Influence of the core polarization on the dielectric properties of polyvalent metals

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Abstract. We have measured the dispersion of plasmon excitations in polycrystalline Sn, Pb, Cd and Zn using electron energy-loss spectroscopy (EELS) in transmission. These metals show a remarkable deviation of their plasmon behaviour from standard theoretical expectations which can be attributed to the presence of shallow core levels in the energetic neighborhood of the plasmon energy. The position of the plasmon resonance in the long wavelength limit is in line with predictions from model assumptions taking into account the core level polarization effects. We show that not only the plasmon energy in the optical limit but also the plasmon dispersion is altered by the interaction of the charge carrier plasmon and the core level excitations.

PACS. 71.45.Gm Exchange, correlation, dielectric and magnetic functions, plasmons

1 Introduction

It is well-known that the core polarization may influence the dielectric properties of a metal in the energy range of the free charge carrier plasmon excitation [1]. Nevertheless, metals have mainly been described in the nearly free electron approximation within the random phase approximation (RPA) [2] and deviations thereof were mostly attributed to exchange and correlation effects between the conduction electrons [3] or to band structure effects [4]. The influence of core polarization has usually been described as an energy and momentum independent background dielectric constant because it is small as long as $E_{core} \gg E_{pl}$, where E_{pl} is the plasmon energy of an electron system with density n and E_{core} denotes the energy of the core level excitation. This assumption fails for several simple metals, especially for the post transition metals, as their most weakly bound d-electrons have binding energies of the order of 10 eV, *i.e.* they are energetically close to the charge carrier plasmon and a dynamic interaction of the two excitations is to be expected.

A theoretical description of the influence of such core excitations onto the plasmon properties in the long wavelength limit has been established recently [5]. This approach could in principle be extended to finite momentum transfers, but the numerical effort has hindered a detailed calculation up to now. Concerning the momentum dependent plasmon properties of post transition metals only scarce and sometimes wide-spread experimental data can be found in the literature. Therefore, it seemed desirable to us to investigate the momentum dependent di-

electric properties of a selection of post transition metals with high resolution. We have chosen Sn, Pb, Cd and Zn because in these metals the ratio E_{core}/E_{pl} is near unity. Hence, these metals offer the possibility to study the interaction of plasmons and core polarization in detail. Additionally, the four metals chosen show quite flat d-bands [6,7], with a bandwidth smaller than 0.2 eV, which makes their classification as shallow core levels reasonable. A detailed analysis of the Zn data has recently been presented in a separate publication [8].

2 Experimental

Polycrystalline films of Sn, Pb, Cd and Zn with a thickness of about 1000 Å were prepared by evaporating high purity metal (99.999%) under high vacuum conditions. In order to avoid oxidation of the highly reactive films and to prepare free standing samples without any substrate, we followed a method outlined for the preparation of thin Pb films by Imbusch [9]. As substrate, frozen methanol on a fine-mesh copper grid at a temperature of about 100 K was used. To remove the methanol, the samples were carefully heated to the melting point of the methanol (180 K) and kept at this temperature until the methanol had disappeared. This low temperature prevents any degradation of the films. Subsequently, the films were quickly transferred into the spectrometer. The phase purity of the films was checked by elastic electron scattering and no signs of other phases, especially metal oxides, could be detected.

The EELS measurements were performed in transmission with a spectrometer described in detail elsewhere [10].
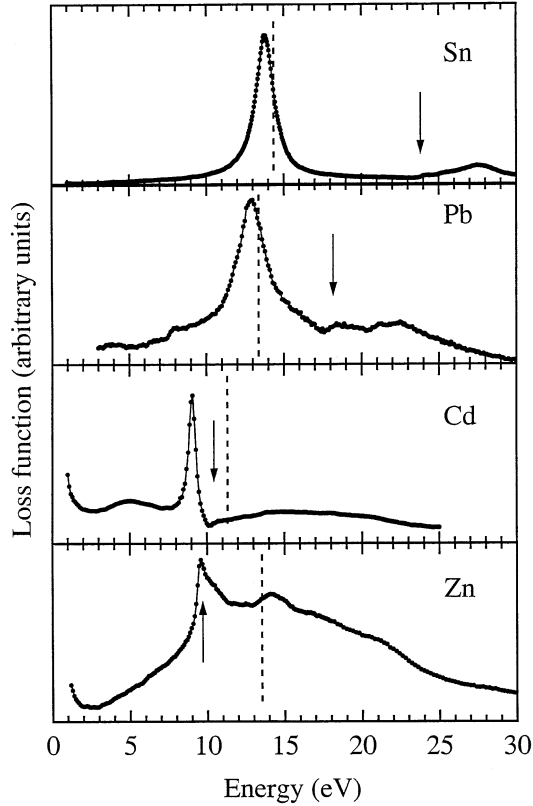
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Fig. 1. The loss function of Sn, Pb, Cd and Zn for a momentum transfer $q = 0.1$ Å^{-1} as measured by EELS. The Drude plasmon energy $\hbar\omega_{pl}^{Drude}$ (see text) is marked by the dashed lines and the onset of core level excitations E_{core} by the vertical arrows.

The primary electron beam energy was 170 keV. The energy and momentum resolution was chosen to be 160 meV and 0.06 Å^{-1}, respectively. EELS is a direct probe of the loss function $\mathrm{Im}(-1/\epsilon(\mathbf{q}, \omega))$ in which plasmon excitations appear as clear peaks at the plasmon excitation energy. The investigated metal films were polycrystalline, hence leading to an averaged information about the dielectric response. The anisotropy of the response in different crystallographic directions, however, is expected to be small in metals due to their cubic or quasi-cubic symmetry, which only gives rise to a small broadening of the plasmon excitations.

3 Results and discussion

3.1 The long wavelength limit

Figure 1 shows the loss function of the selected metals Sn, Pb, Cd and Zn at a momentum transfer of $q = 0.1$ Å^{-1}. This momentum transfer is low enough to be considered as the long wavelength limit because it is much smaller than the size of the first Brillouin zone, which is typically of the order of ~ 2 Å^{-1} for these metals. On the other hand, it is still sufficiently high to avoid strong contributions from surface excitations and the quasi-elastic line [1,10].

The spectra can be divided into two groups. The spectra of the first group including Sn, Pb and Cd, show the typical shape which is expected for a simple metal [1]. The spectra are dominated by a sharp and well-defined plasmon peak. The half width of these features is mainly determined by interband transitions which offer a possible decay channel [11]. The nature of these interband transitions can be quite different for the different metals as they depend upon the details of the band structure of the material under consideration. Therefore, we will not further discuss the width of the plasmon peaks. In addition to the volume plasmon, a feature at lower energy can be observed in the case of Pb and Cd which is due to surface plasmon excitations. Its corresponding position is not directly connected to the volume plasmon position according to the free electron expectation $\hbar\omega_{SP} = \hbar\omega_{pl}/\sqrt{2}$, but it is found to be significantly lower. This deviation is related to the unavoidable oxidation of the surface layer during the preparation process. This very thin oxide layer leads to a dielectric coating of the metal film and a shift of the surface plasmon energy according to the relation $\hbar\omega_{SP} = \hbar\omega_{pl}/\sqrt{\epsilon + 1}$ where ϵ is the dielectric constant of the surface layer [1]. We emphasize that this oxide surface layer does not alter the information on the bulk properties.

At energies higher than the volume plasmon energy, edge-like features can be observed which are related to the excitation of electrons from the shallow core levels. In Figure 1 the onset energy of the core excitation, E_{core}, is marked by vertical arrows. In Sn an additional feature in the same energy region as the core excitations is related to a double plasmon loss. On going from Sn to Cd, a systematic decrease of the core level energy with respect to the plasmon position occurs. The decreasing energy distance of the two types of excitations is accompanied by an increasing deviation of the plasmon energy from its free electron (Drude) value $\hbar\omega_{pl}^{D} = (\hbar^2 n e^2/\epsilon_0 m)^{1/2}$ to lower energies (n is the electron density). When the core level excitation is lower than the plasmon energy, as it is the case for Zn, a qualitative change in the loss function can be observed compared to the spectra described above. The shape of the loss function of Zn has been discussed in detail in a previous publication [8] and only the most important results shall be summarized here: the sharp peak at 9.6 eV is related to the onset of core level excitations while the broad feature at 14.2 eV is attributed to the charge carrier plasmon. The spectral shape of the loss function results from a complex interplay between the real and imaginary part of the dielectric function in this energy range. Compared to the results obtained for the other metals the charge carrier plasmon is shifted to higher energy compared to the Drude value.

The observed values for the plasmon positions are summarized in Table 1 and Figure 2 where further results are added which can be found in the literature for elements of the groups 1B-5B of the periodic table, *i.e.* for elements with weakly bound d-bands in the same energy region as the plasmon energies. In Figure 2 the experimentally determined position of the plasmon is compared to the onset energy of the core level excitations. In order

Table 1. Plasmon energy of some post transition metals and semiconductors: Drude plasmon energy $\hbar\omega_{pl}^{Drude}$, experimental plasmon energy $\hbar\omega_{pl}^{exp}$ and the theoretically expected plasmon energy $\hbar\omega_{pl}^{theor}$ taking into account core polarization effects [5]. Also included is the onset energy of the shallow core levels, E_{core}. The values determined in this work are underlined.

element	$\hbar\omega_{pl}^{Drude}$	$\hbar\omega_{pl}^{exp}$	$\hbar\omega_{pl}^{theor}$	E_{core}
As	17.8	18.7 [13]	-	41.7 [7]
Sb	15.1	15.2 [14, 15]	-	32.1 [7]
		15 [16]		
		15.3 [17, 18]		
Ge	15.6	16.0 [16, 19, 20]	-	29.2 [7]
		16.5 [13, 21]		
Bi	14	14 [16, 22]	-	23.8 [7]
		14.4 [23]		
Sn	14.3	13.7 [16, 24, 25]	13.7	23.9 [7]
In	12.6	11.4 [12, 26, 27]	11.3	16.9 [7]
		12.3 [15]		
Pb	13.5	13.0 [1, 28]	-	18.1 [7]
		13.25 [29]		
Ga	14.5	13.8 [25]	-	18.7 [7]
		14.2 [30]		
Tl	10.9	9.6 [31]	-	12.5 [7]
Cd	11.3	9.01	8.5	10.5 [7]
		9.07 [32]		
		9.2 [12]		
Hg	15.1	6.3 [33]	8	7.8 [7]
		7.3 [34]		
Zn	13.5	14.2 [8]	-	10.1 [7]
		14.3 [32]		
Ag	9.0	3.8 [12, 35]/7.8 [12]	-	4.2 [6, 36]
Au	9.0	2.95 [37]/5.8 [38]	-	2.5 [36, 38]
Cu	10.8	2.2 [37]/7 [39]	-	2 [36]

to compare the data for different elements, all values are normalized to the corresponding Drude plasmon energy. For completeness we have added the data for some noble metals in which d-levels form bands several eV below the Fermi level.

Analyzing the data from right to left, *i.e.* with successive lowering of the core level binding energy, the subsequent lowering of the plasmon energy from its Drude value is demonstrated. Approaching the crossing point of the two solid lines which represent the non-interacting case, a non-crossing behaviour can be seen which is reminiscent of the interaction of two quasiparticles and which follows from quantum mechanical non-crossing requirements. In other words, the energy shift is a consequence of the interaction of two electronic excitations, the free charge carrier plasmon and the core level excitation, which then gives rise to "new" eigenfrequencies of the system in question. The noble metals obviously continue the behaviour given by the post transition metals in spite of their different type of core polarization. The fact that their plasmon energies all come to lie below the Drude value is a result of a higher dielectric background in the noble metals [1, 12]

arising from higher lying electronic transitions. We note that the loss function of Cd and, to some extent, of Zn shown in Figure 1 resemble a Fano line shape [40]. This provides further indication that the two types of electronic excitations discussed above significantly interact and cannot be considered independently.

The experimental results summarized here are in qualitative and even quantitative agreement with refined theoretical calculations [5] (see also Tab. 1). These calculations, however, were only performed for the elements In, Cd, Sn and Hg, *i.e.* for elements which lie on the lower branch of Figure 2 where the plasmon energy is below the core level excitation energy. The reason for the lowered plasmon energy is found in the calculation to be not only due to a simple screening by the core polarization but to be caused by a complex interplay between an upward shift due to an enhancement of the effective valence electron density and a downward shift due to the dielectric screening of the core dipoles. This means that the underlying interaction mechanism, although it can qualitatively be described in the framework of a simple Drude-Lorentz approach, is more complicated.
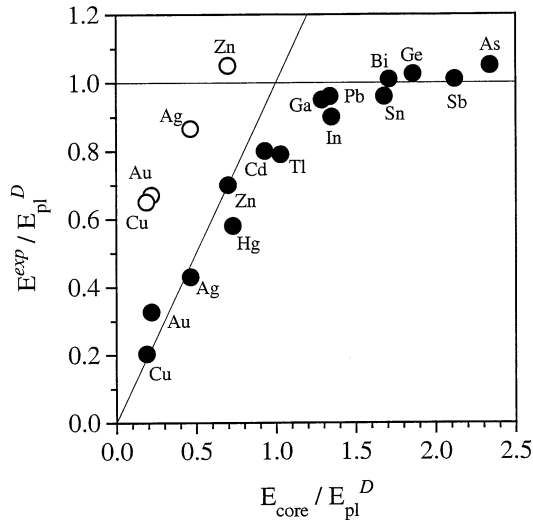
Fig. 2. Deviation of the experimental plasmon (solid circles) and core (open circles) excitation energies (E^{exp}) from the expectation without interaction for different elements as a function of the onset energy of the core level excitations. All energies are normalized with respect to the Drude plasmon energy of the respective material. The two solid lines depict the non-interacting case.

3.2 Finite momentum transfers

We now turn to the momentum dependent loss function of the metals discussed in this study. Figure 3 shows the plasmon dispersion of Sn (Fig. 3a) and Cd (Fig. 3b) in a wide range of momentum transfer. For both materials a positive dispersion of the plasmon excitation can be observed with increasing momentum transfer. Additionally, the plasmon peaks become broader up to a critical momentum q_c where they disappear completely. For Sn, this critical momentum q_c is about 1.4 Å^{-1}, while in the case of Cd the plasmon has already disappeared at 0.8 Å^{-1}. In simple metals, this plasmon decay is caused by intraband transitions within the conduction band which become possible above q_c. Within a free electron consideration q_c can be estimated by $q_c \sim (m\omega_{pl})/(\hbar q_F)$ [1] which yields $\sim$ 1.3 Å^{-1} and 1.4 Å^{-1} for Sn and Cd, respectively. While this simple approach provides a reasonable understanding for the plasmon decay in Sn, it fails for Cd. The reason for this difference lies in the shallow core level excitations. For Sn their energy position is relatively far above the plasmon energy (see also Fig. 1) and they therefore do not impact the lifetime of the charge carrier plasmon. In the case of Cd, however, the dispersing plasmon enters the energy range of the core level excitations at about 0.7–0.8 Å^{-1} which then offer an additional decay channel and cause the plasmon peak to essentially vanish. We note that with increasing momentum transfer the loss function of Pb (not shown) closely parallels the behaviour of Cd shown in Figure 3. In addition to the dispersive plasmon line, an undispersive feature becomes visible at higher momentum transfers in Figure 3. This feature is due to double scattering processes: quasielastic scattering of the
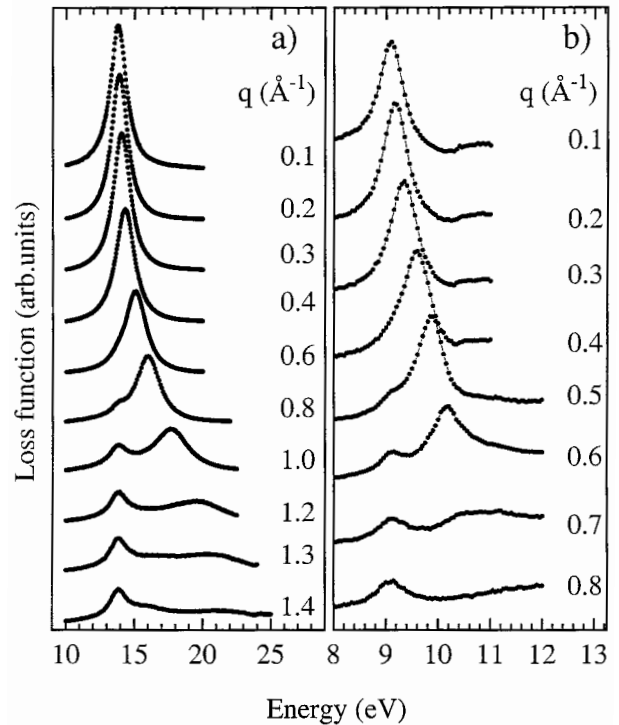

Fig. 3. Momentum dependent loss function of (a) Sn and (b) Cd.

Table 2. Comparison of the plasmon dispersion coefficients, α_{exp}, derived in this study to the values expected within RPA (α_{RPA}).

element	α_{exp}	α_{RPA}	$\alpha_{exp}/\alpha_{RPA}$
Sn	0.43	0.44	0.97
Pb	0.36	0.44	0.81
Cd	0.41	0.5	0.82
Zn	0.51 [8]	0.39	1.3

primary electrons by imperfections or phonons and subsequent inelastic scattering without considerable momentum transfer, a phenomenon often present in EELS studies in transmission. The plasmon dispersion of Zn has been discussed in detail recently [8]. There, the dispersion itself is strongly influenced by the shallow core level excitations which are energetically located below the charge carrier plasmon and exhibit a considerably momentum dependent excitation intensity. Taking these intensity changes into account within a simple Drude-Lorentz approach the actual plasmon dispersion of Zn could be shown to be positive and proportional to the square of the momentum transfer. The dispersion coefficient is presented in Table 2.

The plasmon dispersion of the three other metals discussed here is shown in Figure 4 where the plasmon peak positions are plotted *versus* the squared momentum transfer, q^2. From Figure 4 it is clear that for all three metals the plasmon dispersion is proportional to q^2 at low momentum transfers. The dispersion coefficients
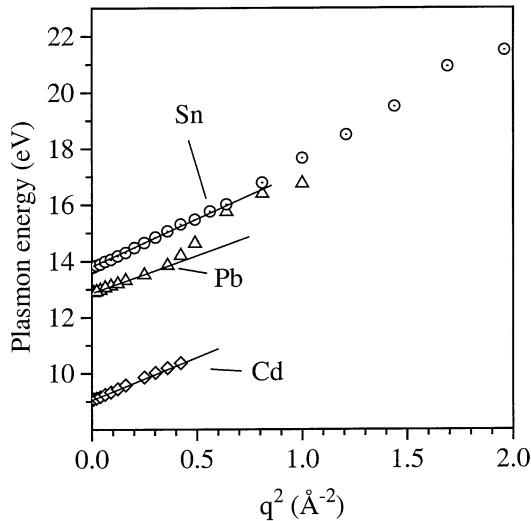
Fig. 4. Measured plasmon energies *versus* squared momentum transfer, q^2. The solid line is a fit to the low-q data.

have been derived by fitting a straight line to the low-q data points, as it is shown in Figure 4. The resultant dispersion coefficients α as determined from the relation $\hbar\omega_{pl}(q) = \hbar\omega_{pl}(0) + (\hbar^2/m)\alpha q^2 + O(q^4)$ which represents the long wavelength expansion of the plasmon dispersion are also included in Table 2, where we compare the measured dispersion coefficients to the value one would expect within RPA: $\alpha_{RPA} = 3E_{Fermi}/5\hbar\omega_{pl}(0)$.

Interestingly, only the plasmon dispersion of Sn agrees with the expectation from RPA, the other dispersion coefficients, however, deviate significantly from the RPA prediction. Moreover, the results shown in Table 2 again suggest a splitting of the metals into two groups: for Pb and Cd, where the shallow core level excitations occur at energies (E_{core}) higher than the plasmon energy $\hbar\omega_{pl}^{exp}$, the dispersion coefficient α_{exp} is considerably smaller than α_{RPA} whilst for Zn the plasmon energy lies above E_{core} and α_{exp} is much larger than α_{RPA}. This observation can be qualitatively understood considering the results shown in Figure 2 and discussed above. There, it has been demonstrated that the nearer the core level excitations move towards the charge carrier plasmon the more they exert a repulsive impact. As the plasmon dispersion also alters the energy distance between the two excitations it directly experiences this repulsion. Consequently, the dispersion is hindered, *i.e.* suppressed, when the plasmon disperses towards E_{core}, as it is the case for Cd and Pb, and the dispersion is enhanced, *i.e.* supported, when the plasmon withdraws from the shallow core level like in Zn. Finally, a core level which is at high enough energies (much higher than $\hbar\omega_{pl}^{exp}$) does not visibly influence the plasmon dispersion as it is observed for Sn. We note that a full, quantitative description of the momentum dependent interaction of charge carrier plasmons and shallow core level excitations is much more complicated. For the optical limit it has already been shown [5] that the interaction leads to a change of the effective valence electron density. Further-

more, the plasmon dispersion might also be affected by other parameters like the actual band structure of the material or electronic correlation effects like local field corrections.

4 Summary

We have investigated the momentum dependent dielectric response of post transition metals, where the excitation from the most weakly bound *d*-level is in the energetic neighborhood of the free charge carrier plasmon. In the long wavelength limit we find a systematic shift of the plasmon energy from its free electron Drude value which exhibits the mutual repulsion of electronic excitations in the loss function. This also impacts the plasmon dispersion depending upon the ratio of the plasmon and the core level energy. A quantitative theoretical description of these effects has not yet been achieved but could probably give important insight in the electronic properties of various systems and into the importance of different parameters used in the model.

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