Optical Absorptions in Metal Sodium: The Temperature Dependence in the Liquid State

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The temperature dependence of optical absorptions in liquid Na is calculated. The electron energy values are obtained to second order in perturbation theory which are then used to determine the electron density of states. The density of states plots show some structure similar to those noted in the solid state. The optical conductivity in the liquid state is found to increase with the temperature as in the solid state. The present calculation for the optical conductivity gives a rather sharp peak around $\hbar\omega = 1.7$ eV. These results are in better agreement with the existing experimental results.

1. Introduction

The study of optical properties of alkali metals[1, 2] is of substantial theoretical and experimental interest. This is because, in one hand, the alkali metals are good candidates for nearly free electron system, on the other hand, they exhibit experimentally some strong absorption in the intermediate region $1 < \hbar\omega < 2$ eV followed by marked interband transitions above the interband threshold $\hbar\omega > 2$ eV. This is somewhat unusual, because the results obtained for other liquid metals thus far agree generally with the Drude theory which is based purely on the free electron model. Furthermore, most liquid metals do not show any absorption edges except in the far ultraviolet region where excitation of the core electron becomes possible. It might be pointed out, however, that the density of states of liquid metals are not necessarily free electron-like.

The experimental work of Mayer and Hietel[2] showed that the optical absorptions in liquid Na has two sharp peaks, one relatively strong peak at $\hbar\omega = 1.65$ eV and the other interband transition peak at $\hbar\omega = 3.2$ eV. This result is rather new and important, since the metals upon melting are expected to lose their periodic lattice, and the concept of the Bloch theorem and sharp Brillouin zone boundaries have no validity[3]; this should be especially true for simple metals[4]. Although experimentally it is extremely difficult[5] to measure any optical absorptions in such a low energy region, the occurrence of the above peak might be real, if some of the solid state characteristics are retained in the liquid state (see, for example, solid Na at 20 °C). The sharpness of such peaks will of course increase with temperature. On the theoretical side, the series of publications made by Faber[6–8], more importantly the review article on optical properties in his excellent book on liquid metals, seem to suggest that the optical absorptions in liquid Na should be free electron-like. Smith[4] has calculated the optical absorption of liquid Na at 100 °C and obtained a smooth curve for the optical conductivity between the photon energy $1.5\ \text{eV} < \hbar\omega < 6$ eV.

We find from the foregoing remarks that there are some unanswered questions in the study of optical absorptions of liquid Na. The purpose of this paper is to calculate the temperature dependence of the optical absorptions of liquid Na, using the pseudopotential theory of Smith[4] and more accurate experimental data for atomic structure. This sort of investigation has not been done, and is, therefore, quite worthwhile for two clear reasons. One is to recheck, whether the peak observed by Mayer and Hietel[2] at $\hbar\omega = 1.65$ eV is indeed real, and second is to compare the temperature dependence of optical conductivity in the liquid state with that in the corresponding solid state. Hopefully, the latter point will show the gradual effect of the change from the nearly free electron behavior to a free electron behavior in liquid Na. We shall mainly be interested here in (i) the exact calculation of the density of states[9, 10], (ii) the comparison between the theoretical results to be obtained and the available experimental values, and (iii) finding out the relationship, if there is any, between the optical absorptions in the solid and liquid Na. The format of our paper will be as follows. In Section 2 we shall review the

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theory relevant to this investigation. In Section 3 we shall present our results. Finally, in Section 4 we will describe the important conclusions.

2. Theoretical Considerations

For the sake of brevity, we shall briefly outline the Smith[4] theory to be used in this paper and introduce some modifications in our approach.

For the calculation of the optical properties of any solid or liquid metals, one is most certainly concerned with the imaginary part of the dielectric constant ε_2. The optical conductivity for a crystalline solid can be determined using the Kubo[11] and Greenwood[12] formula

$$\sigma(\omega) = \frac{\omega}{4\pi}\varepsilon_2 = \frac{2\pi e^2 \hbar^2}{m^2 \omega} \sum_{k' k} \mathrm{f}_{k'}(1-\mathrm{f}_k) \cdot |D(\hbar\omega_{kk'}, \hbar\omega)|^2 \times \delta(\hbar\omega_{kk'} - \hbar\omega), \qquad (1)$$

where $f_{k'}$ and f_k are the Fermi-Dirac distribution functions and $D(\hbar\omega_{kk'}, \hbar\omega)$ is the oscillator strength or the optical matrix element,

$$|D(\hbar\omega_{kk'}, \hbar\omega)|^2 = \left| \int \psi_{kk'}(\hbar\omega) \frac{\partial\psi}{\partial x}(\hbar\omega)\, \mathrm{d}\Omega \right|^2. \qquad (2)$$

Here k and k' denote the occupied and unoccupied bands respectively, and the integration should be carried over the Wigner-Seitz cell. The above form should be applicable[13] to liquid state as well, noting the difference between the solid and liquid in that there is no special anisotropy introduced by the momentum condition $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{q}$. Furthermore, the δ-function should have to be replaced by some other appropriate function. By replacing the summation, it is easy to obtain an analogous formula for liquid metals

$$\sigma(\omega) = \frac{2\pi e^2 \hbar^2}{\Omega m^2 \omega} \int g(E)\, g(E + \hbar\omega) \cdot |D(E, E + \hbar\omega)|^2\, \mathrm{d}E. \qquad (3)$$

The limits of the integrations range between $E_F + \Delta E$ and $E_F - \hbar\omega$, where ΔE is a small change in energy so that can be determined and we shall discuss about it later. There are however, two major problems that need to be worked out. One is the evaluation of the oscillator strength and the other is an exact calculation of the density of states. We first discuss the former one.

Smith[4] has essentially extended the idea of Faber[6] and developed an approach to obtain ε_2. Under some reasonable approximations, i. e., neglecting the interference term (the second term in Eq. (8) of Ref.[4]), since its contribution is expected to be less than 5% of the dominating term, the oscillator strength turns out to be

$$|D(E_a, E_b)|^2 = \frac{1}{3} \frac{\Omega^3 k_F{}^3}{2\pi^2} \frac{1}{(\pi\Omega E_F)^2} \cdot \int \varkappa^4 \varrho(E_a, \varkappa)\, \varrho(E_b, \varkappa) \left[g(E_a)\, g(E_b)\right]^{-1} \mathrm{d}\varkappa, \qquad (4)$$

where the spectral distribution functions can be written as

$$\varrho(\varepsilon, \varkappa) = \frac{\Gamma/E_F}{(\varkappa^2 - \varepsilon - A/E_F)^2 + (\Gamma/E_F)^2}. \qquad (5)$$

The two functions A and Γ contain the details of the liquid structure and the form factors of the chosen electron-ion potentials. These functions are rather complicated and possess logarithmic singularities as can be seen from the following forms:

$$A(\varepsilon, \varkappa) = \frac{3 E_F}{2\varkappa} \int_0^\infty \left| \frac{u(q)}{E_F} \right|^2 \cdot I(q)\, q\, \mathrm{d}q \ln \left| \frac{\varepsilon - (\varkappa + 2q)^2}{\varepsilon - (\varkappa - 2q)^2} \right| \qquad (6)$$

and

$$\Gamma(\varepsilon, \varkappa) = \frac{3\pi E_F}{2\varkappa} \int_0^\infty \left| \frac{u(q)}{E_F} \right|^2 I(q)\, q\, \mathrm{d}q\, \Theta(x), \qquad (7)$$

where

$$x = [E - (\varkappa^2 + 4q^2)]/4\varkappa q. \qquad (8)$$

The function $\Theta(x) = 1$ for $-1 < x < 1$, otherwise it is zero everywhere. We shall see later the significance of the various functions as described above. In the above equations, the symbols have the same meaning as in Smith[4].

First, it is important to be able to obtain the actual density of states in a liquid metal. We should not take it for granted to be a simple free electron-like. To the knowledge of this author, this sort of calculation has not been done from the first principle point of view, while studying the optical properties of Na. Secondly, what is the oscillator strength appropriate to the liquid metal under study? This is the term of crucial importance as it should contain the effect of temperature and density fluctuations in the liquid state[9, 10]. Additionally, the final shape and structure of the optical absorption curve will strongly depend on how we extract the oscillator strength. The effect of temperature will be introduced through the interference function $I(q)$.

The central quantity of our immediate interest is the density of states. The general expression for the density of states is

$$g(E) = \frac{2\,\Omega_0}{(2\,\pi)^3} \int \frac{\mathrm{d}S_k}{|\nabla_k E|}\,, \tag{9}$$

which for liquid metals with spherical Fermi surface reduces to

$$g(E)/g_0(E) = 2\,k\,(\partial E/\partial k)^{-1}\,. \tag{10}$$

g_0 is the free electron density of states. By expanding[14] the electron energy to second order in perturbation theory, we obtain

$$E(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2\,m} + \langle \boldsymbol{k} | U | \boldsymbol{k} \rangle + \sum_q{}' \cdot \frac{\langle \boldsymbol{k}+\boldsymbol{q} | U | \boldsymbol{k} \rangle \langle \boldsymbol{k} | U | \boldsymbol{k}+\boldsymbol{q} \rangle}{(\hbar^2/2\,m)\,(|\boldsymbol{k}|^2 - |\boldsymbol{k}+\boldsymbol{q}|^2)}\,. \tag{11}$$

The prime over the summation excludes the term with $q = 0$. It is generally argued that a calculation beyond the second order energy is unnecessary and it seldom justifies the computer time required.

In the spirit of 'rigid ion model' approximation the matrix elements may be written as

$$\langle \boldsymbol{k}+\boldsymbol{q} | U | \boldsymbol{k} \rangle = S(\boldsymbol{q})\,\langle \boldsymbol{k}+\boldsymbol{q} | u | \boldsymbol{k} \rangle \tag{12}$$

where

$$\langle \boldsymbol{k}+\boldsymbol{q} | u | \boldsymbol{k} \rangle = \Omega_0^{-1} \int \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{r}\}\, u(\boldsymbol{r})\,\mathrm{d}^3 r\,, \tag{13}$$

$$S(\boldsymbol{q}) = N^{-1} \sum_j \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{r}_j\}\,, \tag{14}$$

and N is the number of ions in the volume Ω_0. Here $S(\boldsymbol{q})$ is the usual structure factor, depending only on the ion position, and $\langle \boldsymbol{k}+\boldsymbol{q} | u | \boldsymbol{k} \rangle$ is the form factor, which depends only on the ion potential. Using this type of form factor, the first order energy $E^{(1)}$ may be expressed as

$$E^{(1)} = \lim_{q\to 0} N^{-1} \sum_\nu \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{R}_\nu\}\, u(q) = u(0) \tag{15}$$

where $u(0)$ has been normalized to include the dielectric constant factor. The second order energy $E^{(2)}$ can be obtained in the same manner,

$$E^{(2)} = \sum_{\boldsymbol{k}'}{}' \frac{I(|\boldsymbol{k}-\boldsymbol{k}'|)\,u^2(|\boldsymbol{k}-\boldsymbol{k}'|)}{(k^2 - k'^2)} \tag{16}$$

where

$$I(q) = N^{-1} \langle \sum_{\nu,\omega} \exp\{i\,\boldsymbol{k}\cdot(\boldsymbol{R}_\nu - \boldsymbol{R}_\omega)\} \rangle\,, \tag{17}$$

is the interference function. A more comprehensive form for $E^{(2)}$ can be found elsewhere[14, 15]. It should be pointed out, however, that a numerical differentiation of $E^{(2)}$ is no longer necessary, since an exact form of the energy derivative can easily be derived:

$$\frac{\partial E^{(2)}}{\partial k} = -\frac{E^{(2)}(k)}{k} - \frac{\Omega_0}{2\,\pi^2 k}\,\mathcal{P}_0 \int_0^\infty \mathrm{d}q\, \frac{q\,F(q)}{q^2 - 4\,k^2} \tag{18}$$

where, $F(q) = q\,I(q)\,u^2(q)$. A method for calculation of the principal value integration has been suggested earlier[14]. The above equation must also satisfy the requirement $(\partial E^{(2)}/\partial k)_{k=0} = 0$. The functions A and Γ depend on the second order energy through Eq. (11) because $\varepsilon = E(k)/E_F$. Since, the first order energy $E^{(1)}$ does not depend on k, we may write our density of states as

$$g(E)/g_0(E) = \left[1 + \frac{1}{2\,k}\left(\frac{\partial E^{(2)}}{\partial k}\right)\right]^{-1}. \tag{19}$$

3. Results and Discussions

In this section we shall discuss the various results obtained with the pseudopotential[16] and temperature dependent interference functions. We have used the most recent data[17] for Na at two temperatures, 100 and 200 °C. We also computed[18] the hard sphere interference functions at these two temperatures to compare our results with those of Smith[4].

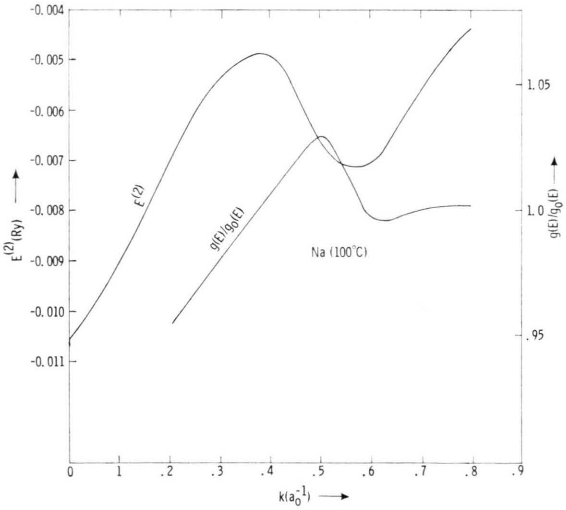

Fig. 1. The plots of the second order correction to energy $E^{(2)}$ and the density of states $g(E)/g_0(E)$ for liquid Na near the melting temperature.

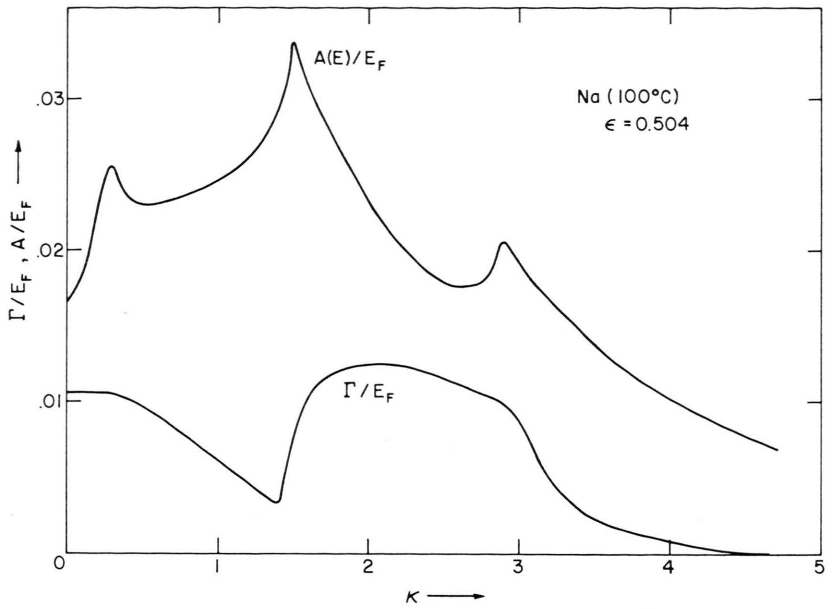

Fig. 2 a. The plots of the two functions Γ/E_F and A/E_F at 100 °C. The experimental $I(q)$ data were used.

The calculated energy spectrum $E^{(2)}$ and the density of states $g(E)/g_0(E)$ are shown in Fig. 1 for one temperature, 100 °C. The $E^{(2)}$ curve has a kink at $k \cong 0.40\, a_0^{-1}$ and a minimum at $k \cong 0.57\, a_0^{-1}$. Similar results were found for liquid Li by Shaw[19]. The $g(E)/g_0(E)$ curve likewise shows some structure indicating a marked deviation from the simple free electron-like behavior at this temperature. With increasing temperature, of course, these sharp features gradually smear out and the curve merges with the free electron-like plot. This type of behavior has been noted earlier[14] for several other liquid metals as well.

In Figures 2 a and 2 b we illustrate the trend of the functions A and Γ plotted as functions of $\varkappa = k/k_F$, k_F being the appropriate Fermi momentum. We have used the free electron value for E_F, although in reality it is a little different from the free electron value as has been discussed by Smith[4]. As can be seen the effect of temperature is to dampen

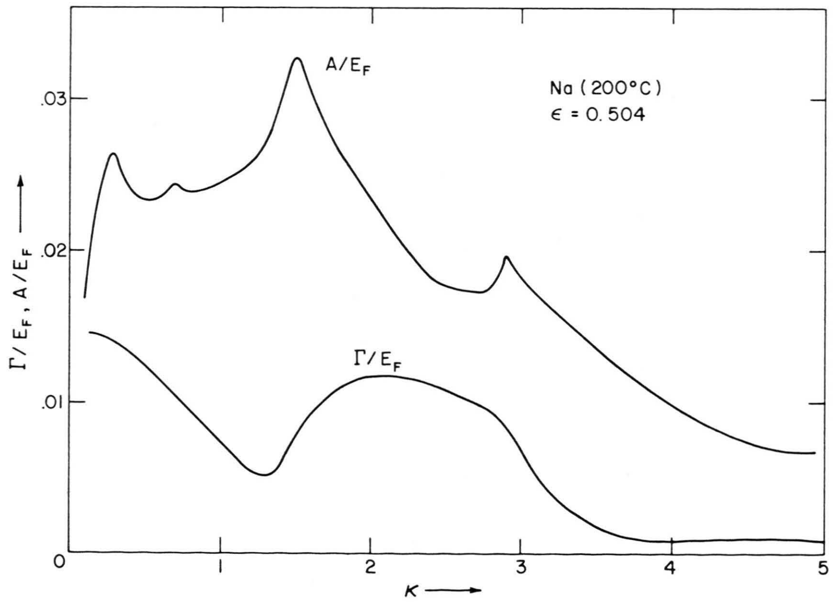

Fig. 2 b. The plots of the two functions Γ/E_F and A/E_F at 200 °C, The experimental $I(q)$ data were used.

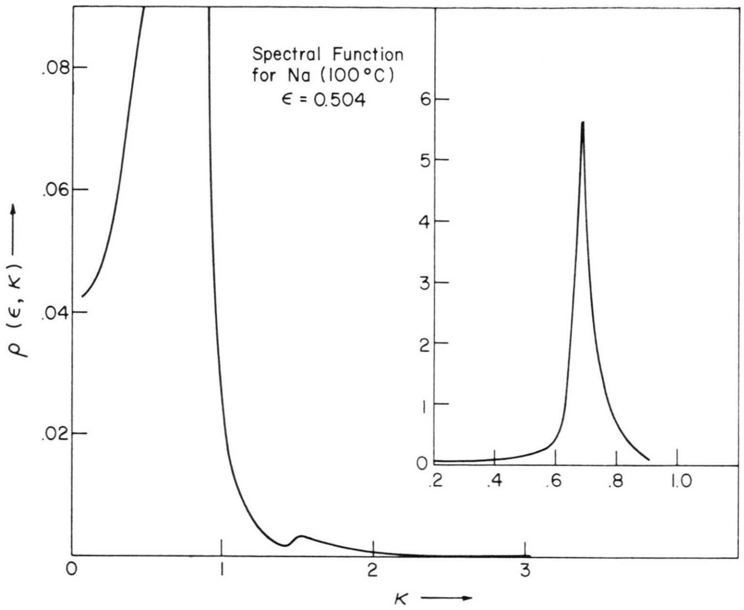

Fig. 3 a. The plots of the spectral function ϱ at 100 °C obtained with experimental $I(q)$.

both the functions A and Γ. The oscillations in these two functions diminish, but the broadening of the peaks becomes more extensive with temperature. These changes could be attributed to the changes in atomic interference functions $I(q)$ of Na. The increase of temperature, in general, causes a lowering of the first peak maximum accompanied by decreasing of the shallowness of the first minimum in $I(q)$. For Na it is particularly important because the Fermi diameter $2\,k_F = 0.95\,a_0^{-1}$ falls closely to the first peak maximum of $I(q)$. Both the functions A and Γ sharply fall to zero after $\varkappa = 3.0$, Γ falling more rapidly than A. This would then determine a limit for the calculation of the spectral function ϱ which should die down to zero after about $\varkappa \cong 3.0$. From the practical standpoint, it is advantageous since one can cut off the limit of integration from infinity to a practical value 3.0. The spectral func-

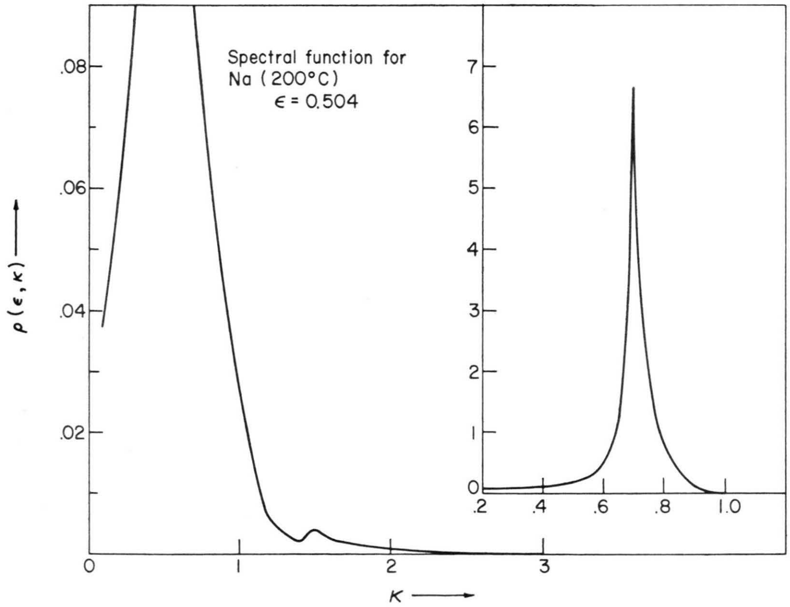

Fig. 3 b. The plots of the spectral function ϱ at 200 °C obtained with experimental $I(q)$.

tion ϱ were obtained for several values of $\varepsilon = E_a/E_F$, but we have plotted a typical pattern of ϱ for $\varepsilon = 0.504$ at two temperatures. There is a very strong peak in this function at $\varkappa \cong 0.70$ for 100 °C, which moves to $\varkappa \cong 0.72$ for 200 °C accompanied by some increase in the peak height.

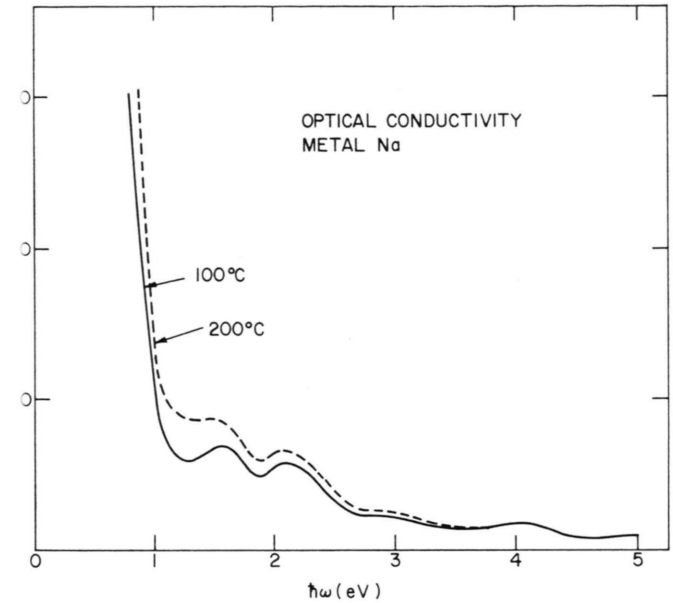

Fig. 4. The plots of the calculated optical conductivity at 100 and 200 °C obtained with experimental interference functions of Reference 17. The hard sphere results are not shown here as they were less satisfactory compared to the present results.

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ and the optical conductivity $\sigma(\omega)$ are directly obtained from Eqs. (1) and (3) respectively. The plots of $\sigma(\omega)$ are shown in Figure 4. Once again, the effect of temperature is clearly visible. For the sake of better understanding of the various results, we can compare the three sets of $\sigma(\omega)$ near the melting temperature 98 °C. The extent of correctness of the experimental $I(q)$ used was rechecked by introducing the Debye-Waller--corrected-hard-sphere $I(q)$. The theoretical $\sigma(\omega)$ curves obtained with experimental $I(q)$ and model $I(q)$ are in good agreement within the first order approximation; these results are closer to the experimental values than previous investigations[4]. The sharpness of the plots in the infrared region and the slow fall in the ultraviolet region are seen quite markedly. The evidence of two peaks, one at $\hbar\omega = 2.1$ eV and the other at $\hbar\omega = 1.7$ eV, together with some structure in the ultraviolet region brings up some important questions. We shall attempt to explain these features in what follows next.

As pointed out before in the introduction Mayer and Hietel[2] experimentally observed two peaks, one at $\hbar\omega = 1.65$ eV and other at $\hbar\omega = 3.2$ eV. The works of Smith[4] and Animalu[13] did not reveal any such structure. In other words, these calculations favor a simple Drude-type formula rather strongly for liquid Na. However, the present calculation shows the total characteristics of the observed pattern, and it does differ from the earlier investigations in two respects. The first one is the second order perturbation calculation of the energy term in liquid Na, which shows some positive evidence of the presence of a few solid state characteristics of the density of states into the liquid after melting of Na at 98 °C. It should be emphasized that both the density of states and the optical conductivity behave quite analogously with regard to retaining some of their crystalline properties even after melting. Nonetheless, above and away from the melting temperature the optical conductivity is seemingly influenced by the Drude-type formula. The second one is the temperature dependence of $\sigma(\omega)$ itself. The present calculation for liquid Na shows an increase of $\sigma(\omega)$ with temperature. A similar result was measured for solid Na as well by Mayer and Hietel[2] which was recently theoretically tested by Miskovsky and Cutler[20]. The latter have studied the phonon aided optical absorption in the alkali metals and obtained the temperature dependence of $\sigma(\omega)$ from OPW calculation.

The second peak in $\sigma(\omega)$ at $\hbar\omega = 2.1$ eV is due to the interband transition and is well understood for both solid and liquid metals. It is believed[6, 7] that the absorptions that are associated with the excitation of core electrons below the Fermi level can persist even after melting, but that associated with the band gaps should not occur in liquid metals. The first peak at $\hbar\omega = 1.7$ eV might be the consequence of other mechanism, such as the electron-phonon interaction. To establish this point unequivocally it will be necessary to make a detailed calculation[20, 21] for this mechanism including all other second order important contributions.

4. Conclusions

In summary, the present investigation shows some new results not reported earlier. The density of states plot has some structures which are attributed to the remnants of some solid state characteristics. These calculations indicate that there are two resonance peaks in the optical absorption spectrum for liquid Na. These peaks were first observed in the experimental work of Mayer and Hietel[2]. It is further demonstrated that the temperature dependent interference functions predict correctly the expected temperature dependence of the optical absorptions in liquid Na in that $\sigma(\omega)$ increases with temperature. The appearance of the resonance peak at $\hbar\,\omega = 1.70$ eV in this work results from the characteristic pattern of the density of states and the final shapes of the two important functions A and Γ.

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