ON THE PARALLEL BANDS AND OPTICAL ABSORPTION OF POLYVALENT NON-TRANSITION METALS

О ПАРАЛЛЕЛЬНЫХ ЗОНАХ И ПОГЛОЩЕНИИ СВЕТА В МНОГОВАЛЕНТНЫХ МЕТАЛЛАХ НЕПЕРЕХОДНОЙ ГРУППЫ

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Several causes that can remove parallel band structure in polyvalent metals are examined with respect to their effect on optical absorption edge singularity.

By now it is generally accepted that the observed optical absorption edges in polyvalent non-transition metals are associated with parallel band structures. This state of knowledge began with the observation by Ehrenreich et al. [1] while interpreting optical reflectance data of aluminium. They noted that away from symmetry points two bands may be nearly parallel, and thus contribute appreciably to the joint density of states. Subsequently, Harrison [2] used a pseudopotential approach to identify the position of such edges (at photon energy $\hbar\omega = 2\,V_{ps}(\mathbf{g})$, where $V_{ps}(\mathbf{g})$ is the Fourier component of the pseudopotential) for all polyvalent metals which, in the case of aluminium at least, compare favourably with the experimental observations [1, 3].

On the basis of perfectly parallel band structures the contribution to conductivity $\sigma(\omega)$ from interband absorption is infinite at the edge, as demonstrated by Ashcroft and Sturm [4]. The singularity is removed only after including the collision broadening of the conduction electrons that undergo transitions. In fact, it is a customary procedure [5] that one chooses a resonable value of electron lifetime in analyzing the absorption data. In this way the optical experiment permits a concomittant measurement of the magnitude of the Fourier components of the pseudopotential and the (phenomenological) relaxation frequency. Moreover, for the stated functions the optical method is superior to its counterparts such as the de Haas van Alphen effect or the cyclotron resonance method in that it requires neither complicated mathematical deduction nor the use of low temperature. The latter feature furthermore allows the temperature variation of the physical quantities to be studied.

The above mentioned advantages associated with investigating the optical properties of polyvalent metals depend largely on the existence of parallel bands. A more or less cursory examination of the energy band curves presented in literature [6, 7] reveals that the bands are not strictly parallel. This is especially true near the intersections of the relevant Bragg planes and the Fermi surface, which are the pertinent regions of phase space available for absorption in the absence of collisions. It is thus of enormous interest to ascertain whether the observed broadening of the absorption peak should be ascribed to collisions or to deviation from parallel band structures. It is the purpose of the present note to give the result of the investigation or some possible causes that may remove perfect parallelism and their consequences on the optical absorption. These include a nonlocal effect, multiwave correction and

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symmetry consideration. As it will be shown later none of these are effective in removing the singularity at the absorption edge.

To make the following discussions meaningful, a brief indication of the origin of parallel bands is, at this point, in order. For this purpose it is necessary to recapitulate some principal results of the pseudopotential theory of metals [8, 9]. To begin, the energy of a valence state $|v\rangle$ may be obtained by solving a Schrödinger-like equation

$$(\mathbf{p}^2/2m + V_{ps})|v\rangle = \varepsilon|v\rangle . \tag{1}$$

Here $\mathbf{p}^2/2m$ is the one-electron kinetic energy operator and V_{ps} is the pseudopotential, which is the sum of the one electron potential $V(\mathbf{r})$ and a projection operator $\hat{P}_c$ (over the core state $|c\rangle$) modified by any linear operator $\hat{O}$ that has the periodic symmetry of the crystal, i.e.

$$V_{ps} = V(\mathbf{r}) + \hat{P}_c\hat{O} \tag{2}$$

with

$$\hat{P}_c = \sum_c |c\rangle\langle c| . \tag{3}$$

In general the pseudopotential is not local.

The valence state satisfies Bloch's theorem and may be expanded in terms of orthogonalized plane wave (OPW) states $|\mathbf{k}-\mathbf{g}\rangle$:

$$|v\rangle = \sum_g a_g|\mathbf{k}-\mathbf{g}\rangle , \tag{4}$$

the summation being over all the reciprocal lattice vectors $\mathbf{g}$. When Eq. (4) is substituted into Eq. (1), one obtains a set of simultaneous equations for a_g. The existence of non-trivial solutions requires that the following secular equation should be satisfied:

$$\begin{vmatrix} E_k - \varepsilon + \langle \mathbf{k}|V_{ps}|\mathbf{k}\rangle & \langle \mathbf{k}-\mathbf{g}_1|V_{ps}|\mathbf{k}\rangle & \langle \mathbf{k}-\mathbf{g}_2|V_{ps}|\mathbf{k}\rangle & \cdots \\ \langle \mathbf{k}|V_{ps}|\mathbf{k}-\mathbf{g}_1\rangle & E_{k-g_1} - \varepsilon + \langle \mathbf{k}-\mathbf{g}_1|V_{ps}|\mathbf{k}-\mathbf{g}_1\rangle & \langle \mathbf{k}-\mathbf{g}_2|V_{ps}|\mathbf{k}-\mathbf{g}_1\rangle & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0 \tag{5}$$

where

$$E_{k-g} = \hbar^2|\mathbf{k}-\mathbf{g}|^2/2m . \tag{6}$$

It is customary in band calculations (Harrison 1960, Ashcroft 1963) to assume that the pseudopotential is local so that $\langle \mathbf{k}-\mathbf{g}_1|V_{ps}|\mathbf{k}-\mathbf{g}_2\rangle = \langle \mathbf{k}-\mathbf{g}_2|V_{ps}|\mathbf{k}-\mathbf{g}_1\rangle = V_{ps}(\mathbf{g}_1-\mathbf{g}_2)$ where $V_{ps}(\mathbf{g}_1-\mathbf{g}_2)$ is the Fourier-component of the pseudopotential associated with the reciprocal lattice vector $(\mathbf{g}_1-\mathbf{g}_2)$. It is a further simplification to take only a finite number of states in solving Eq. (5) for the energy. One is then in the so-called several OPW approximation. In particular the two OPW method, with the locality assumption, is the usual nearly free electron (NFE) approximation which yields parallel bands at every Bragg plane, as shown in Ref. [4]. The stage is now set to begin examining the various corrections to this approximation.

Let us first of all incorporate nonlocality in the two OPW approximation. This is equivalent to solving the following secular equation,

$$\begin{vmatrix} E_k - E & \langle \mathbf{k}|V_{ps}|\mathbf{k}-\mathbf{g}\rangle \\ \langle \mathbf{k}-\mathbf{g}|V_{ps}|\mathbf{k}\rangle & E_{k-g} - E - \Delta_{k,g} \end{vmatrix} = 0 . \tag{7}$$

In obtaining Eq. (7) from Eg. (5) we have defined the zero of energy via

$$E = \varepsilon - \langle \mathbf{k}|V_{ps}|\mathbf{k}\rangle \tag{8}$$

and used the notation

$$\Delta_{k,g} \equiv \langle \mathbf{k}-\mathbf{g}|\hat{P}_c\hat{O}|\mathbf{k}-\mathbf{g}\rangle - \langle \mathbf{k}|\hat{P}_c\hat{O}|\mathbf{k}\rangle . \tag{9}$$

The solution to Eq. (7) is easily found to be

$$E_\pm = \frac{1}{2}(E_k - E_{k-g} - \Delta_{k,g}) \pm \{(E_k - E_{k-g} - \Delta_{k,g})^2 - 4[E_k(E_{k-g} - \Delta_{k,g}) - \langle \mathbf{k}|V_{ps}|\mathbf{k}-\mathbf{g}\rangle\langle \mathbf{k}-\mathbf{g}|V_{ps}|\mathbf{k}\rangle]\}^{1/2} .$$

The nonlocality has two effects. Firstly, the off-diagonal elements in Eq. (7) are now in general unequal. Secondly, it introduces an additional term $\Delta_{k,g}$ not present in the NFE approximation. The latter quantity can be evaluated using the Phillip–Kleinman form, in which $\hat{O} = \varepsilon_v - H$. Then

$$\Delta_{k,g} = \sum_{ck'} \langle \mathbf{k}-\mathbf{g}|ck'\rangle\langle ck'|\varepsilon_v - H|\mathbf{k}-\mathbf{g}\rangle - \langle \mathbf{k}|ck'\rangle\langle ck'|\varepsilon_v - H|\mathbf{k}\rangle \tag{11}$$

$$= \sum_c (\varepsilon_v - \varepsilon_c)[\langle \mathbf{k}-\mathbf{g}|ck\rangle\langle ck|\mathbf{k}-\mathbf{g}\rangle - \langle \mathbf{k}|ck\rangle\langle ck|\mathbf{k}\rangle] ,$$

where we made use of Bloch's theorem $\langle ck'|\mathbf{k}\rangle = \delta_{k',k}\langle ck|\mathbf{k}\rangle$, for the core state $|ck'\rangle$ and the valence state $|\mathbf{k}\rangle$. In the tight-binding approximation

$$|ck\rangle = N^{-1/2}\sum_c e^{i\mathbf{k}\cdot\mathbf{r}_c}\Phi_c^a(\mathbf{r}-\mathbf{r}_c) ,$$

where $\Phi_c^a(\mathbf{r})$ are atomic wave functions. Then it is easy to show that

$$\langle \mathbf{k}|ck\rangle = (N/\Omega)^{1/2}\Phi_c^a(\mathbf{k}) ,$$

where $\Phi_c^a(\mathbf{k})$ are atomic wave functions in the momentum space. Inserting the above into Eq. (11) one obtains

$$\Delta_{k,g} = \left(\frac{N}{\Omega}\right)\sum_c (\varepsilon_v - \varepsilon_c)[|\Phi_c^a(\mathbf{k}-\mathbf{g})|^2 - |\Phi_c^a(\mathbf{k})|^2] .$$

It will be noted that at the Bragg plane $\mathbf{k} = \mathbf{g}/2$, $\Delta_{k,g}$ vanishes identically and the off-diagonal elements that appear in Eq. (7) are the same. Eq. (10) in this case is precisely the same as the NFE result. Thus nonlocality has no effect in removing the singularity in the optical absorption.

The next consideration concerns the fact that the NFE approximation includes the effect of one Bragg plane at a time, when in fact each point in the reciprocal lattice space contributes to the energy at any one plane. Mathematically this is equivalent to the statement that the energy value is determined by solving Eq. (5) which is infinite in order. With the assumption of a local pseudopotential, Eq. (5) may be written as

$$\begin{vmatrix} E_k - E & V_{ps}(\mathbf{g}_1) & V_{ps}(\mathbf{g}_2) & \cdots \\ V_{ps}(\mathbf{g}_1) & E_{k-g_1} - E & V_{ps}(\mathbf{g}-\mathbf{g}_2) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0 . \tag{12}$$

Rather than finding the entire energy spectrum, it is more convenient to group as a class the elements in both the first two rows and the first two columns (which give rise to parallel bands) and treat the remaining elements in Eq. (12) as a perturbation on it. We may then use the perturbation theory developed by Löwdin [10] and convert Eq. (12) into

$$\begin{vmatrix} E_k - E & V_{ps}(\mathbf{g}_1) + \sum_{l \neq 1} \frac{V_{ps}(\mathbf{g}_l)\, V_{ps}(\mathbf{g}_l - \mathbf{g}_1)}{E - E_{k-g_l}} + \dots \\ V_{ps}(\mathbf{g}_1) + \sum_{l \neq 1} \frac{V_{ps}(\mathbf{g}_l)\, V_{ps}(\mathbf{g}_l - \mathbf{g}_1)}{E - E_{k-g_l}} + \dots & E_{k-g_1} - E \end{vmatrix} = 0 \qquad (13)$$

The quatities under the summation signs in Eq. (13) can be regarded as a multiwave correction. For order estimation, it suffices to carry out the first order interaction by letting $E = E_k$ in the denominators of the summands. In a rather different context Animalu [11] calculated this correction and found the maximum magnitude not to exceed 0.01 eV. In view of its small magnitude and weak **k**-dependence, it is apparent that the multiwave correction can only cause a slight shift in the pseudopotential component and, hence, in the position of the absorption peak, but does not effect the removal of the singularity. In this connection mention may be made of a similarly oriented approach [12], in which it is argued that multiwave correction can indeed eliminate the absorption singularity. This difference in conclusion can most likely be attributed to the overestimation in the expansion parameter employed in the above-cited reference.

There remains the discussion about the circumstance that the energy band curves presented in literature are generally not perfectly parallel. The state of this affair is due to the fact that these band calculations are performed at symmetry points or along symmetry lines, where the two OPW approximation is not adequate. However, in the optics of metals, only that part of phase space which is on the Fermi surface is relevant. Now the Fermi surface intersects the symmetry lines only at a finite number of points, hence the deviation from the two OPW approximation occurs only in a negligible region, and the NFE approximation must again be regarded as sufficiently accurate to be used here.

REFERENCES

[1] Ehrenreich, H., Phillipp, H. R., Segal, B.: Phys. Rev. *132* (1963), 1918.
[2] Harrison, W. A.: Phys. Rev. *147* (1966), 467.
[3] Bos, L. W., Lynnch, D. W.: Phys. Rev. Lett. *25* (1970), 156.
[4] Ashcroft, N. W., Sturm, K.: Phys. Rev. *B3* (1971), 1898.
[5] Dresselhaus, G., Dresselhaus, M. S., Beaglehole, D.: *Proc. Symp. on Density of States.* Washington, D. C. Nov. 1969.
[6] Harrison, W. A.: Phys. Rev. *118* (1960), 1182.
[7] Ashcroft, N. W.: Phil. Mag. *8* (1963), 2055.
[8] Harrison, W. A.: *Pseudopotential in the Theory of Metals.* Benjamin. New York 1966.
[9] Ashcroft, N. W.: *Proc. Michigan St. U. Summer School on Metal Physics* (1970).
[10] Löwdin, P.: J. Chem. Phys. *19* (1951), 1396.
[11] Animalu, A. O. E.: Phil. Mag. *11* (1965), 379.
[12] Udoyev, Yu. P.: Fiz. Met. Metallov (USSR) *35* (1973), 1152; Engl. transl. Phys. Met. Metallogr. *35* (1973), 28.

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