Energy Loss Spectra and Plasmon Dispersions in Alkali Metals: Negative Plasmon Dispersion in Cs

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We present *ab initio* calculations of the energy loss spectra and plasmon dispersions of the alkali metals Na, K, Rb, and Cs within the random phase approximation, including band structure effects and core electrons as well as local field effects, due to inhomogeneity in the induced charge density. Band structure effects are found to cause a negative dispersion in Cs.

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The plasmon dispersions of the heavy alkali metals, Rb and Cs, have been a subject of controversy for many years. The electronic properties of the alkali metals have been thought to be well represented by those of an electron gas. Within the random phase approximation (RPA) [1], the plasmon dispersion of an electron gas for small momentum transfer $\mathbf{q}$ is positive and quadratic in $\mathbf{q}$. The light alkali metals, Li, Na, and K, are in agreement with this prediction, although the predicted value of the q^2 coefficient in the case of K deviates significantly from experiment [2]. However, anomalous behavior is observed in Rb and Cs [2]. Rb is the first element that shows no dispersion for small q, and in Cs, the dispersion becomes *negative*. Some workers [2–6] claim that the RPA, which is exact in the limit of high electron density ($r_s \ll 1$), fails for this system because its density is very low ($r_s = 5.6$). Band structure effects are regarded to be small and the negative dispersion is assigned to a large short-range exchange and correlation (SXC), which is not included in the RPA.

A different viewpoint would be to assign the negative dispersion to band structure effects. When going from Na to Cs, the d band approaches the Fermi level and becomes simultaneously narrower. Since the plasmon energies lie in these interband transitions, the d band can be responsible for the anomalous behavior in Rb and Cs as also suggested by Taut and Sturm [5]. However, no realistic calculations have been performed so far to substantiate this argument. The RPA works reasonably well in Na with $r_s = 3.9$, a value which is already outside the limits of the RPA. Even in K with $r_s = 4.8$, the RPA still gives sensible results. It seems unlikely that the RPA suffers a serious breakdown in Cs with $r_s = 5.6$, which is only 15% larger than the value for K. The band structure of Na is in good agreement with the free-electron bands, whereas the band structures of K, Rb, and Cs show increasing deviations from the free-electron bands. This suggests that band structure effects can be important in determining the plasmon dispersions.

In this Letter, we investigate to what extent the band structure and core electrons influence the plasmon dispersion. For this reason, we have performed *ab initio* calculations of the energy loss spectra for the alkali metals in the series Na to Cs, for several $\mathbf{q}$ values along the (1 1 0) direction, within the RPA. The calculations take fully into account the band structure, local field effects [7–9], as well as core excitations.

The energy loss spectrum, $S(\mathbf{q},\omega)$, is given by the imaginary part of the inverse microscopic dielectric function [1,10]:

$$S(\mathbf{q},\omega) = -\mathrm{Im}\,\epsilon^{-1}(\mathbf{q},\omega), \tag{1}$$

where $\epsilon^{-1}(\mathbf{q},\omega)$ is the Fourier transform of $\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega)$. In most calculations, $S(\mathbf{q},\omega)$ is approximated by $\mathrm{Im}\,1/\epsilon(\mathbf{q},\omega)$. This is exact in the homogeneous limit, but neglects the local field effects, which arise from the inhomogeneity of the *induced* density $\delta\rho$, when the system is perturbed by an external field V^{ext}. However, inhomogeneity in the *unperturbed* charge density itself does not necessarily lead to large local field effects [11]. Within the self-consistent Hartree approximation, the dielectric function is given by $\epsilon = 1 - vP^0$, where v is the bare Coulomb potential and P^0 is the propagator for the density-density response function. In the RPA, the propagator P^0 is approximated by the response function of a noninteracting system [12]. Calculating P^0 in real space is not feasible for solids. The usual approach is then to introduce a Bloch basis $B_{\mathbf{q}i}$, in which P^0, v, and ϵ are expanded. The main computational task is the calculation of $P^0_{ij}(\mathbf{q},\omega)$:

$$\begin{aligned} P^0_{ij}(\mathbf{q},\omega) = \sum_{\mathbf{k}} \sum_{n}^{\mathrm{occ}} \sum_{n'}^{\mathrm{unocc}} &\langle B_{\mathbf{q}i}\psi_{\mathbf{k}n}|\psi_{\mathbf{k}+\mathbf{q}n'}\rangle\langle\psi_{\mathbf{k}+\mathbf{q}n'}|\psi_{\mathbf{k}n}B_{\mathbf{q}j}\rangle \\ &\times \Big[(\omega - \epsilon_{\mathbf{k}+\mathbf{q}n'} + \epsilon_{\mathbf{k}n} + i\delta)^{-1} \\ &\qquad - (\delta + \epsilon_{\mathbf{k}+\mathbf{q}n'} - \epsilon_{\mathbf{k}n} - i\delta)^{-1}\Big], \end{aligned} \tag{2}$$

where $\{\psi_{\mathbf{k}n}, \epsilon_{\mathbf{k}n}\}$ are the LDA Bloch states and the corresponding eigenvalues, respectively. We have developed a scheme using a localized product basis [9], based on the LMTO method [13]. The number of basis functions used is 123, in contrast to the pseudopotential method which would require a very large number of plane waves. The number of $\mathbf{k}$ points in the entire zone is 512, which corresponds to 29 points in the irreducible zone. The delta function in the imaginary part of P^0 is replaced by a Gaussian [14] $(\sqrt{\pi}\,\sigma)^{-1}\exp(-\omega^2/\sigma^2)$ with $\sigma = 0.55$ eV. For further computational details we refer to Ref. [9].

Our results are displayed in Fig. 1. As expected, the energy loss spectra of Na show no particular structure apart from a finite plasmon width, which is due to band structure effects. The core electrons are found to lower the plasmon energy by 0.15 eV for the smallest q considered, which is somewhat smaller than the ionic value [15], and become less important for increasing q. Local field effects are almost negligible. The loss spectra of K have a structure around 7.5 eV. The core electrons lower the plasmon energy by 0.35 eV for the smallest q, and the shift decreases for larger q. The local field shifts the plasmon peaks to higher energies. However, without core electrons, the local field is negligible. This phenomena will be discussed in detail below. In the spectra of Rb a structure is found at around 8 eV. In addition, Rb also exhibits a shoulder structure around 5 eV. The shoulder is more pronounced as q is increased, but disappears at the largest q, which is greater than the critical momentum transfer q_c (the plasmon excitation starts to merge with the single-particle excitations). The shoulder structure arises from interband transitions to the d band. The core electrons have significant effects, not only in lowering the plasmon energy, but also in modifying the shape of the spectra and reducing the plasmon widths. The core excitation energies are closer to the plasmon energies than in the previous two cases, which enlarges its influence. The effects of the local field are also more pronounced than in Na and K. The energy loss spectra of Cs are rather similar to the spectra of Rb, with a shoulder structure at 4 eV (transitions to the d band) and a second peak around 6 eV.

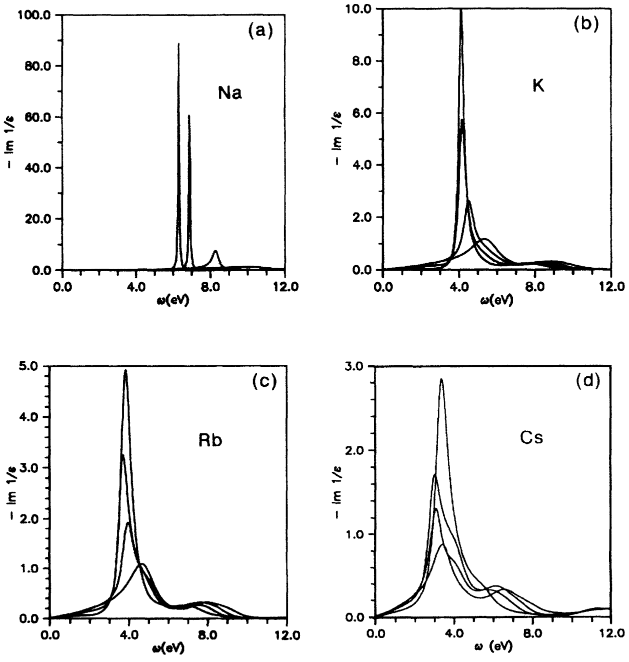

FIG. 1. Energy loss spectra of Na, K, Rb, and Cs, including local field effects and core electrons, for $\mathbf{q} = \alpha(1, 1, 0)2\pi/a$ with $\alpha = 0.125$, 0.25, 0.375, and 0.5. For Na $\alpha = 0.5$ is not shown. Decreasing plasmon peak height corresponds to increasing $\mathbf{q}$.

From the positions of the plasmon peaks in the energy loss spectra, we deduce the corresponding plasmon dispersions $\omega_p(\mathbf{q})$, which are shown in Fig. 2. The plasmon dispersion of Na for small $\mathbf{q}$, apart from a lowering due to core electrons, is in good agreement with the electron gas dispersion predicted by the RPA. The plasmon dispersion of K, on the other hand, shows a significant deviation. Without the core electrons, the dispersion is almost zero. However, a small positive dispersion is found when the core electrons are included, in good agreement with experiment. Local field effects do not change the dispersion except for $q > q_c$. Similar effects due to the core electrons are found in Rb as in the case of K. The dispersion is negative without the core electrons and becomes flat (slightly negative) when the core electrons are included, in fair agreement with experiment. The local field influences the dispersion at large q, while, for small q it only gives a constant shift to higher energy. Most interesting is the plasmon dispersion in Cs: it exhibits a *negative* dispersion which is also confirmed experimentally. Without the core electrons, the negative dispersion is in fact over emphasized. The q dependence of the core contribution to the plasmon dispersion appears to be quite general.

To facilitate our discussions, we consider the Kramers-Kronig relation between the real and imaginary part of the dielectric function:

$$\epsilon_1(\mathbf{q}, \omega) = 1 - \frac{2}{\pi}\int_0^\infty d\omega' \frac{\omega'\epsilon_2(\mathbf{q}, \omega')}{\omega^2 - \omega'^2}, \tag{3}$$

where ϵ_1 and ϵ_2 are the real and imaginary part of ϵ, respectively. It is useful to rewrite the last term as

$$D(\omega_p) = \frac{2}{\pi}\left\{\int_{\omega_p}^\infty d\omega' \frac{\omega'\epsilon_2(\omega')}{\omega'^2 - \omega_p^2} - \int_0^{\omega_p} d\omega' \frac{\omega'\epsilon_2(\omega')}{\omega_p^2 - \omega'^2}\right\} \tag{4}$$

so that $\epsilon_1(\omega_p) = 1 + D(\omega_p)$. The $\mathbf{q}$ dependence is dropped for clarity. With this definition, we observe that for a lowering of the plasmon energy, the contribution to $D(\omega_p)$ from frequencies above ω_p must be greater than the contribution from frequencies below ω_p. In that case, $\epsilon_1(\omega_p)$ will increase, and consequently the plasmon energy (the zero of ϵ_1) will be shifted to lower frequency,

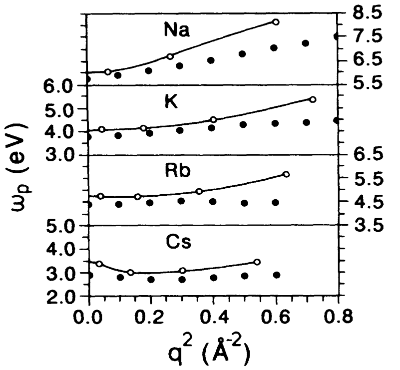

FIG. 2. Plasmon dispersions of Na, K, Rb, and Cs, including local field effects and core electrons. The open and filled circles correspond to theory and experiment [2], respectively.

due to the fact that the slope of ϵ_1 at ω_p is positive. What we actually consider is changes in D due to a change in $\mathbf{q}$ or inclusion of core states.

The systematic lowering of the calculated plasmon dispersion, in the series Na to Cs, is a band structure effect. The increasing deviation from free-electron bands, is due to a lowering of the d band, which approaches the Fermi level in Cs. As a result, the plasmon energy of Cs lies within the interband transitions to the d band (in contrast to Na). This can alter the plasmon dispersion. For $q = 0$ the transitions to the d band should be minor. However, for larger q the transition probability will be enhanced. We consider the transition probability, which involves integrals $\int d^3\mathbf{r}\ \psi^*_{\mathbf{k}n}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \psi_{\mathbf{k}-\mathbf{q}n'}(\mathbf{r})$. When $\mathbf{q} \rightarrow 0$, we expand $e^{i\mathbf{q}\cdot\mathbf{r}} \approx 1 + i\mathbf{q}\cdot\mathbf{r} - 1/2(\mathbf{q}\cdot\mathbf{r})^2$. The s-p transitions are induced by the dipole term $i\mathbf{q}\cdot\mathbf{r}$, while the quadratic term contributes to the s-d transitions. Note that the lowest order dipole contribution is q independent, because $v(q)$ cancels the q^2 term for s-p transitions but not the q^4 term for s-d transitions. As can be seen in Fig. 1, the shoulder structure due to the d band becomes more pronounced as q increases. Since this structure lies just above the plasmon peak, it has the effect of lowering the plasmon energy as follows from Eq. (4). The lowering is more significant for larger q, resulting in a negative dispersion.

This structure above the plasmon energy has also been observed experimentally [16] but it has not been adequately explained so far. As an illustration, we compare the theoretical and experimental ϵ_2 for Cs in Fig. 3. The structure is well reproduced but the magnitude is not in good agreement. However, the experimental error is estimated to be about 30% and the experimental curve below 4 eV was obtained by interpolation from other experimental data. The structure arises from interband transitions from s to d as well as s to p. A similar structure is also found in Rb at 7 eV and a broader structure is found in Na and K at 11 and 8 eV, respectively.

As mentioned, there are suggestions that SXC is responsible for the negative dispersion in Cs. The effects of SXC can be estimated by adding the exchange-correlation kernel $K_{\mathrm{xc}} = vG_{\mathrm{xc}}$ (LDA) to the Coulomb potential. Calculations on electron gas including also the effects of band structure in a perturbative manner show a significant decrease (30%–40%) of the dispersion coefficients of the alkali metals [5]. In one of the approximations used, a minimum in the plasmon dispersion of Cs is found at the right position but it is exaggerated and the dispersion at small q is not correct. Another calculation using the best available Fermi liquid theory that goes beyond the RPA [2] requires $r_s = 12$ to obtain a negative dispersion. This value is only one tenth of the Cs density, which is unrealistically low. A recent calculation on the plasmon dispersion in Na, including band structure and K_{xc} [17], shows that the effect of SXC is significant only for large q. To further clarify the role of the d band in Cs, we calculate the plasmon dispersion using only s and p orbitals as a basis for the band structure. The plasmon dispersion turns out to be positive, which clearly shows that the d band is responsible for reducing the plasmon dispersions.

Finally we consider the influence of the core electrons and the local field. The highest lying p core electrons play an important role in determining the position of the plasmon peak, as well as its shape, particularly in the heavier alkali metals Rb and Cs. Because of the presence of a d band just above the Fermi level, transitions from p core states to the d states are very strong. There are three features associated with the core electrons: (i) A $\mathbf{q}$ dependent lowering of the plasmon energy for all cases studied. (ii) The shape of the valence (low energy) spectra in Rb and Cs is modified. (iii) An indirect enhancement of the local field effects on the valence

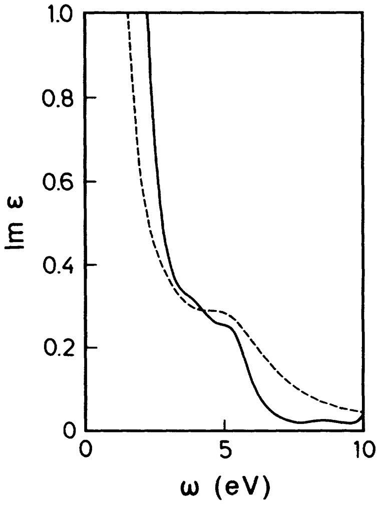

FIG. 3. The imaginary part of ϵ of Cs for $\mathbf{q} = 0.125(1, 1, 0)2\pi/a$. The solid and dashed lines correspond to theory and experiment [16], respectively.

spectra in K, Rb, and Cs, i.e., excluding the core electrons gives rise to negligible local field effects.

The spectral modifications in Rb and Cs are consistent with the relatively small energy separation between the core excitations and the plasmons (in contrast to the Na and K cases), and can be understood by considering the quantity D in Eq. (4). According to the *f-sum rule* [1], the ratio of core to valence weight of the first moment of ϵ_2 is 6 (6 p core electrons and 1 valence electron). Thus, the weight in ϵ_2 originating from the core electrons is much larger than the weight from the valence electrons, which implies a large effect. The third feature is probably the most unexpected. Without local field, the core electrons are easy to polarize, provided there are unoccupied states which can be strongly coupled to the core states by polarization. The underlying reason is that the induced density is assumed to be almost uniformly distributed, thus its Coulomb energy is much less than the true value. When the local field is taken into account, the localized nature of the core electrons makes them hard to polarize because the induced density is very localized, which results in a larger Coulomb energy [11]. Therefore, it is not energetically favorable to strongly polarize the core electrons. As a consequence, the local field effects in ϵ around the core excitation energy are very large, particularly when the final unoccupied states are also localized, as in the cases with a d band in Rb and Cs. In general, the local field effects tend to redistribute the weight in the loss spectra towards higher energy. The reason is that the local field reduces screening so that the Coulomb interaction increases, leading to higher plasmon energy. When the core excitation energies are not so far away from the plasmon energies, this redistribution of weight modifies the real part of ϵ, not only around the core excitation energies, but also in the region of the valence plasmon energy via the Kramers-Kronig relation. This results in a modification of the valence spectra. When the core electrons are not included, the local field effects are small because there are no localized transitions in the region of the valence spectra, in agreement with the theory in Ref. [11]. The influence of core electrons on the dielectric functions of simple metals has also been studied by Zaremba and Sturm [18].

In summary, we have calculated the energy loss spectra of Na, K, Rb, and Cs within the RPA, including band structure and local field effects as well as core electrons. From the positions of the plasmon peaks in the energy loss spectra we deduce the corresponding plasmon dispersions. Our main conclusions are the following: (i) Because of lowering of the d band, band structure effects become increasingly important in the series Na to Cs. Further we found that the d band causes the *negative* dispersion in Cs. Because of the use of the LDA Bloch states in our calculations, SXC is partly included in the response function. However, the use of LDA states rather than Hartree states as in the pure RPA, only modifies the Green function but not the basic RPA polarization diagrams and therefore it does not introduce diagrams associated with SXC. Thus, it is unlikely that our calculations contain a significant SXC. (ii) The core excitations have a significant influence on the shape of the valence spectra and the plasmon dispersions. The core electrons reduce the plasmon energy (the effect is largest for small $\mathbf{q}$). Exclusion of core electrons results in a negative dispersion even for K, a trend which is overemphasized in Cs. (iii) Local field effects are negligible when core electrons are excluded. With core electrons the local field effects are large around the core excitation energy. In fact, considerable influence on the valence spectra was found for Rb and Cs.

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