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ELECTRON STRUCTURE AND PROPERTIES OF DISORDERED METALS *

Abstract: Energy spectra and densities of electron states of disordered metals (amorphous metals, liquid metals) have been determined using variation principle and Green's function methods. It was shown that taking into into account the higher order perturbation calculation and nonlocal effects considerably influences the density of electron states near Fermi energy.

1. Introduction

It is known that a lot of electronic properties of metals (electro- and thermal conductivity, heat capacity, entropy etc.) are determined by density of electron states [1]. Evidently, it causes the scientific interest in studying the energy spectrum and density of states of disordered metals. Apart from the above, these objects have some untraditional properties that are not proper for the crystalline metals.

Due to the disordered metals theory, the appearance of pseudo-slit [2,3] in the density of electron states is worth of careful investigation. Two different approaches to solving this problem are considered in this work. The first approach is based on the variation principle [4] using the one-parameter probe conduction electron wave function. The second one is based on use of the Green's function method and the standard perturbation theory for the model potential (MP) [3,5].

2. The variation calculation of electron structure of disordered metals

The calculation of energy spectrum and states density of liquid and amorphous metals based on variation principle [4] uses the following probe function:

$$\psi_k = \chi_k \psi_0, \quad \chi_k = \frac{1}{\sqrt{C_k}} e^{i\mathbf{kr}} \left[1 + \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\neq 0} u_k(\mathbf{q}) \rho_{\mathbf{q}} e^{i\mathbf{qr}} \right] \quad (1)$$

Here:

$$\rho_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{qR}_j}$$

Obviously, the condition for finding normalizing constant *Ck* is:

$$\left\langle \left| \chi_k \right|^2 \right\rangle = 1 \quad (2)$$

The brackets mean the averaging both by the configuration and by the main state. The variation function introduces the electron scattering on ions and it must satisfy the minimum condition of energy.

Applying the integrating in the parts for expression of average value of Hamiltonian for *k*-th state, expression for energy takes the following form:

$$E_k = E_0 + \frac{\hbar^2}{2m} \left\langle \left| \nabla \chi_k \right|^2 \right\rangle \quad (3)$$

After calculation of energy spectrum using the probe function we neglect all double summing members of equation and obtain:

$$E(k) = \frac{\hbar^2 k^2}{2m} + \frac{1}{NC_k} \sum_{\mathbf{q}\neq 0} u_k(\mathbf{q}) \left\{ \frac{\hbar^2}{2m} (\mathbf{k}+\mathbf{q})^2 S_{ei}(q) + 2u_k(\mathbf{q}) \frac{\hbar^2}{2m} \mathbf{k}(\mathbf{k}+\mathbf{q}) S(q) \right\} \quad (4)$$

and

$$C_k = 1 + \frac{1}{N} \sum_{\mathbf{q}\neq 0} u_k(\mathbf{q}) \left\{ 2S_{ei}(q) + u_k(\mathbf{q}) S(q) \right\} \quad (5)$$

The minimum condition of energy is satisfied by one-parameter probe function that takes such form:

$$u_k(q)=\frac{S_{ei}(q)\ [E(\mathbf{k})-\hbar^2\mathbf{k}(\mathbf{k}+\mathbf{q})/2m]}{S(q)\ \ [\hbar^2(\mathbf{k}+\mathbf{q})^2/2m-E(\mathbf{k})]}. \qquad (6)$$

Here: $S(q)=<\rho_{\mathbf{q}}\rho_{-\mathbf{q}}>$ – structure factor of the disordered metal,

$S_{ei}(q)$ – electron-ion structure factor:

$$S_{ei}(q)=\sqrt{N}<\rho_{\mathbf{q}}e^{i\mathbf{qr}}>=\frac{N}{V}\int e^{i\mathbf{qr}}\{F_{ei}(\mathbf{R})-1\}d\mathbf{R}, \qquad (7)$$

Here $F_{ei}(R)$ is the pair correlation function that describes electron-ion interaction in system. It is remarkable, if the shape-factor of screened MP is small, this value is equal to:

$$S_{ei}(q)=-\frac{2(N/\Omega)\omega(q)S(q)}{\hbar^2q^2/2m} \qquad (8)$$

After all these procedures we can integrate the equation for energy spectrum and get the following:

$$E(k)=\hbar^2(k^2+\Delta_k)/2m \qquad (9)$$

$$\Delta_k=\frac{\Omega}{8\pi^2NI_k}\int_0^\infty dqq^2\frac{S_{ei}^2(q)}{S(q)}\left\{q^2-\frac{q^4-\Delta_k^2}{4kq}\ln\left|\frac{q^2-\Delta_k+2kq}{q^2-\Delta_k-2kq}\right|+\frac{\Delta_k(q^2+\Delta_k)^2}{\left[(q^2-\Delta_k)^2-(2kq)^2\right]}\right\} \qquad (10)$$

$$I_k=1+\frac{\Omega}{8\pi^2N}\int_0^\infty dqq^2\frac{S_{ei}^2(q)}{S(q)}\left\{-3+\frac{q^2+\Delta_k}{4kq}\ln\left|\frac{q^2-\Delta_k+2kq}{q^2-\Delta_k-2kq}\right|+\frac{(q^2+\Delta_k)^2}{\left[(q^2-\Delta_k)^2-(2kq)^2\right]}\right\} \qquad (11)$$

The expression for density of states divided to density of states in free electron approximation is the following:

$$g(E)=\left[1+\frac{\Omega}{16\pi^2Nk^2I_k}\int_0^\infty dqq^2\frac{S_{ei}^2(q)}{S(q)}\left\{\frac{(q^2+\Delta_k)^2}{4kq}\ln\left|\frac{q^2-\Delta_k+2kq}{q^2-\Delta_k-2kq}\right|-\frac{(q^2-\Delta_k)(q^2+\Delta_k)^2}{\left[(q^2-\Delta_k)^2-(2kq)^2\right]}\right\}\right]^{-1}_{E=E(k)} \qquad (12)$$

Now, if we put Ik =1 and Δk=0, we get the result of the Rayleigh-Schrödinger perturbation theory:

$$E^{R-S}(k)=\frac{\hbar^2k^2}{2m}+\frac{V\hbar^2}{16\pi^2N}\int_0^\infty dqq^2\frac{S_{ei}^2(q)}{S(q)}\left\{q^2-\frac{q^3}{2k}\ln\left|\frac{q+2k}{q-2k}\right|\right\} \quad (13)$$

$$g^{R-S}(E)=\left[1+\frac{V\hbar^2}{16\pi^2Nk^2}\int_0^\infty q^2dq\frac{S_{ei}^2(q)}{S(q)}\left\{\frac{q^3}{4k}\ln\left|\frac{q+2k}{q-2k}\right|-\frac{q^4}{q^2-4k^2}\right\}\right]^{-1}_{E(k)=E} \quad (14)$$

And if we put Ik =1 and Δk=0 everywhere except the logarithm, we obtain the result of the Brillouin-Wigner perturbation theory:

$$E^{B-W}(k)=\frac{\hbar^2k^2}{2m}+\frac{V\hbar^2}{16\pi^2N}\int_0^\infty dqq^2\frac{S_{ei}^2(q)}{S(q)}\left\{q^2-\frac{q^3}{2k}\ln\left|\frac{q^2-\Delta_k+2kq}{q^2-\Delta_k-2kq}\right|\right\} \quad (15)$$

$$g^{B-W}(E)=\left[1+\frac{V\hbar^2}{16\pi^2Nk^2}\int_0^\infty q^2dq\frac{S_{ei}^2(q)}{S(q)}\left\{\frac{q^3}{4k}\ln\left|\frac{q^2-\Delta_k+2kq}{q^2-\Delta_k-2kq}\right|-\frac{q^4}{q^2-4k^2}\right\}\right]^{-1}_{E(k)=E} \quad (16)$$

3. The Green's function approach

Another approach to study electron structure of disordered metals is the use of the Green's functions and the perturbation theory [3,5].

Within this approach, energy spectrum of the conduction electrons of disordered metal can be determined as the pole of the Green's function averaged by the configuration of ions. The density of electron states is done by the imagine part of :

$$N(E)=\frac{1}{\pi}\sum_{\mathbf{k}}\mathrm{Im}\left\langle G(\mathbf{k},E-i\varepsilon)\right\rangle_{conf,\varepsilon\to 0}. \quad (17)$$

The averaged Green's function can be written as:

$$\left\langle G(\mathbf{k},E)\right\rangle_{conf}=\frac{1}{E-\frac{\hbar^2k^2}{2m}-\left\langle\Sigma(\mathbf{k},E)\right\rangle_{conf}} \quad (18)$$

Here $\langle\Sigma(k,E)\rangle_{conf}$ is the average value of the mass operator, that in the second term of perturbation theory takes such form:

$$\left\langle \Sigma(\mathbf{k},E)\right\rangle_{conf} = \left\langle \mathbf{k}\left|\mathcal{W}\right|\mathbf{k}\right\rangle + \frac{1}{N}\sum_{\mathbf{q}\neq 0} S(q)\frac{\left\langle \mathbf{k}\left|\mathcal{W}\right|\mathbf{k}+\mathbf{q}\right\rangle\left\langle \mathbf{k}+\mathbf{q}\left|\mathcal{W}\right|\mathbf{k}\right\rangle}{E-\dfrac{\hbar^2(\mathbf{k}+\mathbf{q})^2}{2m}} \tag{19}$$

Transforming the sum into the integral and using the angular averaging, we obtain the following expressions for real and imagine parts of the mass operator:

$$\mathrm{Im}\left\langle \Sigma(\mathbf{k},E)\right\rangle_{conf} = -\frac{\Omega_o m}{4\pi\hbar^2}\int_{\left|k-\sqrt{\frac{2mE}{\hbar^2}}\right|}^{k+\sqrt{\frac{2mE}{\hbar^2}}} \frac{q}{k}\,dqS(q)\left|\left\langle \mathbf{k}+\mathbf{q}\left|\mathcal{W}\right|\mathbf{k}\right\rangle\right|^2_{\theta,\varphi} \tag{20}$$

$$\mathrm{Re}\left\langle \Sigma(\mathbf{k},E)\right\rangle_{conf} = \left\langle \mathbf{k}\left|\mathcal{W}\right|\mathbf{k}\right\rangle_{\theta,\varphi} -$$

$$-\frac{\Omega_o m}{4\pi\hbar^2}\int_0^{\infty}\frac{q}{k}\,dqS(q)\left|\left\langle \mathbf{k}+\mathbf{q}\left|\mathcal{W}\right|\mathbf{k}\right\rangle\right|^2_{\theta,\varphi}\ln\left|\frac{E-\dfrac{\hbar^2(k+q)^2}{2m}}{E-\dfrac{\hbar^2(k-q)^2}{2m}}\right| \tag{21}$$

Significant, we can easily get the terms of higher order of perturbation theory .

The final result for density of electron states is:

$$N(E) = \frac{1}{\pi^3}\int_0^{\infty}\frac{\mathrm{Im}\left\langle \Sigma(\mathbf{k};E)\right\rangle_{conf}k^2\,dk}{\left[E-\hbar^2k^2/2m-\mathrm{Re}\left\langle \Sigma(\mathbf{k};E)\right\rangle_{conf}\right]^2+\left[\mathrm{Im}\left\langle \Sigma(\mathbf{k};E)\right\rangle_{conf}\right]^2} \tag{22}$$

The energy spectrum is determined in a similar way:

$$E(\mathbf{k})-E(0) = \frac{\hbar^2k^2}{2m}+\sum_i E^{(i)}(\mathbf{k}) \tag{23}$$

Here are the corrections of the standard perturbation theory introduced by the second part of the expression (23). Its calculation gives us:

$$E^{(1)}(\mathbf{k}) = \langle \mathbf{k}|W|\mathbf{k}\rangle - \langle 0|W|0\rangle \tag{24}$$

$$E^{(2)}(\mathbf{k}) = -\frac{2m\Omega_0}{\pi^2\hbar^2}\int_0^\infty q^2 dq S(q)\left\{\frac{\langle \mathbf{k}|W|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{\mathbf{k}^2-(\mathbf{k}+\mathbf{q})^2} - \frac{\langle 0|W|\mathbf{q}\rangle\langle \mathbf{q}|W|0\rangle}{\mathbf{q}^2}\right\} \tag{25}$$

The electron-ion interaction is described by nonlocal screened MP in the following form:

$$W(r) = -\frac{Z}{r} + \sum_{l=0}^{l_0} e^{\frac{r}{R_l}}\left(A_e + \frac{Z}{r}\right)P_e \tag{26}$$

Here P_e is the projection operator that select only the l-th partial wave function of the full electron wave function. A_e and R_l are the fitting parameters of MP determined in [7]. The sum includes only the electrons' valent states.

The structure factor is determined by the Ashcroft-Lekner theory based on hard-sphere approximation.

4. Results and discussion

We have done the computing of energy spectra and densities of electron states for series of nontransition metals. Also the influence of the MP nonlocal properties was investigated. Remarkable, the deflection of the density of states near the Fermi state is sensitive to the nonlocal properties contribution. It can be easily seen comparing the results obtained by the quasi-local Fermi sphere approximation and the result received by the nonlocal angular averaging. Now we can conclude, that contribution of both the nonlocality of MP and higher orders of perturbation theory play a crucial role in the formation of energy spectra and densities of electron states of the disordered metals. Data of the Fermi energies (E_f), densities of electron states on the Fermi level ($N(E_f)$) and the effective masses are shown in Table1.

Table 1
Comparison of the Fermi energies, densities of electron states on the Fermi level and the efective masses

Metal	Li	Na	K	Mg	Zn	Cd	Al	In	Tl
N(Ef), 1/erg	0.239	0.307	0.470	0.278	0.210	0.283	0.272	0.358	0.359
Ef	7.329	4.991	3.243	11.687	15.120	12.86	18.05	14.69	14.33
Ef MFE	7.244	4.889	3.192	10.693	14.242	11.34	17.08	12.87	12.54
Ef exp	7.6459	——	——	——	15.167	12.22	——	——	——
g(Ef)	1.08	1.016	0.995	0.986	0.997	0.899	0.987	0.984	0.971
m'/m	——	1.021	1.003	——	1.020	0.827	0.982	1.014	0.936

The comparison of the corresponding experimental and computed data allows to make conclusion of a good correlation of these values.

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Struktura elektronowa i właściwości metali nieuporządkowanych

Streszczenie: W pracy wyznaczono widma i gęstości stanów elektronów swobodnych dla metali nieuporządkowanych (metale amorficzne, ciekłe metale) stosując podejście wariacyjne oraz metody funkcji Greena. Pokazano, że uwzględnienie wyższych rzędów rachunku zaburzeń oraz efektów nielokalnych wpływa w istotny sposób na gęstość stanów w pobliżu energii Fermiego.