LOCALIZATION IN YBa$_2$Cu$_3$O$_7$ INDUCED BY THE SELF-INTERACTION CORRECTION TO THE DENSITY FUNCTIONAL THEORY

V.I. ANISIMOV and M.A. KOROTIN

Institute of Metal Physics, Sverdlovsk, USSR

I.I. MAZIN *

P.N. Lebedev Physical Institute, Moscow 117924, USSR

We address the question whether intra-atomic repulsion U in YBa$_2$Cu$_3$O$_7$ is strong enough to provide electron localization. We use a recently proposed self-interaction-correction (SIC) based approach which provides a qualitative criterion (symmetry breaking) for electron localization. Using a first-principle LMTO-Green-function technique we show that only d$_{xy}$, d$_{yz}$ and d$_{zx}$ orbitals of Cu in the CuO$_2$ plane get localized; localized orbitals have ~ 4.5 eV smaller energy then itinerant ones (which gives an estimate of U). d$_{x^2-y^2}$ and d$_{3z^2-r^2}$ orbitals of Cu and p-orbitals of O are stable against localization.

The recent discovery of the high-T_c copper oxides revived the interest in the Coulomb-induced localization of electrons in solids. The essential physics of this phenomenon is usually described in terms of the Mott–Hubbard parameters [1], namely intrasite Coulomb repulsion U and hopping integral t. Then, a large U/t ratio leads to "localization" of each electron near its nucleus and an attempt to localize another electron with opposite spin on the same atom leads to an increase of the energy by U. When $U/t \ll 1$, however, the electrons are itinerant and the effect of Coulomb interaction (yet strong) is accurately described by the renormalisation of the effective one-electron potential. It is known that such a situation takes place in simple metals for instance. Transition metals represent a step towards the Mott–Hubbard picture; one cannot neglect completely the "Hubbard-like" effects, but they result only in quantitative distortion of the band shapes, first of all in narrowing of the d-bands. However, qualitative effects, like strong Hubbard splitting do not exist in these metals. Finally, there are some examples of the Mott insulators (NiO, MnO) where U/t is quite

large, bands are split by Coulomb repulsion, the magnetic moments are nearly integer and so on. The main problem with high-T_c materials is to know as to which group they belong.

The appearance of strong magnetism in nearly-superconducting copper oxides is an indication of strong electronic correlations. It is not easy to tell, however, whether they belong to the same class as 3d magnetics ("correlation-induced band distortions") or to the class of "doped Mott insulators". There are no ways to determine either theoretically or experimentally the criterion U/t and to decide if it is large enough. For instance the semi-empirical Zaanen–Sawatzky–Allen approach may be very successful but to apply it one should be sufficiently sure in the experimentally photoemission spectra and in the interpretation of corresponding sattelites. Unfortunately, this is not the case for high-T_c materials. The 9.5 eV sattelite in the 1-2-3 compound which has been so widely discussed in this connection was recently proved to be due to surface deterioration ([2])! A formalism is wanted which would allow to deal with "U–t competition" directly.

It was recently proposed by Svane and Gunnarsson to use for this purpose the so-called SIC (self-

---

* To whom all correspondence should be addressed.

interaction correction) formalism [3]. The formalism was introduced by Perdew and Zunger [4] in order to obtain a correct and simple description of free atoms and ions. It consists of using local density functional theory with artificial removing of the Hartree and (local) exchange-correlation self-interactions. The effective SIC potential for the ith eigenstate is

$$V_i(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[\rho](\mathbf{r}) + V_{\text{xc}}[\rho](\mathbf{r})$$
$$- V_{\text{H}}[\rho_i](\mathbf{r}) - V_{\text{xc}}[\rho_i](\mathbf{r}) , \qquad (1)$$

where V_{ext} is an external potential, $\rho_i = |\psi_i(\mathbf{r})|^2$ is the "ith" electron density, $\rho = \sum_{\text{occ}} \rho_i$. Self-interaction correction gives very good results for atomic-like systems (localized electrons) and vanishes with the delocalization. Svane and Gunarsson [2] have mentioned that the potential (1) may break the translational symmetry and lead to self-localization of an electron, due to the orbital dependence of eq. (1). This self-localization is governed by the same criterion U/t and has essentially the same physical origin as the Mott–Hubbard localization. Indeed, Svane and Gunnarsson [3] have applied SIC to the so-called "discrete LDA model" [4] for the one- and two-dimensional Hubbard model and obtained excellent agreement with Monte-Carlo results in a wide region of U/t. They also applied the same model to La$_2$CuO$_4$ and obtained antiferromagnetism; however, somewhat too large. It should be noted in this connection that the approach seems oversimplified in the following aspects: (1) As well shall see below, the third dimension is important for localization. (2). The disadvantage of the quantitative application of the Hubbard model is a too indirect estimate of u and t. (3) We agree with the recent criticism of Sham and Schlüter [5] against the "discrete-LDA" Hubbard model" in connection with real systems.

That is why we tried to apply the SIC formalism to an electron in a real material (YBa$_2$Cu$_3$O$_7$) and to look for a broken-symmetry localized solution.

Concretely, we extract an electron of a particular site (Cu or O) and with a given symmetry ($d_{x^2-y^2}$ etc.). Then we assume that it is localized inside its own atomic sphere *. Then a self-interaction correction is switched on (only for this particular electronic state). The resulting problem is solved by the LMTO Green-function impurity method. If the obtained "impurity level" is localized we recalculate the self-interaction correction and iterate to self-consistency. Therefore, all but one electron states feel the same ordinary self-consistent LDA potential. The state in question, labeled i, feels the potential with the correction:

$$V_i = V_{\text{LDA}} - V_{\text{H}}[\rho_i] - V_{\text{xc}}[\rho_i] . \qquad (2)$$

In principle we should also take into account the change of V_{LDA} on the site in question due to the redistribution of the ith electron density. This is, however, a much weaker effect than the SIC for the ith electron.

We have found that, according to the idea of Svane and Gunnarsson [2], the SIC formalism may distinguish between "localized" and "non-localized" states; in fact, for no oxygen state we have found a localized solution. For copper, d_{xy}, d_{yz} and d_{zx} states get localized with the position of the localized level ~ 1.5 eV below the bottom of the valence band or ~ 4.5 eV below the center of the corresponding bands. This number corresponds well with other estimates of U. $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ do not localize. However, if we extract the CuO$_2$ plane from the crystal and apply the formalism to it, $d_{3z^2-r^2}$ localize too, which shows the sensitivity to three-dimensionality.

Our conclusions are as follows:

(1) SIC-LDA formalism may serve as a tool for distinguishing the "localized" Mott–Hubbard states from the delocalized ones.

(2) In YBa$_2$Cu$_3$O$_7$ the partially filled $d_{x^2-y^2}$ states as well as $d_{3z^2-r^2}$ are delocalized. This suggests that the extreme Hubbard limit with large splitting between occupied and empty states is not appropriate; however it seems quite probable that the shape of the Cu–O bands in LDA is distorted and especially their width is overestimated. Such an overestimate may be responsible for the incorrect paramagnetic ground state in YBa$_2$Cu$_3$O$_6$ and in La$_2$CuO$_4$. The assumption that the whole band structure of La$_2$CuO$_4$ in LDA is correct but too wide is also confirmed by optical measurements [6].

(3) The tendency to localization is greatly favoured by the two-dimensionality; in an isolated CuO$_2$ plane electrons are more localized than in the bulk crystal.

---

* We use a neutral atomic sphere as is usual in the LMTO method.

(4) In estimates of Hubbard parameters U and t from band structure calculations and/or from experiments it should be taken into account that they may be different for states with different symmetry and that maximal U/t corresponds to the filled d_{xy}, d_{yz} and d_{xz} states and not to (anti-)bonding $d_{x^2-y^2}$ orbitals.

Acknowledgement

References

[1] N.F. Mott. Metal–Insulator Transition (Taylor and Francis, London, 1974).

[2] A.J. Arko, R.S. List, Z. Fisk, S.-W. Cheong, J.D. Thomson, J.A. O'Rourke, C.U. Olson, A.-B. Yang, Tun-Wen, Pi, J.E. Schirber and N.D. Shinn, to be published.

[3] A. Svane and O. Gunnarsson, to be published.

[4] J.P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.

[5] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. 56 (1986) 1968.

[6] L.J. Sham and M. Schlüter, Phys. Rev. Lett. 60 (1988) 1582.

[7] E.G. Maksimov, I.I. Mazin, S.N. Rashkeev, S.Y. Savrasov and Y.A. Uspenski, in: Proc. Conf. Towards the Theoretical Understanding of the High-T_c Superconductivity, Trieste, 1988, to be published.