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# Electron correlation in low-carrier-density metals: Photoemission study of the hole-doped Mott insulator $Li_xZn_{1-x}V_2O_4$

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We have measured photoemission spectra of $Li_xZn_{1-x}V_2O_4$ which is a Mott-Hubbard insulator at $x=0$ and becomes a metal by doping with holes for $x \gtrsim 0.35$. The V $3d$ band is broadened and shifted to higher binding energy compared to band theory. The density of states at the Fermi level is low even in the metallic phase, which we attribute to the effect of long-range Coulomb interaction. Implications of these results on polaron effects and superconductivity in metallic oxides are discussed.

Electron correlation in partially filled narrow bands has usually been studied using as a starting point the Hubbard model,[1,2] which is characterized by two parameters: namely, intra-atomic Coulomb energy $U$ and one-electron bandwidth $W$. For the nondegenerate Hubbard model, a gap is opened at the Fermi level ($E_F$) at half-filling in the strong correlation limit, $U/W \gg 1$ (Mott-Hubbard insulator). This system can be made metallic either by decreasing $U/W$ or by doping with extra electrons or holes. Electronic properties of such strongly correlated metals are of great interest and their single-particle density of states (DOS) as measured by valence-band photoemission spectroscopy would give valuable information on the nature of electron correlation, although detailed interpretation of the spectra has not been made so far.

In this work, we have studied the spinel-type $Li_xZn_{1-x}V_2O_4$, in which Li and Zn atoms at the tetrahedral sites are ionized to $Li^+$ and $Zn^{2+}$ and donate electrons to V $3d$ orbitals at the octahedral sites. $ZnV_2O_4$ is a Mott-Hubbard insulator with localized $3d^2$ ($V^{3+}$) configuration (corresponding to half-filling) and orders antiferromagnetically below $T_N=45$ K.[3] For $x>0$ the system is doped with holes ($V^{4+}$:$d^1$) and shows metallic conductivity at $x \gtrsim 0.35$,[4,5] although the carrier density is low (0.2–0.5 per V atom) and the magnetic susceptibility obeys the Curie-Weiss law.[6] Thus $Li_xZn_{1-x}V_2O_4$ with $x \gtrsim 0.35$ is not an ordinary metal and is an interesting system with which to study the effect of electron correlation in narrow bands. Indeed, the present study suggests significant electron correlation in this system. In particular, an observed low DOS near $E_F$ implies the importance of long-range Coulomb interaction as well as short-range interaction $U$ considered in the Hubbard model.

Sintered pellets of $Li_xZn_{1-x}V_2O_4$ ($x=0$, 0.5, and 1) were prepared by solid-state reaction as described in Ref. 5. They were introduced into the ultrahigh vacuum chamber of the spectrometer (base pressure $\sim 1\times10^{-10}$ Torr) through an airlock entry. Clean surfaces were obtained by scraping *in situ* with a diamond file. A He resonance lamp ($h\nu=21.2$ and 40.8 eV) and a Mg x-ray source ($h\nu=1253.6$ eV) were used to excite ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) spectra. The total resolution was $\sim$0.15 eV and $\sim$0.9 eV for UPS and XPS, respectively. Satellites of the He and Mg sources have been numerically subtracted.

Valence-band UPS spectra are shown in Fig. 1. They are compared with the (paramagnetic) one-electron band-theoretical DOS (Ref. 7) corrected for photoionization cross sections[8] and broadened for the instrumental and energy-dependent lifetime widths.[9] While the shape of the O $2p$ band at binding energy $E_B=3$–9 eV is in reasonable agreement with the band theory (for $x \neq 1$, interaction with the Zn $3d$ level somewhat distorts the O $2p$ band), the broad V $3d$ emission with a low DOS at $E_F$ cannot be accounted for by band theory which predicts a high DOS at $E_F$. (Magnified views in Fig. 1, however, show a small but finite DOS for the metallic $x=0.5$ and 1 samples.) Also, one notices that the experimental $d$ bandwidth increases with $x$.

Since band theory, which is appropriate in the weak correlation limit, has failed to describe the $d$-band spectra, we take an opposite view that the $d$ electrons are strongly correlated and nearly localized: The V sites in $Li_xZn_{1-x}V_2O_4$ are assumed to be fluctuating between $d^1$ and $d^2$ configurations in a time scale longer than that of photoemission ($\sim 10^{-15}$ sec).[10] Then $d$-electron emission produces two kinds of final states, $d^0$ and $d^1$, with $d^1$ located closer to $E_F$. Hence, the broadening of the $d$ band width $x$ is attributed to the appearance of a $d^1 \rightarrow d^0$ feature on the high-binding-energy side of the dominant $d^2 \rightarrow d^1$ one. We have decomposed the spectra of $x=0.5$ and 1 into $d^2 \rightarrow d^1$ and $d^1 \rightarrow d^0$ components as shown in Fig. 1, where we have assumed the same line shape for the $d^2 \rightarrow d^1$ component of all $x$ and intensity ratios $(d^1 \rightarrow d^0):(d^2 \rightarrow d^1)=1:6$ and 1:3 for $x=0.5$ and 1, respectively, as expected from the ground-state $d^1$:$d^2$ ratios. From the position of the $d^1 \rightarrow d^0$ component, $U$ is estimated to be $\gtrsim 2$ eV (or possibly $\lesssim 2$ eV if the effect of long-range Coulomb interaction is taken into account as described below), which is similar to previous estimates for $VO_2$ ($U=1.2$ eV)[11] and $V_2O_3$ ($U \lesssim 2$ eV).[12]

The localized $d$-electron picture is consistent with the

 

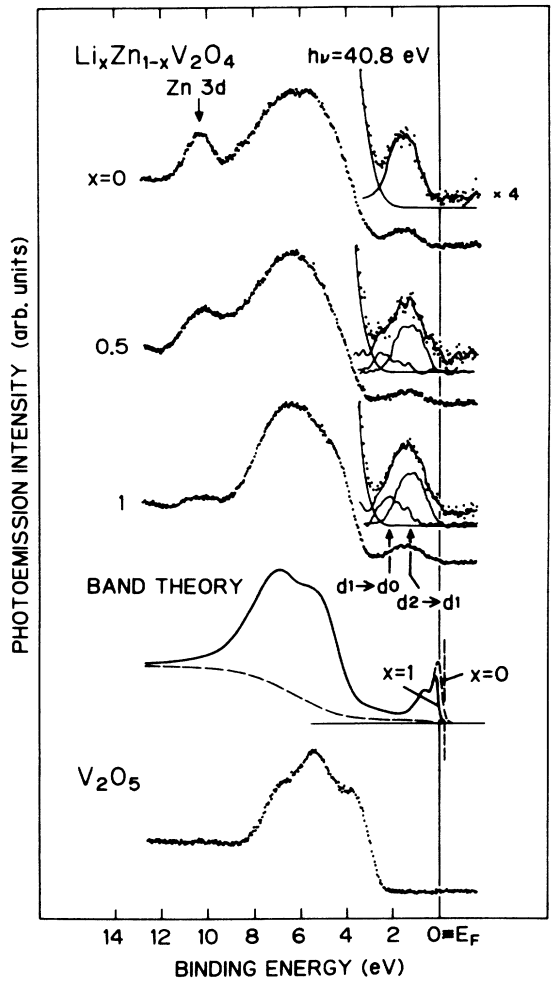


FIG. 1. Valence-band UPS spectra of $Li_xZn_{1-x}V_2O_4$ taken with $h\nu=40.8$ eV. Theoretical spectra deduced from the band-structure calculation (Ref. 7) are compared with experiment. Emission at $E_B\sim 10$ eV is due to the Zn 3$d$ level. The spectrum of $V_2O_5$ which has no electron in the V 3$d$ band is also shown.

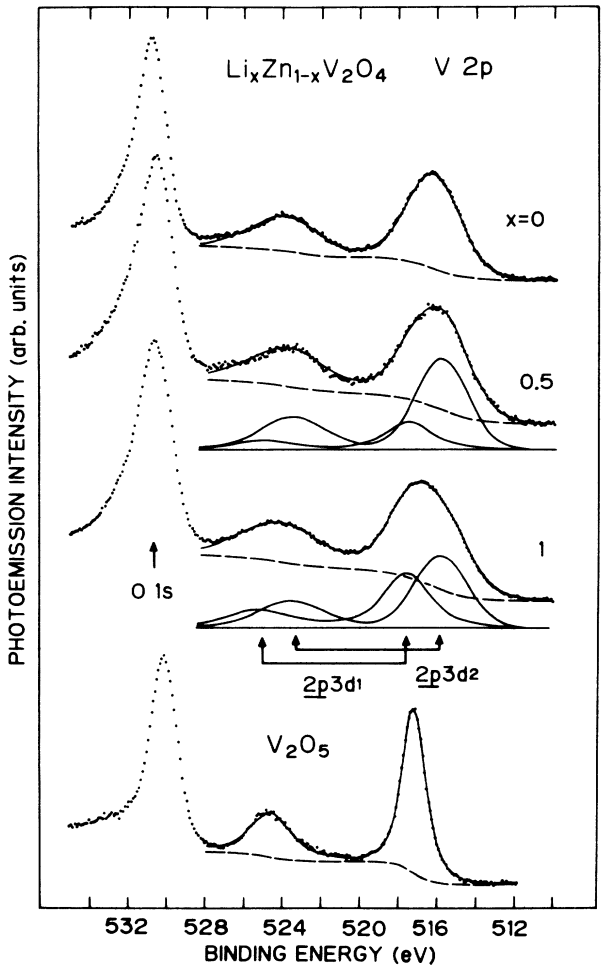


FIG. 2. V 2$p$ core-level XPS spectra of $Li_xZn_{1-x}V_2O_4$. As we do not know the line shapes of the $\underline{2p}3d^1$ and $\underline{2p}3d^2$ multiplets, we have used in the line-shape analyses Gaussian functions whose widths have been assumed proportional to the square root of the total spin of the $d^n$ configuration, $S$.

vanadium core-level XPS spectra in Figs. 2 and 3, where each spectrum has been decomposed into $\underline{c}3d^1$ and $\underline{c}3d^2$ components ($\underline{c}$ denotes core hole). The energy of the $\underline{c}3d^2$ configuration is lower than that of $\underline{c}3d^1$ by the intra-atomic core-hole-3$d$ Coulomb energy. The relative intensity of the $\underline{c}3d^1$ and $\underline{c}3d^2$ components reflects approximately the ground-state $d^1$:$d^2$ ratio, although the $\underline{c}3d^2$ weight has been found a little too high probably because of a final-state effect, i.e., core-hole screening by $d$ electrons. The splitting and intensity ratio of the doublet structure in the V 3$s$ core-level XPS of $ZnV_2O_4$ (Fig. 3) indicate that its $d^2$ ground state is in the high-spin ($S=1$) state.[13] Here, we note that both the valence-band $d^2\rightarrow d^1$ and core-level $\underline{c}3d^2$ binding energies are shifted by the same amount, $\sim$0.5 eV, between $x=0$ and $x>0.5$,[14] so that all the spectral features associated with the $d^2$ ground-state component are rigidly shifted upon hole doping whereas the O 2$p$ band and the O 1$s$ core level are not.

According to the above assignment, the unoccupied part of the V 3$d$ DOS would consist of $d^1\rightarrow d^2$ and $d^2\rightarrow d^3$ components as shown in Fig. 4, leading to a dip in the DOS around $E_F$ not only for the insulating $x=0$ but also for $x>0$. Although the localized $d$-electron picture is generally thought to be equivalent to the $U/W\gg 1$ limit of the Hubbard model, the model would predict an upward shift of the lower Hubbard band across $E_F$ with hole doping and would not explain such a suppressed DOS near $E_F$. We thus consider long-range Coulomb interaction which is neglected in the Hubbard model but becomes important when the carrier density is low. This interaction would shift the DOS away from $E_F$ by the average hole-hole or electron-electron repulsion for the occupied or unoccupied $d$ band, respectively, and would consequently lower the DOS near $E_F$ for arbitrary band filling. So far, it has been established that long-range Coulomb interaction leads to a "soft" gap at $E_F$ (Coulomb gap) irrespective of band filling for localized electrons in disordered systems.[15] While the single-particle DOS near $E_F$ appears to be suppressed by the long-range Coulomb in-

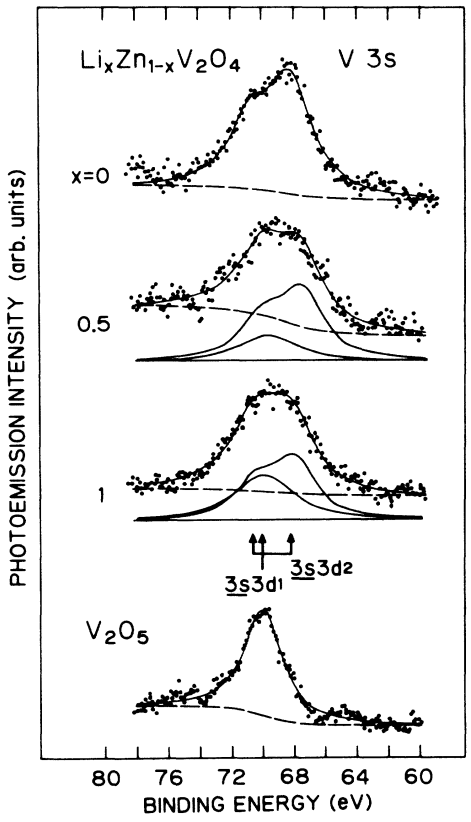


FIG. 3. V 3$s$ core-level XPS spectra of $Li_xZn_{1-x}V_2O_4$. The multiplet of each configuration is simply a doublet, corresponding to final states with spins of $S+\frac{1}{2}$ and $S-\frac{1}{2}$.

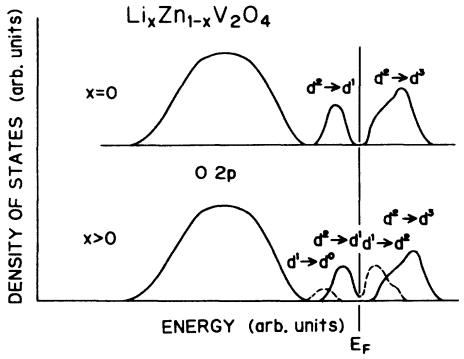


FIG. 4. Schematic single-particle DOS of $Li_xZn_{1-x}V_2O_4$. For the V 3$d$ states, only $t_{2g}$ electrons are shown for simplicity.

teraction, the same interaction in the ground state leads to electronic polaron effects. Namely, doped carriers are "dressed" with electronic excitations of other electrons and become "heavy" carriers. Phononic polarons could also lead qualitatively to the same effect, but phonon energies alone are generally too small to account for the observed width of the low DOS region around $E_F$.

The present localized $d$-electron picture is consistent with the Curie-Weiss behavior of mixed $d^1$ ($S=\frac{1}{2}$) and $d^2$ ($S=2$) configurations observed at high temperatures, $T>500$ K.[6] In the semiconducting region $x \lesssim 0.35$, the large negative Weiss constant ($\sim -500$ K) and the suppression of the magnetic susceptibility at low temperature, $T<500$ K, compared to the high-temperature Curie-Weiss law, suggest a strong antiferromagnetic coupling between the local moments.[6] In the metallic region $x \gtrsim 0.35$, on the other hand, although the Weiss constant at high temperatures is the same as that in the semiconducting region, the low-temperature susceptibility is enhanced relative to the high-temperature Curie-Weiss law.[6] Such a behavior can be understood as an effect of doped holes which become itinerant and induce ferromagnetic coupling between local moments,[16] thereby weakening the antiferromagnetic coupling. Hence the enhancement of the magnetic susceptibility below $\sim 500$ K suggests that the polaron "band" width of the doped holes is of the order of 500 K and that they become itinerant below this temperature.

Discrepancy between band theory and photoemission spectra similar to the present work, i.e., low DOS at $E_F$ and shift to higher binding energy of the $d$ band, has been reported for $LiTi_2O_4$.[17] In the light of the present results, this would also be attributed to short-range and long-range Coulomb correlation within the Ti 3$d$ band. In this sense, $LiTi_2O_4$ is a correlated, low-carrier-density metal and its superconductivity ($T_c=13.7$ K) may not be explained within the conventional BCS mechanism based on one-electron band theory.

Finally, we would like to suggest that the suppression of the single-particle DOS near $E_F$ due to long-range Coulomb interaction can be significant also at half-filling: If the system is on the metallic side of the Mott transition but is close to it, screening of the long-range Coulomb interaction by itinerant carriers would not be so effective, leading to a suppression of the DOS near $E_F$ compared to what would be expected for a closing of the Mott-Hubbard gap. The mysterious, very low DOS at $E_F$ observed in the photoemission spectra of metallic $CrO_2$ (Ref. 18) and $BaPb_{1-x}Bi_xO_3$ (Ref. 19) might be explained along this line. [As for $BaPb_{1-x}Bi_xO_3$, $U$ is large both for the Bi/Pb 6$s$ (Ref. 20) and O 2$p$ (Ref. 21) electrons unlike what is widely believed.] Recently, it has been suggested that long-range Coulomb interactions plays an important role in the superconductivity of low-carrier-density metals including doped Cu oxides.[22] Indeed, doped holes in these oxides enter the O 2$p$ band but the DOS at $E_F$ as observed by photoemission is too low for an O 2$p$ band whose top is cut off at $E_F$.[23]

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[1]J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963); **227**, 237 (1964); **281**, 401 (1964).

[2]W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970); M. Cyrot, J. Phys. (Paris) **33**, 125 (1972); T. Moriya and H. Hasegawa, J. Phys. Soc. Jpn. **48**, 1490 (1980); J. Spalek, A. Datta, and J. M. Honig, Phys. Rev. Lett. **59**, 728 (1987).

[3]S. Niziol, Phys. Status Solidi A **18**, K11 (1973).

[4]B. Reuter and K. Müller, Naturwissenchaften **54**, 164 (1967). These authors have reported a higher critical concentration, $x \sim 0.55$.

[5]K. Kawakami, Y. Sakai, and N. Tsuda, J. Phys. Soc. Jpn. **55**, 3174 (1986).

[6]F. Takagi, K. Kawakami, I. Maekawa, Y. Sakai, and N. Tsuda, J. Phys. Soc. Jpn. **56**, 444 (1987); Muhtar, F. Takagi, K. Kawakami, and N. Tsuda, *ibid.* (to be published).

[7]As no band-structure calculation is available for $ZnV_2O_4$ or $LiV_2O_4$, that of the isostructural $LiTi_2O_4$ [S. Satpathy and R. M. Martin, Phys. Rev. B **36**, 7269 (1987)] has been employed by appropriately shifting $E_F$. We believe that such a rigid-band assumption is a good approximation for the present purpose.

[8]J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[9]A. Fujimori, M. Sekita, and H. Wada, Phys. Rev. B **33**, 6652 (1986).

[10]Since the metal-insulator boundary is not clear in the $Li_xZn_{1-x}V_2O_4$ system, one cannot exclude localization at $V^{3+}$ and $V^{4+}$ sites in the $x=0.5$ sample because of the disorder at the tetrahedral sites. Photoemission cannot distinguish the localization from the valence fluctuation. The V valence would indeed fluctuate in $LiV_2O_4$ since there is no tetrahedral-site disorder nor evidence for charge ordering: The single crystal shows metallic conductivity [D. B. Rogers, J. L. Gillson, and T. E. Gier, Solid State Commun. **5**, 263 (1967)].

[11]C. Sommers and S. Doniach, Solid State Commun. **28**, 133 (1978).

[12]C. Castellani, C. R. Natoli, and J. Ranninger, J. Phys. (Paris) Colloq. **37**, C4-199 (1976).

[13]D. A. Shirley, Phys. Scr. **11**, 177 (1975).

[14]Actually, the V $2p$ and $3p$ core levels show this behavior but V $3s$ does not, probably because of interaction with the Zn $3p$ level at $E_B \sim 90$ eV.

[15]A. L. Efros, J. Phys. C **9**, 2021 (1976); J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. B **29**, 4260 (1980); J. H. Davies and J. R. Franz, Phys. Rev. Lett. **57**, 475 (1986).

[16]Y. Nagaoka, Phys. Rev. **147**, 392 (1966).

[17]P. P. Edwards, R. G. Egdell, I. Fragala, J. B. Goodenough, M. R. Harrison, A. F. Orchard, and E. G. Scott, J. Solid State Chem. **54**, 127 (1984).

[18]K. P. Kämper, W. Schmitt, G. Güntherodt, R. J. Gambino, and R. Ruf, Phys. Rev. Lett. **59**, 2788 (1987).

[19]G. K. Wertheim, J. P. Remeika, and D. N. E. Buchanan, Phys. Rev. B **26**, 2120 (1982); H. Sakamoto, H. Namatame, T. Mori, K. Kitazawa, S. Tanaka, and S. Suga, J. Phys. Soc. Jpn. **56**, 365 (1987).

[20]K. Takegahara and T. Kasuya, J. Phys. Soc. Jpn. **56**, 1478 (1987).

[21]P. Humbert and J. D. Deville, J. Phys. C **20**, 4679 (1987).

[22]Y. Takada, in *Superconducting Materials,* Japanese Journal of Applied Physics, Series 1, edited by S. Nakajima and H. Fukuyama (Publication Office of Japanese Journal of Applied Physics, Tokyo, 1988), p. 240.

[23]A. Fujimori, E. Takayama-Muromachi, and Y. Uchida, Solid State Commun. **63**, 857 (1987); A. Fujimori, S. Takekawa, E. Takayama-Muromachi, Y. Uchida, A. Ono, T. Takahashi, Y. Okabe, and H. Katayama-Yoshida (unpublished).