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ANOMALOUS X-RAY SCATTERING*

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Anomalous X-ray Scattering.^{x)}

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Abstract

The availability of tunable synchrotron radiation has made it possible systematically to perform X-ray diffraction studies in regions of anomalous scattering near absorption edges, e.g. in order to derive phase information for crystal structure determination. We give an overview of recent experimental and theoretical work and discuss the properties of the anomalous atomic scattering factor, with emphasis on threshold resonances and damping effects. The results are applied to a discussion of the very strong anomalous dispersion recently observed near the L_3 edge in a cesium complex [11]. We also give an overview of elements and levels where similar behaviour can be expected. Finally, we discuss the influence of solid state and chemical effects on the absorption edge structure.

1. Introduction

The great value of anomalous elastic X-ray scattering for obtaining phase information and improving contrast in X-ray crystallography has been recognized for a long time (see [1-7] and references therein), and the possibility of varying the atomic scattering factors has been of practical importance in protein crystallography [4,6]. The availability of high intensity tunable synchrotron X-ray radiation has greatly added to the importance of this technique, and the field appears to be expanding rapidly [7-14]. Anomalous scattering methods utilize variation of the atomic scattering power as function of photon energy near inner shell absorption edges. From a crystallographer's point of view, particularly interesting and relevant questions concern (i) which elements show large anomalous scattering for X-ray energies used in diffraction studies and (ii) what are the limits on useful resolution in order to obtain largest possible variation in atomic scattering factors around an X-ray absorption edge.

When discussing structure determination one must distinguish between local structure and extended, periodic structure. Information about local structure can be obtained from various kinds of EXAFS (Extended X-ray Absorption Fine Structure) measurements. Structure at and above inner shell absorption edges has been known for a long time [15,16] but only recently has such structure been used systematically to obtain information about the local structure around the particular ion associated with the absorption edge [17]. In order to obtain higher sensitivity, instead of measuring small variations in a total absorption cross section one can analyze the variation of a particular emission product originating from the ion in question. E.g., by monitoring a characteristic photon or electron emission line one can measure fluorescence

and Auger EXAFS. Since photons and electrons have very different mean free paths, fluorescence EXAFS will be more bulk sensitive and Auger EXAFS more surface sensitive.

In contrast, X-ray diffraction gives information about periodic, extended structure, and the sample must therefore be crystalline. Tuning close to an absorption edge, the dynamic polarizability of the corresponding sublattice of ions will become non-negligible. This will change the scattering properties by introducing a phase shift and as a result the relative intensities of the diffraction spots will vary with photon energy. However, it should be noted that the anomalous atomic scattering factors also show EXAFS structure, and the diffraction experiment therefore also contains information about local structure.

The key quantity in X-ray diffraction is the structure factor $F(\mathbf{K})$, which is the Fourier transform of the charge distribution of the crystal and which gives the positions and intensities of the diffraction spots. For a particular scattering vector \mathbf{K} and for a crystal with several atoms per unit cell, the structure factor $F(\mathbf{K})$ can be written as ([1,13,18] and references therein)

$$F(\mathbf{K}) = \sum_p F_p(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{r}_p) \quad (1.1)$$

where

$$F_p(\mathbf{K}) = f_p(\mathbf{K}) T_p(\mathbf{K}) G_p(\mathbf{K}) \quad (1.2)$$

is the structure factor for the p-th sublattice. \mathbf{r}_p is a vector specifying the different atoms in the unit cell. $f_p(\mathbf{K})$, the atomic scattering factor, and $T_p(\mathbf{K})$ are the Fourier transforms of the atomic charge distribution and the nuclear smearing amplitude respectively. $G_p(\mathbf{K})$ is a geometric structure factor describing the structure of the empty p-th sublattice.

Since experimentally one measures the intensity of the diffraction spots

$$I \sim |F(\mathbf{K})|^2 \quad (1.3)$$

one can only obtain information about the modulus of the structure factor; the lack of phase information therefore makes it impossible to determine relative positions of the different ions in the unit cell. However, phase information can be obtained if the atomic scattering factors can be varied. This has often been accomplished by isomorphous replacement of the ions of a particular sublattice combined with choosing X-ray energies in regions of anomalous dispersion [2-6]. From a number of measurements of this kind one can derive results for the real and imaginary parts of the atomic scattering factor $f_p(\mathbf{K})$ to be used in eqs. (1.1) and (1.2) in order to calculate the total structure factor $F(\mathbf{K})$ and the diffraction pattern. The anomalous part of $f_p(\mathbf{K})$ can be determined in several ways, e.g. by measuring the complex refractive index $\sqrt{\epsilon(\omega)}$ [1], by measuring the intensity difference or ratio between Friedel pair of reflexions ([8,13] and references therein)

$$\Delta I = |F(\mathbf{K})|^2 - |F(\bar{\mathbf{K}})|^2 \quad (1.4)$$

$$R(\mathbf{K}) = |F(\mathbf{K})|^2 / |F(\bar{\mathbf{K}})|^2 \quad (1.5)$$

or by measuring the photon energy dependence of the angle of total reflexion [12] (which also is a measurement of the refractive index).

The remaining part of this paper will be organized in the following way. In section 2 we discuss anomalous scattering in terms of the atomic polarizability and the macroscopic dielectric function. In section 3 we go on to consider various radiative and non-radiative damping mechanisms of importance near absorption edges. The results are applied in section 4 to a case of recent interest, namely anomalous scattering near the L_3 absorption edge in a Cs complex [11]. Section 5 gives an overview of atoms that can be expected to show strong effects of anomalous dispersion in X-ray energy ranges of interest for X-ray diffraction. Finally, in section 6 we discuss the influence of solid state and chemical effects on anomalous atomic scattering factors.

2. The atomic scattering factor

2.1. Introduction

The theory of the atomic scattering factor has a long and successful history [1,19-24] and we refer to literature for comprehensive discussions. Here we shall only give a brief outline of some basic concepts necessary for the subsequent discussion.

For photon energies much higher than the binding energy of the innermost shell, all atomic electrons scatter like free electrons with an atomic scattering factor

$$f(K) \equiv f_0(K) = \int \rho(r) \exp(iK \cdot r) \quad (2.1)$$

which only depends on the atomic ground state electronic charge distribution

$\rho(\mathbf{r})$. In this limit the atomic scattering factor gives the momentum distribution of atomic electrons. For lower photon energies the bound character of the atomic electrons becomes noticeable and there appears a frequency dependent contribution to the scattering factor due to anomalous scattering

$$f(\mathbf{k}) = f_0(\mathbf{k}) + f'(\mathbf{k}) + i f''(\mathbf{k}) \quad (2.2)$$

f' and f'' are related through Kramers-Kronig relations and can be associated with scattering via absorption and reemission of photons, resulting in a phase shift.

2.2. Atomic polarizability and the anomalous scattering factor

In the case of forward scattering, $\mathbf{k}=0$, we have

$$f(\mathbf{k}=0) = f_0 + f' + i f'' \quad (2.3)$$

$$f_0 \equiv f_0(\mathbf{k}=0) = \int \rho(\mathbf{r}) d\mathbf{r} = Z \quad (2.4)$$

where Z is the number of atomic electrons. We can easily find an expression for the forward part of the anomalous atomic scattering factor by noting that in this limit there must be a direct connection with the complex, macroscopic dielectric function and index of refraction. With N atoms per unit volume having dipole polarizability $\alpha(\omega)$ the dielectric function is given by

$$\epsilon(\omega) = 1 + 4\pi N \alpha(\omega) \quad (2.5)$$

and the refractive index by

$$n(\omega) + i k(\omega) = \sqrt{\epsilon(\omega)} \cong 1 + 2\pi N \alpha(\omega) \quad (2.6)$$

In the high-frequency limit the dielectric function is that of a collection of free electrons with mass m and plasma frequency ω_p

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.7)$$

$$\omega_p^2 = \frac{4\pi N Z e^2}{m} \quad (2.8)$$

For lower frequency we write the deviations from eq. (2.6) with the help of a form factor $f(\omega)$ involving all of the Z electrons of a given atom

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \frac{f(\omega)}{Z} \quad (2.9)$$

Combining eqs. (2.5) and (2.9) we obtain

$$f(\omega) = - \frac{m}{e^2} \omega^2 \alpha(\omega) \quad (2.10)$$

which connects the atomic scattering factor with the polarizability. This relation also follows directly from considering the amplitude for elastic scattering of photons.

2.3. Microscopic properties of the atomic scattering factor

The atomic dipole polarizability can be written as

$$\alpha(\omega) = \frac{e^2}{m} \sum_{ni} \frac{g_{ni}}{\omega_{ni}^2 - \omega^2} \quad (2.11)$$

$$g_{ni} = 2 \omega_{ni} |\langle i | z | n \rangle|^2 \quad (2.12)$$

where g_{ni} is the oscillator strength, $\omega_{ni} = E_n - E_i$ is the exact excitation energy and $\langle i | z | n \rangle$ is the dipole matrix element coupling the initial and excited states i and n . Summation over excited states n also implies integration over the corresponding continuum. Combining eqs. (2.10) and (2.11), we obtain

$$f(\omega) = \omega^2 \sum_{ni} \frac{g_{ni}}{\omega^2 - \omega_{ni}^2} \quad (2.13)$$

$$= Z + \sum_{ni} \frac{\omega_{ni}^2 g_{ni}}{\omega^2 - \omega_{ni}^2} \quad (2.14)$$

where we have made use of the Thomas-Reiche-Kuhn sum rule for the oscillator strength

$$\sum_{ni} g_{ni} = Z \quad (2.15)$$

Eq. (2.14) already is on a properly partitioned form, the normal and anomalous atomic scattering factors (forward scattering) being

$$f_0 = Z \quad (2.16)$$

$$f'(\omega) + i f''(\omega) = \sum_{ni} \frac{\omega_{ni}^2 g_{ni}}{\omega^2 - \omega_{ni}^2} \quad (2.17)$$

$$f'(\omega) = \sum_{ni} \text{PP} \frac{\omega_{ni}^2 g_{ni}}{\omega^2 - \omega_{ni}^2} \quad (2.18)$$

$$f''(\omega) = \frac{\pi}{2} \sum_{ni} \omega_{ni} g_{ni} \delta(\omega - \omega_{ni}) = \frac{\pi}{2} \omega \frac{dg_i}{d\omega} \quad (2.19)$$

Fig. 1 schematically illustrates the behaviour of the atomic scattering factor $f(\omega)$ (eq. (2.14)) in the cases of Z bound electrons with a single discrete excited state (resonance, fig. 1a), a continuum of excited states (fig. 1b), and finally Z' electrons in a discrete transition and $Z-Z'$ in a continuum of transitions (fig. 1c). From this schematic picture we may draw two particularly interesting conclusions, which are corroborated by more realistic calculations: (i) For photon energies not much larger than the highest absorption threshold there is really no region with normal dispersion [22,23]; in other words, the refractive index is complex and shows strong variation with photon energy. (ii) Experimental results are often discussed in terms of an effective number of electrons scattering like free electrons and an effective number of electrons lost as one passes down through an absorption threshold. However, in resonance regions the real part of the scattering factor, $\text{Re } f(\omega)$, is not related to the number of electrons in any simple way. In principle, in terms of $\text{Re } f(\omega)$ one can lose more electrons than there are in the physical atom. Inclusion of damping will of course remove the singularities at resonance and limit the variation in $\text{Re } f(\omega)$. However, in principle, $\text{Re } f(\omega)$ can still go negative also at photon energies above the first ionization threshold, meaning that there can be regions of high reflec-

tivity at high photon energies (see e.g. [25]).

For accurate numerical calculation of oscillator strength distributions and anomalous atomic scattering factors one should use self-consistent field (SCF) type of one-electron methods like Hartree-Fock, Dirac-Fock or Dirac-Fock-Slater (local potential). In much of the earlier work the atomic oscillator strength was expanded in power series of ω^{-1} and the threshold oscillator strength calculated using hydrogenic [1,21-24] or Dirac-Fock-Slater [26] wave functions. The results give a good overall picture of the variation of $f'(\omega)$ and $f''(\omega)$ with photon energy but are not very accurate near absorption thresholds, the region of particular interest at present. Especially for heavy atoms the self-consistent atomic potential is strongly non-Coulombic, and one may have to go a distance of the order of the binding energy above threshold for a power series expansion and a hydrogenic approach to become applicable.

For inner shell excitations a Dirac-Fock-Slater (DFS) one-electron scheme should work well. The core hole is then very deep and compact and exchange effects between the excited state electron and the hole are negligible [27]. Cromer and Liberman [28] have calculated DFS continuum oscillator strength distributions and anomalous atomic scattering factors within a relativistic formulation but neglecting damping effects. The results cover the entire periodic system at selected X-ray energies and seem to be the best available at present.

2.4. Scattering angle dependence of the atomic scattering factor

In an actual experiment not even the low index diffraction spots correspond to forward scattering, and high index spots may correspond to large scattering angles and momentum transfer. The intensity drops off rapidly with

increasing scattering angle because for increasing momentum transfer the diffuse part of the electronic charge distribution becomes ineffective in scattering. The anomalous part of the atomic scattering factor, however, is only weakly dependent on the momentum transfer [1,11,18]. Anomalous scattering occurs in the vicinity of absorption thresholds and the wavelength is therefore much larger than the radius of the absorbing shell, so that effectively the scattering takes place in the forward direction. We can then use a hybrid form of eq. (2.2) where the normal part is treated in full while the anomalous part is taken in the forward scattering limit

$$\begin{aligned} f(\mathbf{k}) &\cong f_0(\mathbf{k}) + f'(0) + i f''(0) \\ &\equiv f_0(\mathbf{k}) + f' + i f'' \end{aligned} \quad (2.20)$$

This seems to imply that the relative importance of anomalous dispersion will be larger for high index reflexions, for which $f_0(\mathbf{k})$ can become quite small.

3. Effects of damping

In order to calculate the effects of anomalous dispersion close to absorption thresholds, one has to include damping effects due to radiative and non-radiative emission processes. Until quite recently it has been the custom to neglect damping effects since these only affect a region close to threshold that used to be inaccessible to experiment (see e.g. [1,22]). However, now that this region is of particular interest from an experimental point of view, the damping problem has to be seriously considered in analysis of experimental X-ray diffraction data [8,29]. Since the real and imaginary parts of the atomic anomalous scattering factor are related through a Kramers-Kronig relation (see eqs. (2.17) to (2.19))

$$f'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' f''(\omega')}{\omega^2 - \omega'^2} d\omega' , \quad (3.1)$$

experimental or theoretical knowledge of the absorption cross section is in principle enough to obtain the anomalous part of the forward scattering factor. The result then contains all effects of damping and threshold effects and can be used directly for crystal structure determination. This approach requires knowledge of the absorption cross section over a very wide range of photon energies, which may experimentally be a problem. However, far away from threshold the cross section can be fairly well represented by a series expansion, and one can this way obtain a reasonably good description of $f'(\omega)$ in the threshold region [8,29].

An accurate first principles calculation of anomalous dispersion has explicitly to consider radiative (Fig. 2a,c,e,f,g) and non-radiative (Fig. 2b,d,h,i) damping processes. The radiative damping is due to

resonance fluorescence, from the elastic scattering process itself (Fig. 2e), and to Raman scattering (Fig. 2f) and characteristic fluorescence (Fig. 2g) connected with inelastic scattering. The non-radiative part of the damping is due to autoionization (Fig. 2h) and Auger decay (Fig. 2i). Fig. 3 demonstrates that a low order digrammatic expansion of the elastic scattering amplitude, i.e. essentially the atomic polarizability (cf eq. (2.10)), contains all of the elementary scattering processes. Taken to infinite order, the result can be expressed in terms of broadening and shift of the electron-hole levels and a complex, frequency dependent effective electron-photon interaction (Fig. 3).

The relative importance of the radiative and non-radiative damping terms depends critically on the type of core level and its binding energy. For deep enough K-levels the fluorescence yield ($\Gamma^x/\Gamma^{\text{tot}}$) tends to unity ([30,31] and references therein), in which case radiative decay of the core hole totally dominates, and already around Cu fluorescence and Auger decay are of equal importance. For $L_{2,3}$ hole levels the fluorescence yield is negligible for, say, $Z \leq 50$ and only reaches ~ 0.3 in the range $Z=70-80$ [31,32]; the L_1 fluorescence yield is even lower [31]. For M-shells and higher, non-radiative processes determine the life-time of the hole, except for outer valence shells where Auger processes are energetically forbidden; the now very long life-time is again determined by fluorescence decay, if allowed [33]. To sum up, for elements of interest in X-ray diffraction and crystallography, as a rule of thumb, for K-shell scattering radiative decay processes must always be included while for L-shell scattering radiative damping may be neglected for atomic numbers $Z \leq 50$. Auger decay must always be included, except perhaps for K-levels for $Z \geq 50$.

Let us consider the most important decay processes in greater detail in

a case of special interest, namely X-ray diffraction near the $L_{2,3}$ edge in a Cs complex [11]. In the Cs ion in the presence of a core hole there appears to be a compact, lowlying 5d-like orbital that the excited electron can occupy, giving rise to a prominent threshold resonance in absorption (cf 5p→5d transitions in Ba [34]). In general, the damping depends on the intermediate excited state (for the threshold resonance $i=2p$, $n=5d$)

$$f'(\omega) + i f''(\omega) = \sum_{ni} \frac{1}{2} \omega_{ni} g_{ni} \left[\frac{1}{\omega - \omega_{ni} - i \Gamma_{ni}} - \frac{1}{\omega + \omega_{ni}} \right] \quad (3.2)$$

For excitations to the continuum well above threshold, we may consider the line width Γ_{ni} in terms of the characteristic fluorescence width Γ^x and Auger width Γ^A of the core hole alone ($i=2p$)

$$\Gamma_{ni} = \Gamma_i = \Gamma_i^x + \Gamma_i^A \quad (3.3)$$

However, this is a region where the absorption normally varies slowly enough that damping need not be considered at all. In the threshold region where damping must be included, the width of the intermediate state cannot in principle be considered in terms of broadening of the core level alone: One also has to consider resonance fluorescence (Fig. 2e) and autoionization (Fig. 2h) which contribute a width to the entire 2p→5d electron-hole excitation. The anomalous elastic scattering process (Fig. 2e, Fig. 3) can then be regarded a resonant absorption and emission, and the scattering amplitude and the partial width due to resonance fluorescence become closely related (see e.g. [35]).

In X-ray diffraction and crystallography inelastic processes contribute

to smearing and background of the diffraction pattern and thus represents unwanted processes. However, as an experimental method inelastic X-ray scattering using synchrotron light is becoming a powerful tool for investigation of the electronic structure and excitation spectrum of solids (see e.g. [36]) in a similar way that light scattering using lasers has been for a long time (see e.g. [37,38]). X-ray excited characteristic X-ray fluorescence can also be regarded as inelastic X-ray scattering and has recently been used for studying line shapes of characteristic emission lines near absorption thresholds [39] as well as EXAFS structure in the excitation function [40].

Actually, a unified approach to the problem of X-ray and light scattering seems to be emerging both from a theoretical and experimental point of view. With the very intense and highly monochromatized synchrotron light sources that are becoming available one will be able to study the emitted X-ray spectrum as a function of incident photon energy, following the development of the elastic peak and the inelastic Raman peaks, which trail the incident photon energy, and the inelastic characteristic peaks, which stay at fixed photon energies. In threshold resonance excitation, characteristic lines can become degenerate with and actually indistinguishable from Raman lines and one might expect to observe resonances in individual Raman lines, in analogy with resonances observed in threshold excited photoelectron satellite spectra (see e.g. [41,42]). Also one might be able to observe shifts and distortions of threshold excited characteristic lines due to post collision interaction (PCI) phenomena (see e.g. [42]).

In the case of X-ray excitation, emission and scattering, the life-time of intermediate excited states is often determined by non-radiative (Auger) processes. However, for valence orbitals in free atoms and molecules decay

is purely radiative. Fluorescence life-time measurements using synchrotron light and time-resolved spectroscopy have been performed [33], and it would be very interesting to study such processes under threshold excitation conditions, in which case the excitation and emission processes no longer are independent. In principle one could expect to see PCI effects because emission of a photon does cause a change in the potential seen by the slowly receding photoelectron. However, unlike the Auger case, there is no net change in the electronic charge, and PCI effects might therefore be very weak.

Finally we note that the problem of correlation and damping in resonant intermediate states, and how this links excitation and emission processes, has been given much attention lately in the context of light scattering and statistical physics [43,44].

4. Application to anomalous X-ray scattering around the L_2 edge in Cs

It seems that almost all theoretical calculations of anomalous X-ray scattering factors have assumed that X-ray absorption edges are step-like. Nevertheless, evidence for sharp threshold peaks has been around for more than forty years, since the discovery of the so called "white lines" in X-ray absorption spectra (see e.g. [45] for a discussion and further references). These white lines appear to be associated with transitions from a deep core level to final states with spatially very compact character, which remain partially localized also in a solid due to the attractive influence of the core hole, forming an exciton-like excitation.

Let us now consider the specific case of excitation of a 2p-electron in atomic Cs, with application to anomalous scattering around the 2p-threshold [11]. In the presence of a 2p-core hole there will be low-lying, very compact

5d-orbitals, spacially similar to the occupied 5d-orbitals in the lanthanides and the 5d-transition metals. As a result, the absorption spectrum will be characterized by a $2p \rightarrow 5d$ resonance transition well below the atomic ionization threshold and carrying appreciable oscillator strength. There could also be some non-negligible contributions from $2p \rightarrow 6s$ transitions. The major part of the 2p oscillator strength, however, goes into slowly varying $2p \rightarrow \epsilon s, \epsilon d$ continuum absorption. As mentioned before (sect. 2.3), Cromer and Liberman [28] have calculated the continuum oscillator strength distribution and anomalous scattering factors within an atomic Dirac-Fock-Slater picture. Since the discrete levels below threshold have fairly small integrated strength, the threshold resonance should only influence the anomalous dispersion in a fairly narrow range around threshold. In that region, however, there will be very strong variation around a mean value determined by the continuum distribution alone.

The magnitude of these variations in $f'(\omega)$ and $f''(\omega)$ will depend on the broadening of the discrete sub-threshold excitations. For Cs the L_3 fluorescence yield is ~ 0.1 , which means that to a fair approximation we may neglect radiative damping processes and consider the L_3 width of ~ 2.5 eV to be due to Auger decay. In principle, the width of the $2p \rightarrow 5d$ excitation is not identical to the width of the 2p-core hole, because e.g. autoionization will give an additional contribution to the width as well as to the dipole excitation matrix element (see e.g. [42] and references therein). If we were interested in studying the detailed energy dependence of various partial photoionization cross sections, autoionization probably has to be considered [42]. However, since only total polarizabilities and absorption cross sections are of interest in elastic scattering of photons, we only need to consider the dominating process of Auger decay of the core level. Note that if Auger decay dominates over auto-

ionization the isolated resonance will have essentially Lorentzian line shape, not asymmetric Breit-Wigner-Fano line shape [42]. In particular, there will be no noticeable interference minimum on the low-energy side of the resonance.

Concerning higher lying discrete structure, the distance between levels will be smaller than the core level width. Therefore the continuum will effectively be lowered down to the region of the main threshold resonance, and even in the free Cs atom the absorption spectrum should consist of an approximately Lorentzian, 2.5 eV broad threshold peak followed by a fairly smooth continuum (cf K-spectra of Ar and other systems [30]). For cesium hydrogen(+) tartrate, the experimental threshold absorption results [11,45] do not seem to suggest any pronounced asymmetry in the absorption peak. However, a clear asymmetry on the high energy side has been observed for La and rare-earth metals and compounds [47,48] and 5d-transition metals [45]. From an atomic point of view, this suggests that the threshold resonance cannot be regarded as isolated; intra- and interchannel interactions ($2p \rightarrow 5d, nd, \epsilon d; ns, \epsilon s$) might transfer excitation strength from the resonance to the weaker discrete and continuum states at higher energy. The resonance region can be regarded as a kind of continuum shape resonance and an asymmetric resonance line shape is to be expected. Also, core level asymmetry and structure due to many-electron effects might of course contribute to asymmetry of the threshold resonance (see e.g. [49,50] and references therein).

The core level width sets a limit to the sharpness of the threshold resonance in $f''(\omega)$ and therefore also to the variation of $f'(\omega)$. The maximum variation of $f'(\omega)$ over a resonance is approximately equal to the maximum jump in absorption $f''(\omega)$. In the actual Cs experiment [46], the absorption jump $f''(\omega)$ was ~ 13 and the measured maximum variation in $f'(\omega)$ was also ~ 13 .

However, since the measurement was performed with energy resolution $\Delta\omega/\omega \approx 10^{-3}$, i.e. 5 eV at 5 keV, it seems that by improving the resolution to about 1 eV or better, so that the natural line width dominates, one should be able to observe a variation in the scattering power by as much as 25 electrons over a photon energy interval $\Delta\omega \approx 2.5$ eV and a minimum value of the anomalous atomic scattering factor as low as $f'(\omega) \approx -35$.

Very recently I have become aware of some closely related work by Burek [25] on diffraction properties of crystals with very large lattice constants, e.g. KAP (potassium acid phthalate) with $2d \approx 26.6$ Å for the 001 planes. Near the oxygen K edge at ≈ 525 eV (23.6 Å) Burek reports very strong effects of anomalous dispersion which can only be reproduced theoretically by inclusion of a prominent 0.75 eV wide threshold resonance in the absorption spectrum. Now, oxygen has an open 2p-shell and there should be a prominent $1s \rightarrow 2p$ type of discrete transition below the ionization edge. In the KAP crystal the environment is molecular and the resonance would rather have $1s\sigma \rightarrow 2p\pi$ character. Strong threshold resonances have been observed at the oxygen and carbon K edges in CO and similar molecules [51] and are also theoretically well established [51], and it seems likely that they are the reason for the very strong anomalous dispersion observed in KAP [25].

5. Overview of systems with strong threshold resonances

Generally speaking, absorption spectra of all open shell atoms will show prominent discrete resonances for transitions from core levels with suitable symmetry into the open shell. Some of the elements preceding such series will also show resonances when the additional attraction of the core hole is taken into account. From such considerations alone $2p \rightarrow 3d$, $2p, 3p \rightarrow 4d$ and $2p, 3p, 4p \rightarrow 5d$ threshold resonances in the $3d, 4d$ and $5d$ -transition metals

as well as $2p, 3p, 4p \rightarrow 5d$ transitions in the lanthanide sequence should be of interest. Even more prominent discrete resonances must be connected with transitions to localized $4f$ -like orbitals, e.g. $3d \rightarrow 4f$ in Ba, La and the rare earths [53] and $3d, 4d \rightarrow 5f$ in the $5f$ -elements. For K, L_1 , M_1 etc. absorption one might expect prominent structure in systems with open p -shells, e.g. C to F, Si to Cl [54], Ge to Br etc.

However, in order to be of practical interest in X-ray crystallography the transition energies should lie in the range 5-25 keV (0.5-2.5 Å wavelength), which gives suitable scattering angles for lattice spacings of normal crystals. Unfortunately this eliminates excitations to $4f$ and $5f$ -like states because the binding energy of the $3d$ core level is not more than ~ 3 keV at the beginning of the $5f$ -series. Also it rules out $2p \rightarrow d$ resonances in the $3d$ -transition metals, because the $2p$ binding energy is in the range 0.5-1 keV. This is perhaps particularly unfortunate in view of the great importance of these elements in biological systems. $4d$ -transition elements are probably also ruled out because the $2p$ binding energy lies in the range 2-3 keV. It seems that the only really good candidates for displaying very strong anomalous dispersion in X-ray diffraction using normal crystals, are the $2p$ edges ($2p \rightarrow 5d$ threshold resonances) in the region from Cs to Pt ($Z=55-78$).

If we instead consider special crystals with very large lattice spacing in one or several directions, such as certain organic crystals [25], the situation becomes entirely different. These crystals diffract in the 5-25 Å (0.5-2.5 keV) wavelength region and most of the elements and edges discarded above now become interesting, if and when they occur in such crystals. E.g., crystals containing Ba or elements from the lanthanide series can be expected to show enormous anomalous dispersion around the $M_{4,5}$ edges. Also, light molecular systems can now become important and excitation to

empty low-lying π -orbitals may lead to strong effects of anomalous scattering around carbon, oxygen and other K edges in organic material.

6. Solid state and chemical effects

So far we have discussed $L_{2,3}$ threshold resonance phenomena in terms of atomic transitions, and one may ask what will be left of such resonances in a solid and in particular in a metal. The answer seems to be that the excited state 5d-orbitals are so compact that an atomic-like threshold resonance survives, although sometimes modified by the local environment. This is clearly demonstrated by a wealth of experimental $L_{2,3}$ absorption data showing "white line" behaviour in the metals and metal compounds in the range $Z=57-75$ ([45,47,48] and references therein). For the metal compounds, the resonance can be discussed in terms of a compact $2p \rightarrow 5d$ excitation hybridized with the valence electrons on the neighbouring atoms. For a given metal atom, depending on the compound the 5d levels may lie outside or inside the band of valence electrons; the hybridization can then be quite different for different compounds and the resulting chemical differences can be clearly observed in the threshold region [48]. Since $f''(\omega)$ is directly proportional to the absorption cross section and $f'(\omega)$ is obtained from $f''(\omega)$ via a Kramers-Kronig relation, anomalous X-ray diffraction must be capable of providing detailed information about the chemical environment of a particular atom in the unit cell much in the same way as EXAFS techniques. In the case of K-shell absorption edges for elements around $Z=30$ it has already been demonstrated that $f'(\omega)$ shows detectable structure that must be related to excited state level structure in the threshold region or to EXAFS [8,12]. However, the experimental uncertainty is presently so large that in practice this type of

chemical information can not be obtained with X-ray diffraction techniques.

For the rare-earth metals, recent band-structure calculations [55] have confirmed the picture of a threshold resonance formed from excitation of 2p-electrons into a nearly empty, narrow 5d-band. It seems that a band picture with inclusion of transition matrix elements can give a good description of the shape and magnitude of the threshold resonance even without taking into account the Coulomb attraction and the width of the 2p-hole [55]. Nevertheless, the core hole should cause considerable localization of the 5d-like band states and make the 2p→5d threshold resonance atomic-like (cf. the 3d-transition metals [41]), and this might influence the absolute absorption cross section at resonance and perhaps also the cross section relative to the smoother background from excitations to extended states.

7. Summary

The problem of calculation of anomalous atomic scattering factors can be reduced, to a reasonable approximation, to calculating the photo-absorption cross section, or equivalently, to calculating the discrete and continuum oscillator strength distribution. This gives directly (eq. (2.19)) the imaginary part $f''(\omega)$ of the anomalous atomic scattering factor, and a Kramers-Kronig relation (eq. (3.1)) then gives the real part $f'(\omega)$. Since strong anomalous scattering in the neighbourhood of core level absorption thresholds is of particular interest, the absorption cross section in such regions has to be well described, and hydrogenic approximations are no longer useful. In real heavy atoms and ions the effective one-electron potential can be strongly non-Coulombic, leading to prominent excitations to

bound states or to resonances in the continuum. Effective one-electron schemes like Hartree (Dirac)-Fock-Slater (HFS, DFS) or Hohenberg-Kohn-Sham (HKS) then have to be employed and, in particular, discrete resonances must be included, as well as damping effects.

In the photon energy interval 5-25 keV, particularly relevant for X-ray crystallography using crystals with normal lattice spacings, the only edges showing very strong anomalous scattering effects seem to be the 2p-edges in the elements Cs to Pt ($Z=55-78$), due to 2p \rightarrow 5d atomic-like absorption edge resonances. For an accurate description of this threshold region one must consider atomic-like localization effects as well as effects of chemical bonding and bandstructure. Furthermore, one must understand the structure of the 2p-core level itself, which involves the problem of relaxation and shake-up in systems with a mixture of localized and extended states. Finally, Auger broadening of the 2p-hole has to be included because it represents the main decay mechanism; however, for the 5d-transition metals radiative broadening also becomes important and has to be included as well.

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Figure captions

- Figure 1. Frequency dependence of the real and imaginary parts of the anomalous atomic forward scattering factor $f(\omega)$ (see text).
- Figure 2. Diagrammatic representations of photon scattering and absorption processes, involving absorption of photons and emission of both photons and electrons.
- Figure 3. Feynman diagrams for the amplitude of elastic scattering of photons.