Plasma resonance of binary amorphous and crystalline Al-transition metal alloys: Experiments and *ab initio* calculations

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ABSTRACT

We report on measurements of the volume plasmon loss energy E_P by electron energy loss spectroscopy of binary *amorphous* Al–(Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Pd, Ce) alloys. In these systems the measured E_P can be described by an *effective* valence of the transition metal *independent* of the particular transition metal. By exploiting *ab initio* calculations for the *crystalline* counterparts in the case of Al–(Ti, V, Fe, Ni) we show that this behavior can be understood in terms of the *full dielectric function* taking into account *intra-* and *interband* transitions mainly due to the presence of d-states close to the Fermi energy. This is validated by the comparison with published experimental data on binary Al systems with the *non*-transition metals Be, Mg, Ca, and Zn. Due to the absence of composition-dependent structural phase changes, amorphous alloys are found to be model-like systems for studying the influence of interband transitions on the plasma resonance.

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1. Introduction

A lot of information about the electronic transitions in a material is contained in its dielectric function $\varepsilon(\vec{q}, \omega)$. In particular, $\varepsilon(\vec{q}, \omega)$ provides the basis for calculating a material's electronic and optical properties, *e.g.* the *(volume) plasma resonance* [1–3]. In the simplest approach based on a homogeneous single-band valence-electron gas model in the optical limit ($\vec{q} \to 0$), the eigenfrequency (plasma frequency) of these quantized collective oscillations (plasmons) is given by

$$\omega_P = \sqrt{\frac{e^2 \bar{n}_e}{\varepsilon_0 m_e}}, \tag{1}$$

which depends, apart from the constants e (elementary charge), ε_0 (permittivity of the vacuum) and m_e (mass of the free electron), only on the *mean valence electron density* $\bar{n}_e$ of a material [2]. In principle, if the mean particle density $\bar{n}_0$ and the mean valence $\bar{Z}$ of a material is known its ω_P can be calculated *via* (1) using $\bar{n}_e = \bar{n}_0 \bar{Z}$. Vice versa, it would be possible to determine $\bar{n}_e$ from measurements of ω_P.

However, in crystalline (c) systems ω_P is strongly affected by band-structure effects and will generally be anisotropic [4–6].

Furthermore, a change of composition can cause significant changes of the crystal structure and therefore the band structure and ω_P, as well. Amorphous (a) systems, on the other hand, exhibit isotropy in real and reciprocal space – a circumstance that turned those materials into ideal model systems for studying e.g., structure formation processes in condensed matter physics [7–9]. In the a-state the often complicated Brillouin zone of crystals is replaced by a pseudo-Brillouin zone which is *spherical* in shape but exhibits a smeared-out boundary [7,10]. Thus, the band structure is also smeared-out.

For so-called "simple" a-alloys (where no d-states are present at the Fermi energy E_F) it was indeed found that it is possible to predict ω_P quite accurately by taking into account $\bar{Z}$ calculated from the "usual" valences from the periodic table [11]. However, if d-states at E_F occur, like in alloys with transition metals (TM), even in a-alloys this simple approach is no longer viable. Especially, for the binary a-Al–TM alloys with TM = Ca, Ti, V, Cr, Mn, Fe, Co, Ni it was shown that the dominant feature seen by electron energy loss spectroscopy (EELS), if indeed interpreted as caused by the excitation of volume plasmons, can be described by the valences $Z_{Al} = 3$ and $Z_{TM} \approx 5$ [11]. While the former value is to be expected, the latter cannot be inferred from the periodic table [11]. Further, Z_{TM} is virtually independent of the particular TM in the alloy [11].

While there have been speculations about different possible origins for this systematics, involving interband transitions or different subsets of electrons involved, no satisfactory explanation could be given [11]. This is partly due to the fact that theoretical

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calculations are difficult to perform for a-systems – an obstruction not present in the crystalline counterparts.

In the present paper we provide a comprehensive study of the plasma resonance for systems with early and late TM from the 3rd, 4th and 5th period. With the help of extensive *ab initio* calculations for c-systems, we show how the measured plasma resonance in the a-systems can be understood. Our experimental data for systems already presented in Ref. [11] have been reanalyzed, mainly in order to provide a consistent fitting procedure for all the systems discussed, extended, and complemented by measurements on further systems [12–14]. The experimental results are compared with theoretical calculations on the c-counterparts, and the influence of interband transitions due to the TM-d-states is demonstrated. This result is further supported by an analysis of published data for Al–(Be, Mg, Zn) (only available for the polycrystalline (pc) state) [15–18].

The paper is organized as follows. In Sections 2 and 3 we outline the basics of our experimental and theoretical methods. Section 4 contains the results of our comprehensive study of plasma resonances in Al–TM systems. Our conclusions are summarized in Section 5.

2. Experimental

Mother alloys of our samples were prepared from high-purity raw materials (Al: 99.9999%, Cr, Ni: 99.999%, Fe: 99.9985%, Mn: 99.99%, Pd: 99.98%, Co: 99.95%, Ce, Y: 99.9%, Sc, Ti, V: 99.8%) by arc-melting under Ar atmosphere. The obtained alloy beads are then crushed to pieces approximately 0.1 mm in size. Quench-condensed thin a-films (thickness $d = 20$–70 nm) have been prepared from the so-produced material by sequential flash evaporation [19] onto substrates held at the temperature of liquid (l) He or l-N_2 in a high vacuum cryostat ($p \lesssim 5 \times 10^{-7}$ mbar). Substrates were either a-C-coated Cu grids ($d_C \approx 15$ nm) or NaCl (the a-films were later floated off the NaCl in water and picked up on Cu grids prior to further investigations). The plasma-resonance data were taken *ex situ*, after annealing the films up to room temperature, by EELS in a Philips CM20FEG transmission electron microscope (TEM) with 200 keV incident energy and a Gatan 678 energy dispersive detector. The background caused by the EELS signal of the C substrate had to be subtracted as described in Section 4.1. The experiments yield the so-called *plasma energy* $E_P = \hbar \omega_P$. No major difference of E_P between measurements of on-C and free-standing films was found. The a-state of the samples has been confirmed by transmission electron diffraction in the TEM.

While the samples from Ref. [15] (Al–Mg) were also prepared as thin films by flash evaporation, the samples from Ref. [16] (Al–Be) were produced by co-evaporation, and from Ref. [20] (Al–Ca) by DC magnetron co-sputtering of the elements. The thin specimens in the case of Al–Mg (Ref. [17]) were obtained by rolling and in the case of Al–Zn (Ref. [18]) by cutting the according bulk alloys, respectively.

3. Theoretical

For c-Al–(Ti, V, Fe, Ni) we performed *ab initio* calculations of the wave-vector and frequency-dependent dielectric function in the random phase approximation (RPA) [5,21,22],

$$\varepsilon(\vec{q}, \omega) = 1 - V_q \sum_{\mu \nu \vec{k}} |B^{\mu \nu}_{\vec{k}\vec{q}}|^2 \frac{f^{\nu}_{\vec{k}} - f^{\mu}_{\vec{k}+\vec{q}}}{\hbar \omega + \epsilon^{\nu}_{\vec{k}} - \epsilon^{\mu}_{\vec{k}+\vec{q}} + i\hbar\gamma}, \quad (2)$$

in the framework of a $\vec{q}$-dependent linear tetrahedron method as outlined in Ref. [5] to accurately evaluate the wave-vector summation in the limit $\hbar\gamma \to 0$. The distribution functions $f^{\mu}_{\vec{k}}$ and energies $\epsilon^{\mu}_{\vec{k}}$ for wave vector $\vec{k}$ and band μ as well as the overlap matrix

Table 1
Crystal structures [24–29] used in the theoretical calculations and computed loss energies E_P^{calc}.

Material		Crystal structure	E_P^{calc} (eV)
Al		fcc	15.3
TiAl$_3$	Al$_{75}$Ti$_{25}$	D0$_{22}$ (bcc)	16.1
TiAl	Al$_{50}$Ti$_{50}$	CsCl (sc)	17.6
Ti		hcp	12.0
VAl$_3$	Al$_{75}$V$_{25}$	Cu$_3$Au (sc)	17.5
VAl	Al$_{50}$V$_{50}$	CsCl (sc)	20.5
V$_3$Al	Al$_{25}$V$_{75}$	Cu$_3$Au (sc)	16.4
V		bcc	20.8–22.6
FeAl$_3$	Al$_{75}$Fe$_{25}$	D0$_{22}$ (bcc)	18.5
FeAl$_2$	Al$_{66.\bar{6}}$Fe$_{33.\bar{3}}$	MoSi$_2$ (tetragonal)	18.2
FeAl	Al$_{50}$Fe$_{50}$	CsCl (sc)	20.9
Fe$_2$Al	Al$_{33.\bar{3}}$Fe$_{66.\bar{6}}$	MoSi$_2$ (tetragonal)	18.7
Fe$_3$Al	Al$_{25}$Fe$_{75}$	Cu$_3$Au (sc)	21.0
Fe		bcc	23.9
NiAl$_3$	Al$_{75}$Ni$_{25}$	D0$_{22}$ (bcc)	17.9
NiAl$_2$	Al$_{66.\bar{6}}$Ni$_{33.\bar{3}}$	CaF$_2$ (fcc)	19.8
NiAl	Al$_{50}$Ni$_{50}$	CsCl (sc)	21.0–25.0
Ni$_3$Al	Al$_{25}$Ni$_{75}$	Cu$_3$Au (sc)	22.6
Ni		fcc	29.6–32.9

elements $B^{\mu \nu}_{\vec{k}\vec{q}} = \langle \psi^{\mu}_{\vec{k}+\vec{q}} | e^{i\vec{q} \cdot \vec{r}} | \psi^{\nu}_{\vec{k}} \rangle$, which denote transitions between the eigenstates $\psi^{\nu}_{\vec{k}}$ and $\psi^{\mu}_{\vec{k}+\vec{q}}$ are extracted from a density functional theory (DFT) calculation using the ELK code [23], which employs a full-potential linearized augmented plane wave (FP-LAPW) basis. $V_q = e^2/(\varepsilon_0 q^2)$ denotes the Fourier transformed bare Coulomb potential.

In Ref. [5] we stressed that there are different definitions of the plasma frequency, depending on the transitions included. In particular, the pure intraband plasma frequency, *i.e.*, the one, where only *intraband* transitions are taken into account, resembles the results of an electron-gas model in the optical limit, but exhibits an unexpected negative dispersion. However, the full plasma frequency, *i.e.*, the one, where *interband* and *intraband* transitions play a role and which corresponds to a peak in the loss function, has a positive dispersion, but does not equal the electron-gas result in the optical limit. Thus, neither of them can be *fully* put into correspondence with a simple electron gas model [5]. Moreover, it has been shown that d-bands close to the Fermi energy have an important influence on the peak in the loss function, in particular in the case of silver and the two Heusler compounds Co$_2$FeSi and Co$_2$MnSi, where so-called optical plasmons occur, which dominate the spectrum in the loss function [5]. Therefore, *ab initio* calculations *including* interband transitions are indispensable for the comparison of the loss function with experimental data.

Table 1 lists the underlying crystal structures for various concentrations of the systems under consideration as well as theoretical results for the position of the peak (E_P^{calc}) in the calculated loss function $S(\vec{q}, \omega) = -\Im(\varepsilon^{-1}(\vec{q}, \omega))$ in the optical limit $\vec{q} \to 0$, where we used 25^3–61^3 $\vec{k}$-points in the full first Brillouin zone. All values were obtained using the $\vec{q}$-dependent linear tetrahedron method [5]. A tendency of an increasing E_P^{calc} with increasing TM concentration becomes obvious, which will be discussed in detail together with the experimental results below. For the NiAl compound as well as for pure V and Ni a whole spectrum of comparable peaks exist in a certain energy range, such that a definition of a *single* plasma resonance is questionable in these materials.