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ISOCHROMAT SPECTROSCOPIC INVESTIGATION OF THE HCP-BCC PHASE TRANSFORMATION OF TITANIUM, ZIRCONIUM, AND HAFNIUM

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Résumé. — D'après les présomptions théoriques la densité d'états électroniques dans la zone centrale de la bande d des métaux de transition diminue, si le réseau change de la structure hexagonale compacte à la structure cubique centrée. Ici on présente des isochromates du rayonnement de freinage des métaux Titane, Zircon et Hafnium mesurées pour la structure hexagonale compacte aussi que pour la structure cubique centrée. On fait voir des différences significantes dans la structure fine de ces isochromates ; elles confirment la présomption théorique.

Abstract. — According to theoretical expectations the electronic density of states in the mid-part of the d-band of transition metals should decrease, when the lattice structure changes from the hcp to the bcc phase. Highly resolved bremsstrahlung isochromats of the hcp and bcc phases of Ti, Zr, and Hf are presented. Significant differences in the fine structures of these isochromats are shown, which confirm the theoretical expectation.

I. Introduction. — The conduction band of transition metals may be described as the superposition of a narrow « d-band » of high density of states with a broad « s-band » of low density of states. This general feature is well confirmed, amongst others by the results of classical X-ray spectroscopy.

Newer calculations of energy bands show, that the density of states in the d-band of transition metals is no smooth curve, but has a marked fine structure with some maxima and minima. This fine structure of the d-band essentially depends on the type of the lattice [1].

One of the features, common to numerous band calculations, is [1]: for bcc structures the d-band is subdivided in a bonding half and an antibonding half, separated by a region of a low density of states. For hcp and fcc lattices this minimum in the mid-part of the d-band is not or at least not so distinctly expected.

How can this theoretical statement be examined experimentally ?

The bcc metals Cr, Mo, W have low values of the density of states at the Fermi level, this may be concluded from measurements of the electronic specific heat γT [2]. Since the Fermi levels of these metals lie in the central part of the d-band, this experimental result may be considered as an indication that the expected minimum in $D(E)$ really exists [1].

Yet this theoretical statement may be tested in a more direct manner by such experiments, which give the density of states not only at the Fermi level, but

in an extended region of the conduction band. Amongst others, the isochromat spectroscopy belongs to these spectroscopic methods [3].

II. Bremsstrahlung isochromats. — A. PRINCIPLE OF THE METHOD. — Highly resolved bremsstrahlung isochromats give a picture of the density of states in the unoccupied part of the d-band above the Fermi level [3].

With the usual assumption — transition probability $P(E) = \text{const}$ — the measured intensity

$$I(E) = P(E) \cdot D(E)$$

is proportional to the density of states. The assumption of a constant transition probability is more reliable for the isochromat spectroscopy than for the classical X-ray spectroscopy in emission or absorption [3], where this assumption is too narrow as has been proved earlier [4].

For the following reasons the transition metals Ti, Zr, and Hf are well suited for the intended special investigation of the fine structure of the d-band :

1) here the interesting states in the mid-part of the d-band are unoccupied and hence can be investigated by the isochromat technique ;

2) these metals have a hcp low-temperature phase and a bcc high-temperature phase ; i. e. the density of states for the two different lattice structures can be investigated at the same probe under equal conditions ; only the temperature of the probe (anode) has to be changed.

B. EXPERIMENTAL RESULTS. — Figure 1 shows the isochromats of the hcp and bcc phase of Ti, Zr and Hf. The temperature of the probes during the measurement was about 70 K below, resp. 70 K above the temperature of the phase transition hcp-bcc.

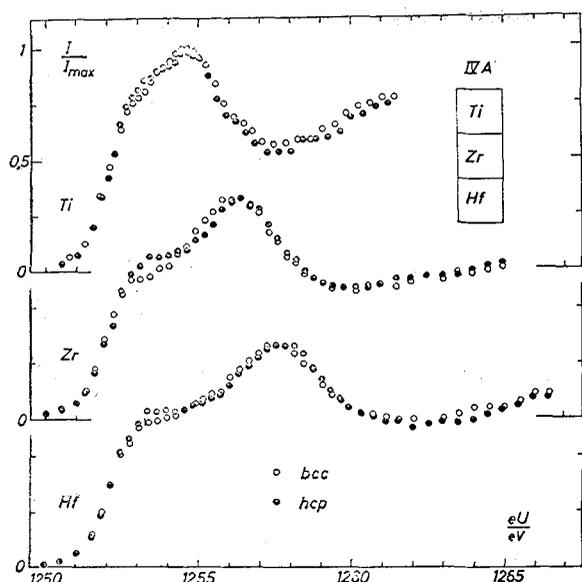


FIG. 1. — Bremsstrahlung isochromats of Ti, Zr, Hf : hcp and bcc phase. All curves are normalized to equal height of the isochromat maximum. The statistical standard deviation is smaller than the diameter of the measuring points.

The maximum of the isochromats corresponds with a region of high density of states in the unoccupied part of the band. These structures in the d-band get broader, when going from the 3 d- to the 5 d-elements in one column of the periodic table [5], [6].

The interesting states in the central region of the d-band, which shall be studied in this investigation, lie on the initial part of the isochromats of Ti, Zr, and Hf, half-way up to the maximum. Here the isochromats of all three metals show a significant difference for the two phases: the intensity of the hcp isochromat is greater than that of the bcc curve.

The identical characteristic feature of all three metals can be seen more clearly in figure 2. Here the differences between the hcp and bcc isochromats of figure 1 are shown; the differences are statistically significant.

The Fermi levels of Ti, Zr, Hf lie in the lower half of the rise to the isochromat maximum: for Zr and Hf halfway up to the step [7]; for Ti nearly halfway up to the point where the slope changes (Fig. 1).

The shape of the isochromat near the onset is essentially determined by the temperature dependent Fermi distribution [8]. Because of the lower measuring temperature the hcp curve starts at a slightly higher voltage, but more steeply.

Yet the differences in the intensity of the isochromats of the two phases cannot simply be explained by the influence of the Fermi distribution; for in this

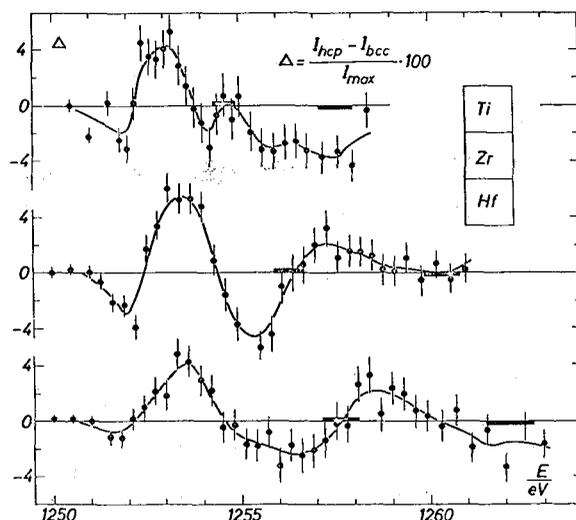


FIG. 2. — Difference of the hcp and bcc isochromats of figure 1. Fully drawn curve: gliding average. The regions of the maximum and of the following minimum of the isochromats are heavily marked on the abscissa.

case the height of the step should not change with temperature and should be the same for the two phases of Zr and Hf.

Thus this isochromat spectroscopic investigation shows directly, that for bcc transition metals the mean density of states in the central part of the d-band is lower than for hcp metals.

III. Discussion of selected examples. — **A. DENSITY OF STATES OF TITANIUM.** — There are different methods, which give information about the density of states [3]. In figure 3 the available newer experimental and theoretical results, concerning the shape and the fine structures in the density of states — both in the occupied and unoccupied part of the d-band — have been collected. Here only the case of Titanium will be discussed as a representative example.

In order to facilitate the comparison between the results of different methods, all curves in figure 3 are normalized to equal height of the maximum; the Fermi level corresponds with the zero point of the abscissa.

Results of those experimental techniques, which are complementary with respect to occupied, resp. unoccupied states [3], are collected in one picture. In figure 3 results of the following methods are compiled:

a) Upper diagram: energy distribution of electrons, released by quanta (PE) — bremsstrahlung isochromats (IS 1, 2).

In both methods no deeply lying atomic level with its disturbing energy width and its atomic symmetry is involved [3].

For Ti no photoemission measurements are known which use quantum energies comparable with those

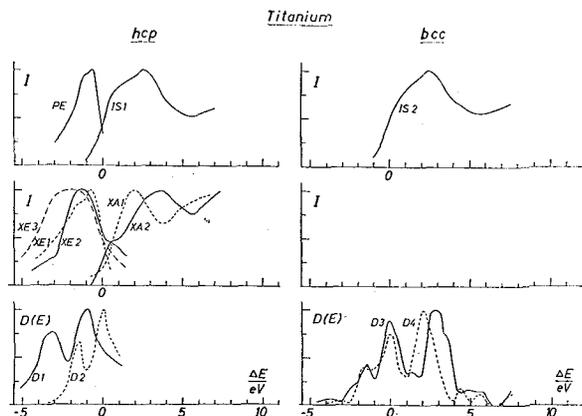


FIG. 3. — Compilation of experimental and theoretical results, concerning the fine structure in the density of states of the d-band of Ti. Methods : photoemission (PE) ; isochromat spectroscopy (IS 1, 2) ; X-ray emission (XE 1-3) ; X-ray absorption (XA 1, 2) ; theoretical densities of states (D 1-4). All curves are normalized ; the Fermi level lies at the zero point of the abscissa. The curves are taken from the following references : PE [9] ; IS 1, 2 this paper figure 1 ; XE 1 [10] ; XE 2 [11] ; XE 3 [12] ; XA 1 [13] ; XA 2 [11] ; D 1, 2 [14] ; D 3, 4 [15].

of the isochromat measurements of this paper (~ 1250 eV). Therefore a measurement in the UV region [9] with its « optical density of states » is cited here.

b) Middle diagram : X-ray spectroscopy in emission (XE 1-3), resp. in absorption (XA 1-2).

Here *K*-spectra (XE 1, XA 1), *L*-spectra (XE 2, XA 2), and a *M*-spectrum (XE 3) are plotted.

c) Lower diagram : theoretical densities of states (DE 1-4).

The calculation for hcp Ti [14] has been performed merely up to the Fermi level ; therefore no comparison with measured isochromats can be made.

This picture too shows, that the fine structure in the density of states substantially depends on the lattice type ; different assumptions concerning the underlying potential chiefly change the width of the structures in the d-band [1].

When comparing the different hcp curves no full agreement can be stated. The calculated hcp curves show two maxima in the occupied part of the band. Accordingly the experimental curves (XE 1 after unfolding) show a double structure ; yet the distance between the two lines is smaller than in the calculation. Possibly this two components are not resolved in XE 2 and XE 3.

For the unoccupied part of the band both the isochromat IS 1 and the X-ray absorption XA 2 show a marked maximum with a change in the slope half-way up to the maximum. The *K*-absorption XA 1 has a different shape : because of the 1-selection rule only p-like states, but not the d-like states, can contribute to the absorption.

B. COMPARISON OF ISOCHROMATS WITH THEORETICAL DENSITIES OF STATES. — Figure 4 shows a more direct comparison of measured isochromats with calculated densities of states (if available). For that, the theoreti-

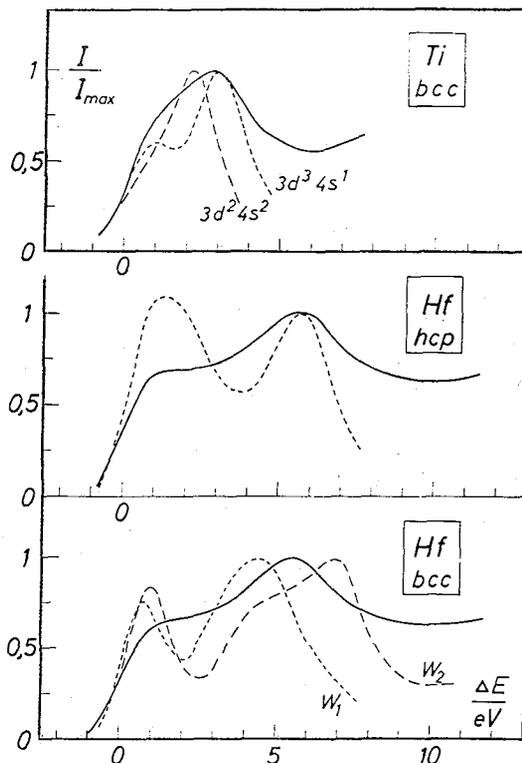


FIG. 4. — Comparison of measured isochromats (fully drawn curves) with theoretical densities of states. Dashed curves : theoretical density of states, folded with the window function of the apparatus. For explanation see text.

cal curves are multiplied with the Fermi function and then are folded with the window function *A*, in order to consider the limited energy resolution of the apparatus [8] :

$$I_{\text{calc}}(E) \propto [D(E) \cdot \{1 - f(E)\}] * A.$$

All curves of figure 4 are normalized to equal height of the maximum.

For Hf no band calculations are known. Therefore here computations for hcp rhenium [16], resp. bcc tungsten [17] are used (after a corresponding change of the position of the Fermi level). According to the conceptions of the rigid band model this should be possible for neighbouring elements with equal lattice structures in one row of the periodic table [5], [6].

The two broad lines in the folded curves are indicated in the measured isochromats. For Hf the first calculated line corresponds to the step in the rise of the isochromat ; in the case of Ti because of the smaller band width no marked step is formed in the isochromat ; however the double structure here leads to a strong asymmetry of the isochromat maximum.

The calculated maxima in the region 0-2 eV above the Fermi level are indicated in the measured curves

in a weakened form only. Possibly this may be due to the smearing out of structures in the density of states on account of the high temperatures during the measurement [8].

Figure 4 shows that for Ti and Hf the distance between the two calculated lines strongly depends on the assumptions concerning the potential. When comparing such distances the result should be independent of special assumptions for the transition probability. Such a comparison yields :

a) *bcc Ti* : the electronic configuration of metallic Ti lies nearer to $3d^3 4s^1$ than to $3d^2 4s^2$ (atomic Ti has the configuration $3d^2 4s^2$).

b) *bcc Hf* : the fine structure calculated with the potential W_1 [17] is too narrow ; the potential W_2 [17]

with a different exchange term gives a d-band which is too broad.

A comparison of the folded curves for hcp and bcc Hf shows, that in the region 0-2 eV above the Fermi level (the region of the step in the isochromats) the total number of states is significantly smaller for bcc Hf than for hcp Hf.

That agrees with the fact, that the intensities differ between the hcp and bcc isochromats in this region of the step (Fig. 1) ; that supports the conclusion, that the mean density of states diminishes in this central part of the total d-band when the phase transformation hcp to bcc occurs.

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DISCUSSION

M. HAGSTRÖM. — Have you made any measurements on liquid metals ?

M. MERZ. — No, but we intend to investigate liquid metals later on.