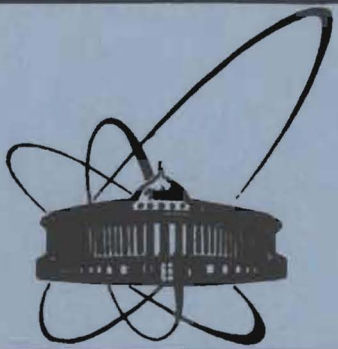


объединенный
институт
ядерных
исследований
дубна

E17-85-213

R.Taranko, A.L.Kuzemsky

CORRELATION EFFECTS IN TRANSITION METALS AND ALLOYS AND PHOTOELECTRON SPECTROSCOPY

Submitted to XV Annual International
Symposium on Electronic Structure
of Metals and Alloys (Dresden, April 15-19, 1985)

1985

1. Photoelectron spectroscopy and X-ray excited Auger spectroscopy[1] have proved to be a very powerful technique to study simple and transition metals, their compounds and alloys, magnetic semiconductors, mixed-valence compounds, etc. Electron spectroscopy has been particularly useful as a probe of the band structure of solids and as a test of theoretical developments in atomic structure and molecular orbital calculations.

Effective-one-electron theory has provided a basis for understanding a wide range of solid state phenomena, especially, for simple metals. The adequacy of the single-particle picture is based on the density-functional theory introduced by Hohenberg, Kohn and Sham. On the other hand, now it seems to be generally accepted that the transition metals provide a thorough test for many aspects of many-body (or correlation) effects in solids. But it is only relatively recently that the Auger and photoemission spectra of 3d transition metals have been investigated carefully[2-7]. After this there has been a great interest in interpretation of the obtained results in connection with the role of the correlation effects. As pointed in paper[3], nickel, from several points of view, is the case for which many-electron effects cannot be ignored. While photoemission reveals well-defined single-particle dispersions curves in nickel, they have a large energy width indicative of short quasi-particle lifetimes. Angle-resolved photoemission experiments providing direct observation of energy band dispersions in cuprum and nickel[8] revealed a few problems for nickel: presence of satellite, narrowing of the d-bandwidth and other discrepancies with standard one-electron-band calculations. The ferromagnetic spin splitting in nickel is particularly interesting because photoemission has made it directly observable, and the local-density approximation interprets it as a property of the homogeneous electron gas; in this case theory and experiment differ by more than a factor of two[3]. The additional information is contained in Auger spectra which provide the possibility for determining directly the local Coulomb interactions in materials[4-6]. While explaining these features the importance of the correlation effects within the unfilled d-band has been generally recognized[9-11].

Effect of the Coulomb correlation on energy bands in ferromagnetic nickel has been investigated recently in papers[10,11] within the degenerate Hubbard model by perturbation theory li-

mited to second order in U/W for T = 0 (U: Coulomb intra-atomic integral; W : band-width). A theory for the resonant 3d-band photoemission spectra in nickel has been developed in paper [7] on the basis of a hybridized s- and d-band model.

In this report we present a new self-consistent and unified approach to consideration of the correlation effects in transition metals like nickel. For this aim we use the novel irreducible two-time thermodynamic Green-function method developed by Kuzemsky [12] for interacting Fermi-systems. The IGF method completely describes the quasiparticle inelastic scattering processes in the many-body systems and finds quasiparticle spectra with damping in a very general way.

2. For the study of the correlation effects in transition metals we use the total Hamiltonian for the degenerate d-band which is given by the following expression:

$$\mathcal{H} = \sum_{ij} \sum_{\mu\nu\sigma} t_{ij}^{\mu\nu} a_{i\mu\sigma}^{+} a_{j\nu\sigma} + \frac{1}{2} \sum_{ij} \sum_{i'j'} \sum_{\mu\nu} \sum_{\mu'\nu'} \sum_{\sigma\sigma'} \langle i\mu\sigma, j\nu\sigma' | \frac{1}{r} | i'\mu'\sigma, j'\nu'\sigma' \rangle \times \tag{1}$$

$$\times a_{i\mu\sigma}^{+} a_{j\nu\sigma'}^{+} a_{i'\mu'\sigma'} a_{j'\nu'\sigma} .$$

One can use the basis orbitals of the canonical bands adapted to cubic symmetry of t_{2g} or e_g type. Those states are represented by $a_{i\nu\sigma}^{+}$ or $n_{i\nu\sigma} = a_{i\nu\sigma}^{+} a_{i\nu\sigma}$, where i is the site index, ν is the type of orbital and σ is the spin index.

We consider here, for example, only the following four contributions

$$\mathcal{H} = \sum_{ij} \sum_{\mu\nu\sigma} t_{ij}^{\mu\nu} a_{i\mu\sigma}^{+} a_{j\nu\sigma} + \frac{1}{2} \sum_{i\mu\sigma} U_{\mu\mu} n_{i\mu\sigma} n_{i\mu-\sigma} +$$

$$+ \frac{1}{2} \sum_{\substack{i\mu\mu' \\ \mu\neq\mu'}} \sum_{\substack{\sigma\sigma' \\ \sigma\neq\sigma'}} U_{\mu\mu'} n_{i\mu\sigma} n_{i\mu'\sigma'} - \frac{1}{2} \sum_{i\mu} \sum_{\substack{\mu'\sigma \\ \mu\neq\mu'}} J_{\mu\mu'} n_{i\mu\sigma} n_{i\mu'\sigma} . \tag{2}$$

It is reasonable to assume that

$$U_{\mu\mu} = U; \quad U_{\mu\mu'} = U'; \quad J_{\mu\mu'} = J. \tag{3}$$

The Hamiltonian (2) is specified by four parameters: bandwidth W and the three integrals U, U′ and J. In addition to the intrasite Coulomb interaction U, which is the only interaction present in the Hubbard model, our Hamiltonian (2) contains two more kinds of interactions, namely U′ and J, which have been taken as an example only to emphasize central ideas of the IGF-method description of the degenerate correlated

Fermi-system. Due to these two additional kinds of interactions crucial differences between the degenerate Hubbard model and generalized degenerate Hubbard model have been highlighted. Additional important interactions, for example, exchange interactions (c.f. [13]) can be included directly.

3. For the calculation of the electronic quasiparticle spectrum of the described model (2) and the electronic density of states let us consider the two-time thermodynamic one-electron Green function

$$G_{ij\sigma\sigma'}^{\mu\nu} = \langle\langle a_{i\mu\sigma} | a_{j\nu\sigma'}^{+} \rangle\rangle = -i\Theta(t) \langle [a_{i\mu\sigma}(t), a_{j\nu\sigma'}^{+}]_{+} \rangle . \tag{4}$$

Following the IGF method [12] the equation of motion for the GF(4) can be exactly transformed into a Dyson equation

$$\hat{G} = \hat{G}^{0} + \hat{G}^{0} \hat{M} \hat{G} \tag{5}$$

with an exact representation of the self-energy operator $\hat{M}$ which is represented by higher-order Green functions. For the model (2) we use here the mean-field renormalization differing from the simple Hartree-Fock renormalizations [14]. As a consequence of the suitable definition of the irreducible GF, the generalized mean-field GF $\hat{G}^{0}$ has the form

$$\sum_{i\gamma} \hat{H}_{ji}^{\mu\gamma} \cdot \hat{G}_{il}^{0\gamma\nu'} = \hat{I} \delta_{jl} \cdot \delta_{\mu\nu'} . \tag{6}$$

The self-energy operator $\hat{M}$ consists of four terms describing all possible electron inelastic processes. Because of a very complicated form it is not written explicitly. To find useful explicit expressions for $\hat{M}$, suitable approximations to evaluate the higher-order Green functions in $\hat{M}$ should be used.

4. To give a physical picture of the calculations to be published elsewhere in the complete form, we now consider what happens in two special limiting cases. First, let us consider the many-band Hubbard model. In this case U′ = J = 0.

In the pair approximation [12] for self-energy operator we obtain

$$M_{k n\sigma}^{+}(\omega) = \frac{U^2}{N^2} \sum_{\mu\nu\nu'} \sum_{\substack{n_1 n_2 n_3 \\ \vec{p}\vec{q}}} \Phi_{\mu\nu\nu'}^{n n_1 n_2 n_3}(\vec{k}, \vec{p}, \vec{q}) \, Q_{\sigma}^{n_1 n_2 n_3}(\omega, \vec{k}, \vec{p}, \vec{q}), \tag{7}$$

where

$$\Phi_{\mu\nu\nu'}^{n n_1 n_2 n_3}(\vec{k}, \vec{p}, \vec{q}) = a_{\mu}^{*n}(\vec{k}) \, a_{\nu}^{n}(\vec{k}) \, a_{\mu}^{n_1}(\vec{k}+\vec{p}) \, a_{\mu}^{*n_2}(\vec{p}+\vec{q}) \times$$

$$\times a_{\mu}^{n_3}(\vec{q}) \, a_{\nu}^{*n_1}(\vec{k}+\vec{p}) \, a_{\nu'}^{*n_3}(\vec{q}) \, a_{\nu'}^{n_2}(\vec{p}+\vec{q}), \tag{8}$$

$$Q_{\sigma}^{n_1 n_2 n_3}(\omega, \vec{k}, \vec{p}, \vec{q}) = (-\frac{1}{\pi})^3 \int_{-\infty}^{\infty} \frac{d\omega_1 d\omega_2 d\omega_3}{\omega + \omega_1 - \omega_2 - \omega_3} \times$$

$$\times \{n(\omega_1)[1 - n(\omega_2) - n(\omega_3)] + n(\omega_2)n(\omega_3)\} \times \tag{9}$$

$$\times \operatorname{Im} G_{p+q,-\sigma}^{n_2}(\omega_1) \cdot \operatorname{Im} G_{k+p,\sigma}^{n_1}(\omega_2) \cdot \operatorname{Im} G_{q,-\sigma}^{n_3}(\omega_3).$$

The $a_{\nu}^{n}(\vec{k})$ are coefficients of the atomic orbitals which form the Bloch basis function

$$\Psi_{\vec{k}n\sigma}(\vec{r}) = N^{-1/2} \sum_{\mu} a_{\mu}^{n}(\vec{k}) \sum_{i=1}^{N} \phi_{\mu\sigma}(\vec{r} - \vec{R}_i) e^{i\vec{k}\vec{R}_i}. \tag{10}$$

As we can see from the above expression for $M_{\vec{k}\sigma n}(\omega)$ (7), the obtained result is quite similar to that one derived in paper /10/.

To gain some more explicit physical insight into the problem, we consider in addition, the second limiting case by analysing the one-band Hubbard model. For the one-band case we find from Eq. (7)

$$M_{\vec{k}\sigma}(\omega) = \frac{U^2}{N^2} \sum_{pq} \int_{-\infty}^{\infty} \frac{d\omega_1 d\omega_2 d\omega_3}{\omega + \omega_1 - \omega_2 - \omega_3} \{n(\omega_1)[1 - n(\omega_2) - n(\omega_3)] + \tag{11}$$

$$+ n(\omega_1)n(\omega_3)\} g_{p+q,-\sigma}(\omega_1) g_{k+p,\sigma}(\omega_2) \cdot g_{q,-\sigma}(\omega_3),$$

where

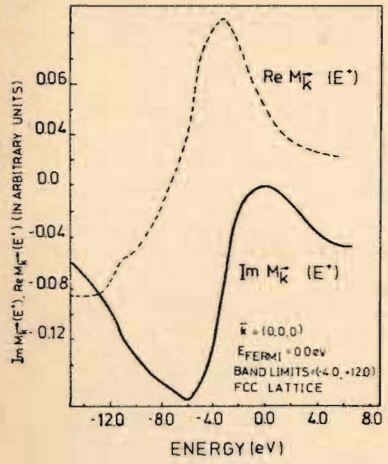
$$g_{k\sigma}(\omega) = -\frac{1}{\pi} \operatorname{Im} G_{k\sigma}(\omega + i\epsilon). \tag{12}$$

Equations (5) and (11) form a closed self-consistent system of equations for the one-electron Green function of the one-band Hubbard model. In principle, we may substitute into the r.h.s. of (11) any relevant initial Green function and solve it by iterations. To obtain explicit analytical expression, one can choose, for the first iteration step, the following simple one-pole expression for (12)

$$g_{\vec{k}\sigma}(\omega) = \delta(\omega - \epsilon(\vec{k}\sigma)). \tag{13}$$

Then we obtain

$$M_{\vec{k}\sigma}(\omega) = \frac{U^2}{N^2} \sum_{pq} \frac{n_{p+q,\sigma}(1 - n_{k+p,\sigma} - n_{q,-\sigma}) + n_{k+p,\sigma} n_{q,-\sigma}}{\omega - \epsilon(\vec{p} + \vec{q}, -\sigma) - \epsilon(\vec{k} + \vec{p}, \sigma) + \epsilon(\vec{q}, -\sigma)}. \tag{14}$$



Typical behaviour of the real and imaginary parts of self-energy for FCC metal.

For the sake of simplicity one can take

$$\epsilon(\vec{k}\sigma) = \epsilon^{HF}(\vec{k}\sigma) = \epsilon_{\vec{k}} + UN^{-1}n_{-\sigma}, \tag{15}$$

where

$$n = n(\epsilon_k) = [\exp(-\beta(\epsilon_k - \epsilon_f)) + 1]^{-1}. \tag{16}$$

In the Figure we show the typical behaviour of the $M_1 = \operatorname{Re} M$ and $M_2 = \operatorname{Im} M$, the real and imaginary parts of $M(\omega)$ calculated with the appropriate set of metal parameters for FCC lattice with

$$\epsilon_k = E_0 - 4t[\cos\frac{ak_x}{2}\cos\frac{ak_y}{2} + \cos\frac{ak_x}{2}\cos\frac{ak_z}{2} + \cos\frac{ak_y}{2}\cos\frac{ak_z}{2}]. \tag{17}$$

For the FCC-tight-binding electrons the band-width is given by

$$W = 16t. \tag{18}$$

The details of the calculations will be published elsewhere. Note that in X-ray photoemission spectra the photoelectron current is proportional to the imaginary part of the Fourier transform of the retarded Green function which can be explicitly calculated on the basis of the developed formalism.

5. In this report we have shown that the IGF method gives a unified and self-consistent formalism for the complete description of the quasiparticle electronic spectra including electron-electron inelastic scattering processes within the realistic many-band model of transition metals. The approach developed here can be extended to the description of the correlation effects in disordered transition metal alloys within the random Hubbard model. Our principal conclusion, therefore, is that the adequate description of electronic quasiparticle spectra in transition metals and their alloys experimentally observed by Auger and X-ray photoemission spectroscopy require a much stronger role of the many-body correlation effects than believed some years ago.

REFERENCES

1. Weightman P. Rep.Prog.Phys., 1982, 45, No.7, p.753.
2. Chazalviel J.N., Yafet Y. Phys.Rev., 1977, B15, No.2, p.1062.
3. Eastman D.E. et al. J.Appl.Phys., 1979, 50, No.11, p.7423.
4. Antonides E., Sawatzky G.A. Inst.Phys.Conf.Ser. 1979, No.39, Ch.2, p.134.
5. Sawatzky G.A., Lenselink A. Phys.Rev., 1980, B21, No.5, p.1790.
6. Drchal V., Kudrnovsky J. phys.stat.sol.(b), 1981, 108, No.2, p.683.
7. Jo T. et al. J.Phys.Soc.Jap., 1983, 52, No.7, p.2581.
8. Himpsel F.J. et al. J.Appl.Phys., 1981, 52, No.3, p.1658.
9. Kleinman L. et al. Phys.Rev., 1980, B22, No.2, p.1105.
10. Kleinman L., Mednick K. Phys.Rev., B24, No.12, p.6880.
11. Treglia G. et al. J.Phys.(Paris), 1982, 43, No.3, p.341.
12. Kuzemsky A.L. Theor.Math.Phys., 1978, 36, No.2, p.208.
13. Stollhoff G., Thalmeir P. Z.Phys., 1981, B43, No.1, p.13.
14. Mizia J. phys.stat.sol.(b), 1976, 74, No.2, p.461.

Received by Publishing Department
on March 26,1985.

COMMUNICATIONS, JINR RAPID COMMUNICATIONS, PREPRINTS,AND PROCEEDINGS OF THE CONFERENCES PUBLISHED BY THE JOINT INSTITUTE FOR NUCLEAR RESEARCH HAVE THE STATUS OF OFFICIAL PUBLICATIONS.

JINR Communication and Preprint references should contain:

- names and initials of authors,
- abbreviated name of the Institute (JINR) and publication index,
- location of publisher (Dubna),
- year of publication
- page number (if necessary).

For example:

1. Pervushin V.N. et al. JINR,P2-84-649, Dubna, 1984.

References to concrete articles, included into the Proceedings, should contain

- names and initials of authors,
- title of Proceedings,introduced by word "In:"
- abbreviated name of the Institute (JINR) and publication index,
- location of publisher (Dubna),
- year of publication,
- page number.

For example:

Kolpakov I.F. In: XI Intern. Symposium on Nuclear Electronics, JINR,D13-84-53, Dubna, 1984, p.26.

Savin I.A., Smirnov G.I. In: JINR Rapid Communications, N2-84,Dubna,1984,p.3.

В Объединенном институте ядерных исследований начал выходить сборник *"Краткие сообщения ОИЯИ"*. В нем будут помещаться статьи, содержащие оригинальные научные, научно-технические, методические и прикладные результаты, требующие срочной публикации. Будучи частью "Сообщений ОИЯИ", статьи, вошедшие в сборник, имеют, как и другие издания ОИЯИ, статус официальных публикаций.

Сборник "Краткие сообщения ОИЯИ" будет выходить регулярно.

The Joint Institute for Nuclear Research begins publishing a collection of papers entitled *JINR Rapid Communications* which is a section of the JINR Communications and is intended for the accelerated publication of important results on the following subjects:

Physics of elementary particles and atomic nuclei.
Theoretical physics.
Experimental techniques and methods.
Accelerators.
Cryogenics.
Computing mathematics and methods.
Solid state physics. Liquids.
Theory of condenced matter.
Applied researches.

Being a part of the JINR Communications, the articles of new collection like all other publications of the Joint Institute for Nuclear Research have the status of official publications.

JINR Rapid Communications will be issued regularly.

Таранко Р., Куземский А.Л. E17-85-213

Корреляционные эффекты в переходных металлах и сплавах и фотоэлектронная спектроскопия

Вычислен спектр электронных квазичастичных возбуждений и их затухание для реалистической многозонной модели переходного металла. Полученные результаты сравниваются с фотоэмиссионными измерениями. Проведены численные расчеты действительной и мнимой части массового оператора электронов.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1985

Taranko R., Kuzemsky A.L. E17-85-213

Correlation Effects in Transition Metals and Alloys and Photoelectron Spectroscopy

The electronic quasiparticle spectra and their damping for the many-band model of transition metals have been calculated in connection with the photoemission phenomena. The numerical calculations of the real and imaginary parts of self-energy operator have been done.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1985