13} \\
0 & H_{22} - E & H_{13} \\
H_{13} & H_{13} & H_{33} - E
\end{vmatrix} = 0, \quad (2.6)$$

where the interaction matrix element $H_{13}$ is the coupling between the $M^+M^-$ and $MM$ state (or $M^-M^+$ and $MM$). The direct coupling between $H_{11}$ and $H_{22}$ vanishes in the MV-3 case. For small coupling $H_{13}$, the solution to the $3\times3$
problem may be obtained as the solution to the $2 \times 2$ problem, where $U$ is added and $Q_0$ exchanged by 0 in the right curve. Again we may choose $H_{13}$ and $Q_0$ to fit previously calculated PESs along a breathing or half-breathing mode. Figures 3 and 4 show a localized and a delocalized case, respectively.

### 3. Softening in MV-2 systems

In NiO, the Ni$^{2+}$ ion is a high-spin 3$d^8$ ion with $(t_{2g}^6e_g^1\uparrow^2)$ configuration. The adjacent valence state Ni$^+$ is an unstable $(t_{2g}^6e_g^3)$ system while Ni$^{3+}$ is a stable $(t_{2g}^6e_g^1)$ system. The latter is formed as a localized site if Li$_2$O is used as a dopant (Johnston 1959). As it is an MV-2 system (Ni$^{2+}$/Ni$^{3+}$) the coupling should be quite large, since the interacting orbitals are $e_g$ orbitals and the reorganization energy is also large, for the same reason. The Li$_2$O-doped state is close to being delocalized with a black colour but with some activation energy for conductivity (Johnston 1959). In pure NiO, the SDW system is obviously the groundstate, and hence a description of this state in terms of bands is impossible. The insulator-to-metal transition is at approximately 500 K, which indicates that the CDW system is at a high energy too, as is also suggested by Mott (1990). Thus we do not expect MV-3 behaviour in Ni$^{2+}$ oxides. In the nickelates, the parent compound is La$_2$NiO$_4$ with Ni in the valence state +2. Doping with Sr leads to La$_{2-x}$Sr$_x$NiO$_4$ where Ni obviously has the average valence state $(2+x)$, thus there is a mixture of Ni$^{2+}$ and Ni$^{3+}$ sites. Ordering (stripe phase) occurs in diagonal directions in an alternating manner (Yoshizawa et al. 2000; Tranquada et al. 2002). Softening is observed in the bond-stretching dispersions compared with those of non-doped La$_2$NiO$_4$.

Tranquada et al. (2002) point out that there is no softening in the [1 1 0] direction (valences are the same), but in the [1 0 0] direction (MV). This may be explained by the fact that exchange of valence is possible only in the [1 0 0] direction according to the MV model.
Another MV-2 system has LaMnO$_3$ as the parent substance, where Mn has the oxidation state Mn$^{3+}$. Doping to La$_{1-x}$Sr$_x$MnO$_3$ needs compensation by lifting $x$ Mn$^{3+}$ to Mn$^{4+}$. The Mn$^{4+}$ is a very stable d$^3$ system so $x=1$ corresponds to a 3d$^1$ while $x=0$ corresponds to a 3d$^4$ configuration. Similar softening is observed for La$_{1-x}$Sr$_x$MnO$_3$ to that observed previously for nickelates. The additional electron goes to an axial 3d orbital. In both systems, decrease of the activation barrier for electron transfer (ET) between two adjacent sites is consistent with anomalies in the bond-stretching vibrations.

4. Softening in MV-3 systems

A model of the same type as MV-3 was suggested by Sleight for the BaBiO$_3$ superconductors, discovered by him and others before the superconducting cuprates (Sleight et al. 1975; Sleight 1988). Doping in bismuthates is achieved by Pb or K and changes the composition to BaPb$_x$Bi$_{1-x}$O$_3$ and Ba$_{1-x}$K$_x$BiO$_3$, respectively. The electronic groundstate of BaBiO$_3$ is a typical CDW state with alternating Bi$^{3+}$ and Bi$^{5+}$ sites (negative $U$). Softening was observed for bismuthates with $x>0$ (Braden et al. 2002).

Another well-defined MV-3 system is Cs$_2$Au$_2$X$_6$ ($X=Cl, Br$; Kojima & Kitagawa 1994; Liu et al. 1999). The metal ions are Au$^+$ and Au$^{3+}$ ($U<0$) judging from the local geometry at the Au sites (Au$^+$ is 5d$^{10}$, linear, two-coordinated, and Au$^{3+}$ is 5d$^8$, square planar). At ambient pressure, the conductivity is low as expected. By increasing the pressure, the conductivity is increased by orders of magnitude. At high pressure, there is a phase transition to the single valence state (Au$^{2+}$) with equal bond lengths (Liu et al. 1999). There is no superconductivity and this is possibly related to the absence of coupling between (Au$^{3+}$/Au$^+$) and (Au$^{2+}$/Au$^{2+}$) for the full-breathing mode (see below for the corresponding copper case).

The cuprates have a superconducting phase if some La$^{3+}$ is replaced by Sr$^{2+}$ in La$_2$CuO$_4$ (La$_{2-x}$Sr$_x$CuO$_4$) and a maximum in $T_c$ for $x=0.125$. There is softening in the half-breathing mode but not in the full-breathing mode, clearly
related to the accidental vanishing of the coupling between $(\text{Cu}^{3+}/\text{Cu}^+)$ and $(\text{Cu}^{2+}/\text{Cu}^{2+})$ in the case of full-breathing mode (A. Klimkäns & S. Larsson 2007, unpublished thesis).

In this and other cuprates stripes are formed. Doping provides Cu$^{3+}$ sites and stabilizes the $(\text{Cu}^{3+}/\text{Cu}^+)$ CDW state, lowering $U$. The softening in the half-breathing mode appears to be a mixed MV-2 and MV-3 effect (Reznik et al. 2006). Reznik et al. (2006) have pointed out that ‘dynamic charge inhomogeneity’ may explain the giant electron–phonon anomaly which they discovered. Most probably the CDW diabatic state is responsible. Although Reznik et al. (2006) believe that this contribution to the understanding of superconductivity is indirect, vanishing of the activation energy in the MV-3 system can be shown to be directly related to activationless electron-pair transfer of the superconducting type (Larsson 1998).

5. Discussion

In the current literature, there are suggestions that oxide superconductivity is related to (i) SDW (antiferromagnetism), (ii) CDW or (iii) electron–lattice coupling. In the present paper, it is demonstrated that these three factors are in operation at the same time and together cause superconductivity (Larsson 1998). The latter arises owing to a quantum mechanical interaction between the SDW and CDW states, via electron–lattice interactions. Phonon interactions are important but, in MV-3 theory, not for the stabilization of the pair state. In MV-3 theory, pairing is directly related to the existence of two valence states which differ by two units and are therefore unsurprising. The Mott–Hubbard $U$ should be defined as the free energy for disproportionation of the central valence state. In the case of a stable CDW (disproportionated) state, $U$ is negative, but if $U$ is defined as electron repulsion, it is always positive of course.

Coupling to the phonons is by the same mechanism as in MV theory in general. This is indeed a most conspicuous feature of MV theory, since reorganization energy ($\lambda$) can hardly be equal to zero. Delocalization occurs if $\lambda > 2H_1$. In the delocalized case, $\lambda$ is still evident in the shape of the PESs, causing phonon interactions. BCS theory is based on a treatment of electron repulsion using harmonic phonons, and is therefore unsuitable in the present case. It is still necessary to obtain quantitative agreement between theory and softening results as measured by INS and IXS. This is not an easy task but can be done in principle if accurate calculation of the electronic structure can be performed along the relevant PESs suggested here. MV-3 theory as a description of high-$T_c$ superconductivity is thus a verifiable theory.

References


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