Mechanism for the valence-band photoemission in Ni: Inclusion of interatomic interactions

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In relation to the valence-band photoemission in Ni, the importance of interatomic interactions is proposed, on the basis of examinations of the correlation effect in the T-matrix approximation. Calculated results show that, in the presence of the interatomic interaction, both the bandwidth and the satellite binding energy become smaller than those in the Hubbard model. This property in the interatomic interaction enables us to explain consistently the experimental result.

Recent experiments of the valence-band photoemission in Ni have shown that a satellite peak exists about 6 eV below the Fermi level[1] for which the bandwidth is about 30% narrower than that in band calculations.[2] This fact indicates an importance of correlation effects between electrons. Several theoretical investigations[3−5] have been devoted to the correlation effect on electronic structure of Ni, within the framework of the Hubbard model in the T-matrix approximation. As has been pointed out by Penn[3] and Liebsch,[5,6] however, these treatments cannot explain consistently both the degree of band narrowing and the satellite binding energy. Namely, the value of the Coulomb integral U determined so as to give the 6-eV satellite peak leads to only half the band narrowing obtained with the photoemission data. Thus a problem provided by the valence-band photoemission in Ni is to find a mechanism by which both the band narrowing and the satellite binding energy can be consistently explained. Liebsch[6] has tried to remove the above inconsistency by taking account of electron-hole interactions, and suggested that this

mechanism leads possibly to an explanation for the above consistency problem. On this point, a recent work by Igarashi[7] also shows a trend similar to the above.

On the other hand, there should be the effect of interatomic interactions which, in the Hubbard model, is not taken into account, and we propose the importance of this mechanism in photoemission. We have recently found a significant contribution of interatomic interactions, by the analysis of momentum-dependent susceptibility of Ni, which leads to comparable magnitudes of intra-atomic and interatomic integrals.[8] In this Brief Report, we take into account only the following matrix elements of the electron interaction v with respect to the real Wannier function in lth band, $w_l(\vec{r} - \vec{R})$, around an atomic site $\vec{R}$:

$$U = (l\vec{R}; l', \vec{R} | v | l, \vec{R}; l', \vec{R}) , \tag{1a}$$

$$U_1/z_1 = (l, \vec{R}; l', \vec{R} + \vec{\rho} | v | l, \vec{R}; l', \vec{R} + \vec{\rho}) , \tag{1b}$$

which are assumed to be independent of l and l', with

$$(l, \vec{R}; l', \vec{R}' | v | l, \vec{R}; l', \vec{R}') = \int \int d\vec{r}_1 d\vec{r}_2 w_l(\vec{r}_1 - \vec{R}) w_{l'}(\vec{r}_2 - \vec{R}') v(\vec{r}_1 - \vec{r}_2) w_l(\vec{r}_1 - \vec{R}) w_{l'}(\vec{r}_2 - \vec{R}') . \tag{2}$$

Here U and U_1 are the intra-atomic and interatomic integrals, respectively, and $\vec{\rho}$ is a position vector tending to one of z_1 nearest neighbors. By noticing the existence of the interatomic interaction, we can understand the above consistency problem in photoemission as follows: First, the bandwidth becomes narrower because the available space of holes moving

around in a crystal is more restricted by the interatomic interaction. Namely, when two holes come to neighboring sites the energy of the electronic system is increased by U_1/z_1, and, to a state with two holes at the same site, in which the energy is increased by U, correspond z_1 states with a hole at each of two neighboring sites. Thus, to the band narrowing, the

interatomic interaction makes a contribution comparable to the intra-atomic one, since U and U_1 are comparable to each other.[8] Second, as for the position of the satellite peak, it is not changed so much by the interatomic interaction, because the satellite arises from a bound state with two holes at the same atomic site. These two characters tend to improve the consistency problem. The purpose of this report is to derive a new character of the interatomic interaction for the consistency problem, by using a simplified model with the fivefold degenerate bands.

If we express the Bloch state $|l, \vec{k}\rangle$ in lth band with momentum $\vec{k}$ in terms of the Wannier function, the matrix element of the electron interaction is written in the present model as

$$N(l, \vec{q}+\vec{k}; l', \vec{q}-\vec{k}|v|l, \vec{q}+\vec{k}'; l', \vec{q}-\vec{k}')$$
$$= U + U_1 a_1(\vec{k}-\vec{k}') \quad , \quad (3)$$

$$a_1(\vec{k}) = \frac{1}{z_1} \sum_{\vec{p}} e^{i\vec{k}\cdot\vec{p}} \quad . \quad (4)$$

Here N is the number of atoms in a crystal. We consider a low-density case with n holes per atom around the R points in the simple cubic structure, taking one of the R points as the origin of $\vec{k}$ and changing the sign of energy. We now calculate in the T-matrix approximation the self-energy part $M(\vec{k};\omega)$ of a hole. For a paramagnetic state, the expression can be

written, within the low-density—limit approximation, up to the first order with respect to n, as

$$M(\vec{k};\omega) = \Big(l, \vec{k}; l', \vec{0}\Big|T(\omega + \epsilon(0))\Big|l, \vec{k}; l', \vec{0}\Big)n$$
$$- \Big(l, \vec{k}; l, \vec{0}\Big|T(\omega + \epsilon(0))\Big|l, \vec{0}; l, \vec{k}\Big)\frac{n}{10}$$
$$\equiv T_c(\vec{k};\omega)\, n - T_{\text{ex}}(\vec{k};\omega)\frac{n}{10} \quad , \quad (5)$$

where $T_c(\vec{k};\omega)$ and $T_{\text{ex}}(\vec{k};\omega)$ correspond to the Coulomb and exchange processes, respectively.

The two types of T matrices in Eq. (5) can both be obtained from the solution for

$$T(\vec{k}_1, \vec{k}) \equiv \Big(l, \vec{k}; l', \vec{0}\Big|T(\omega + \epsilon(0))\Big|l, \frac{\vec{k}}{2} - \vec{k}_1; l', \frac{\vec{k}}{2} + \vec{k}_1\Big) ,$$
$$(6)$$

by the use of

$$T_c(\vec{k};\omega) = T\Big(-\frac{\vec{k}}{2}, \vec{k}\Big) \quad , \quad (7a)$$

$$T_{\text{ex}}(\vec{k};\omega) = T\Big(\frac{\vec{k}}{2}, \vec{k}\Big) \quad . \quad (7b)$$

The equation for $T(\vec{k}_1, \vec{k})$ is written as

$$T(\vec{k}_1, \vec{k}) = V(\vec{k}_1, \vec{k}) - U \sum_{\vec{k}'} T(\vec{k}', \vec{k})B(\vec{k}', \vec{k}) - \frac{1}{z_1} \sum_{\vec{p}} e^{i\vec{k}_1\cdot\vec{p}} \sum_{\vec{k}'} U_1 e^{-i\vec{k}'\cdot\vec{p}} T(\vec{k}', \vec{k})B(\vec{k}', \vec{k}) \quad , \quad (8)$$

in which

$$V(\vec{k}_1, \vec{k}) = U + U_1 a_1\Big(\vec{k}_1 + \frac{\vec{k}}{2}\Big) \quad , \quad (9)$$

and $B(\vec{k}', \vec{k})$ is a two-particle Green's function that is written, in the present low-density—limit approximation, as

$$B(\vec{k}', \vec{k}) = \frac{1}{N} \{\epsilon[(\vec{k}/2) + \vec{k}'] + \epsilon[(\vec{k}/2) - \vec{k}'] - \epsilon(0) - \omega - i\eta\}^{-1} \quad . \quad (10)$$

For simplicity, we consider $\vec{k}$ lying in a direction $[1,1,1]$, and put $\vec{k} = k(1,1,1)$. In this case, $B(\vec{k}', \vec{k})$ in Eq. (8) is invariant for the transformation $\vec{k}' \rightarrow -\vec{k}'$ and for any interchange between k'_x, k'_y, and k'_z, as seen from Eq. (10). Based on this symmetry property, we divide $V(\vec{k}_1, \vec{k})$ in Eq. (8) into symmetric and antisymmetric parts, which are given by

$$V^{(+)}(\vec{k}_1, \vec{k}) = [V(\vec{k}_1, \vec{k}) + V(-\vec{k}_1, \vec{k})]/2$$
$$= U + U_1 \cos\Big(\frac{ka}{2}\Big)a_1(\vec{k}_1) \quad , \quad (11a)$$

$$V^{(-)}(\vec{k}_1, \vec{k}) = [V(\vec{k}_1, \vec{k}) - V(-\vec{k}_1, \vec{k})]/2$$
$$= -U_1 \sin\Big(\frac{ka}{2}\Big)c_1(\vec{k}_1) \quad . \quad (11b)$$

Here

$$a_1(\vec{k}_1) = (\cos k_{1x}a + \cos k_{1y}a + \cos k_{1z}a)/3 \quad , \quad (12a)$$

$$c_1(\vec{k}_1) = (\sin k_{1x}a + \sin k_{1y}a + \sin k_{1z}a)/3 \quad , \quad (12b)$$

with the lattice constant a. If we denote by $T^{(\pm)}(\vec{k}_1)$ the solution to Eq. (8) with $V^{(\pm)}(\vec{k}_1, \vec{k})$ in place of $V(\vec{k}_1, \vec{k})$, we have

$$T(\vec{k}_1, \vec{k}) = T^{(+)}(\vec{k}_1) + T^{(-)}(\vec{k}_1) \quad , \quad (13)$$

and then we can easily obtain the solution as follows. As seen from the equation for $T^{(+)}(\vec{k}_1)$, this T matrix has the same symmetry as $B(\vec{k}_1, \vec{k})$ with respect to $\vec{k}_1$, leading to

$$T^{(+)}(\vec{k}_1) = UX(\vec{k};\omega) + U_1 a_1(\vec{k}_1) Y(\vec{k};\omega) \quad . \quad (14)$$

Here

$$X(\vec{k};\omega) = \left\{1 + U_1\left[B_2(\vec{k};\omega) - B_1(\vec{k};\omega)\cos\frac{ka}{2}\right]\right\}\Big/D(\vec{k};\omega) \ , \tag{15a}$$

$$Y(\vec{k};\omega) = \left\{\cos\frac{ka}{2} + U\left[B_0(\vec{k};\omega)\cos\frac{ka}{2} - B_1(\vec{k};\omega)\right]\right\}\Big/D(\vec{k};\omega) \ , \tag{15b}$$

$$D(\vec{k};\omega) = [1 + UB_0(\vec{k};\omega)][1 + U_1B_2(\vec{k};\omega)] - UU_1B_1^2(\vec{k};\omega) \ , \tag{15c}$$

with

$$B_l(\vec{k};\omega) = \sum_{\vec{k}'}B(\vec{k}',\vec{k})[a_1(\vec{k}')]^l \ . \tag{16}$$

As for $T^{(-)}(\vec{k}_1)$, it is seen that $T^{(-)}(\vec{k}')$ changes its sign for the transformation $\vec{k}' \rightarrow -\vec{k}'$, and is invariant for any interchange between k_x', k_y', and k_z'. By the use of this symmetry property, we have

$$T^{(-)}(\vec{k}_1) = U_1c_1(\vec{k}_1)\sin\left|\frac{ka}{2}\right|Z(\vec{k};\omega) \ , \tag{17}$$

where

$$Z(\vec{k};\omega) = 1/[1 + U_1C_2(\vec{k};\omega)] \ , \tag{18}$$

with

$$C_2(\vec{k};\omega) = \sum_{\vec{k}'}B(\vec{k}',\vec{k})[c_1(\vec{k}')]^2 \ . \tag{19}$$

By combining Eqs. (7), (13), (14), and (17), we obtain

$$\left.\begin{array}{c}T_c(\vec{k};\omega)\\T_{\text{ex}}(\vec{k};\omega)\end{array}\right\} = UX(\vec{k};\omega) + U_1\left[\cos\frac{ka}{2}Y(\vec{k};\omega) \pm \sin^2\frac{ka}{2}Z(\vec{k};\omega)\right] \ . \tag{20}$$

From Eqs. (5) and (20), the spectral function

$$A(\vec{k};\omega) = -\text{Im}\{2/[\omega + i\eta - \epsilon(\vec{k}) - M(\vec{k};\omega)]\} \tag{21}$$

is numerically calculated by taking $\epsilon(\vec{k}) = -a_1(\vec{k})W/2$, which is the s-band energy spectrum, with a width W, in the tight-binding approximation. The quasiparticle energy $\omega = E(\vec{k})$ is obtained from the maximum of $A(\vec{k};\omega)$ with respect to ω for a given $\vec{k}$. The degree of band narrowing, $\Delta W/W$, is defined by

$$\Delta W/W = 1 - [E(\vec{k}_m) - E(0)]/W$$

with $\vec{k}_m = (\pi/a)(1,1,1)$. The satellite binding energy E_b is defined by the position of satellite peak with the maximal density of states, which is measured from the Fermi level. The results are shown in Fig. 1. We can see from the figure the following facts. The contribution of interatomic interaction to the band narrowing $\Delta W/W$ is of the same order as or even larger than that in the Hubbard model. Next, the satellite binding energy E_b becomes smaller than that in the Hubbard model. This result comes from a larger shift of the Fermi level than in the Hubbard model, although the position of the satellite peak remains almost unchanged from that in the Hubbard model. As to the satellite intensity, we define the occupation number per atom by

$$n_b = (1/\pi N)\int d\omega \sum_{\vec{k}}A_b(\vec{k};\omega) \ ,$$

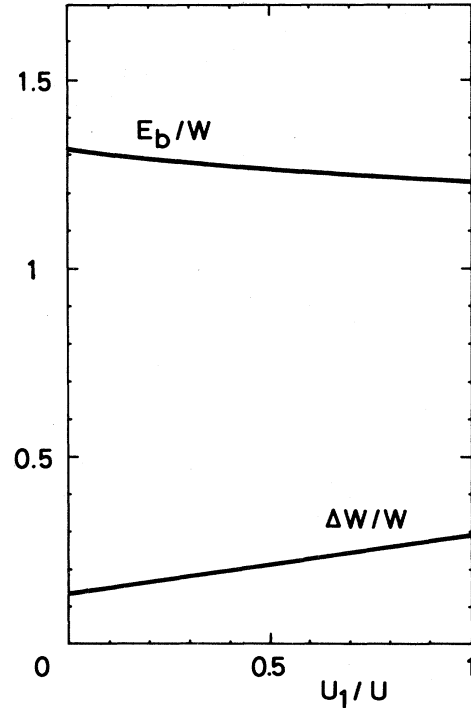where $A_b(\vec{k};\omega)$ represents the contribution of the

FIG. 1. Effects of interatomic interaction on the band narrowing $\Delta W/W$ and the satellite binding energy E_b. The values of parameters are chosen as $n = 0.6$ and $U/W = 0.4$. The results for $U_1/U = 0$ in the figure represent those in the Hubbard model.

satellite peak to $A(\vec{k};\omega)$. Then, in the case in which $U/W=0.4$, we have the result: $n_b=0.10, 0.13, 0.18$ for $U_1/U=0, 0.5, 1.0$, respectively. In addition to the above satellite, there exists another maximum of $A(\vec{k};\omega)$, peculiar to the interatomic interaction. It comes from a bound state with two holes located at neighboring sites. However, its binding energy measured from the band bottom is only about U_1/z_1, and so the intensity curve due to this bound state mixes with the main curve, without being observed as a satellite. From the above facts, it is concluded that the interatomic interaction improves the consistency problem of the band narrowing and satellite binding energy, which the T-matrix approximation calculation in the Hubbard model[3,5] cannot fulfill.

In this Brief Report, we took into account only the nearest-neighbor interaction in interatomic interactions and, in the present Wannier function scheme, there should be a more or less contribution from the more distant interactions[8] with U_ν ($\nu \geq 2$), although the magnitude of U_ν/z_ν may be smaller in comparison with U_1/z_1 because of screenings due to s and d electrons. From the physical meaning for the role of the nearest-neighbor interaction in the consistency problem, the effect of the more distant interactions on the present problem is the same as in the nearest-neighbor interaction. Hence, if we make the calculation for the nearest-neighbor interaction, by taking account of the realistic situation of Ni, then we can obtain information about the strengths of intra-atomic and interatomic interactions by the use of the observed values of E_b and $\Delta W/W$. We confined ourselves to the calculation up to the first order with respect to hole density, and, up to this order, there is no contribution from the electron-hole interaction. In a calculation beyond the first order, we must examine a contribution from the electron-hole interaction, on the basis of the existence of the interatomic interaction. However, from that mechanism on roles of the interatomic interaction, which has been discussed in this paper, the conclusion of its importance should remain unchanged.

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