The L spectra of some iron-group metals

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SUMMARY

In Part I a new kind of X-ray spectrometer is described in which the crystal is bent in the shape of a cylinder. The main features of the instrument are high resolution and a high luminosity. The spectral lines are stigmatic images of the line focus. Shape of the spectral lines and gain in intensity over known spectrometers are calculated. Adjustment and operation are very simple. It may be said that the instrument makes the little-explored region of 10-20 Å much more accessible.

Part II is devoted to the measurements and the discussion thereof. Chapter I contains a short survey of previous X-ray work related with the energy bands of Cu, Ni, Co and Fe, together with a brief description of the principles of methods for calculating the energy bands of metals.

Chapter II describes the measurements. The $L_{II,III}$ absorption spectra of pure Cu, Ni, Co and Fe as well as of some alloys containing these elements have been observed, the greater part for the first time. The $L\alpha$ spectra of pure Cu and Ni have been obtained for different excitation conditions. Some of the more interesting results are:

(1) the L_{III} absorption edges of Ni and Fe shift with increasing temperature to higher frequencies whereas such a shift is not observed for Cu,

(2) the maximum of the Cu $L\alpha$ line shifts to higher frequency and the line broadens with increasing temperature, the same being observed for increasing energy of the incident electrons,

(3) for energy of the incident electrons (= E_{inc}) equal to the excitation energy of the L_I or L_{II} level (= E_{L_I} or $E_{L_{II}}$) the $L\alpha$ lines for Cu and Ni are nearly symmetrical lines, tailing out to both long and short wavelength side; also they do not exhibit an emission edge in contrast to the $L\alpha$ lines for higher energy of the incident electrons,

(4) the CuNi (96, 4) Ni L_{III} absorption still shows a "white line" indicating, contrary to expectation, the presence of $3d$ holes,
(5) such a "white line" is not observed in NiAl (20, 80) Ni L_{III} in accordance with expectation,
(6) FeAl (30, 70) Fe L_{III} shows a "double white line" whereas Fe L_{III} is single for pure Fe in which case a "double white line" might be expected according to theoretical considerations.

Chapter III deals with the views pertaining to the interpretation of the observed emission and absorption band shapes and their connection with the theoretical density-of-states curve. It appears that only for 42 Mo approximate agreement between theory and experiment exists.

Chapters IV and V are devoted to a discussion of the measurements. From a comparison of various measurements the X-ray spectrum is concluded to represent the density-of-states curve. However, interband transitions appreciably influence the shape of Cu $L\alpha$, whereas the influence on Ni $L\alpha$ is only small. The influence of temperature is much larger than expected. An explanation of the observed effects can be given by assuming the screening of the *nearly atomic* $3d$ electrons to depend critically on the measure of hybridization of the *nearly free* $4sp$ electrons. An increase in the measure of s character of the conduction electrons amounts to an increase in the screening of the $3d$ electrons and hence in a shift in the level scheme of the average $3d$ level. A change of only 0.02 in the screening constant of the $3d$ electrons results in a shift larger than 1 eV in the case of copper. A qualitative understanding of the effects is reached. Specifically it is a.o. possible to understand:
(1) the *gradual* change from symmetrical Cu $L\alpha$ line for $E_{inc} = E_{L_I}$ to, with increasing E_{inc}, more and more asymmetrical line,
(2) the *sudden* change from symmetrical Ni $L\alpha$ line for $E_{inc} = E_{L_I}$ ($E_{L_{II}}$) to asymmetrical Ni $L\alpha$ line for E_{inc} differing less than 20 Volt from E_{L_I} or $E_{L_{II}}$,
(3) the shifting of the L_{III} absorption edge for Ni and Fe and the absence of such for Cu,
(4) why the interband transitions so strongly influence the Cu $L\alpha$ line shape but hardly affect the Ni $L\alpha$ line shape.

Although the explanations are rather speculative, it is tempting to investi
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is tempting to investigate whether they permit an understanding of other measurements where such a mechanism might be important. It is shown in Chapter VI that indeed the shifting of $3d$ and $4sp$ band relative to each other enables one to qualitatively understand:

(1) the non-agreement between calculated and observed density-of-states curves for the transition metals and the approximate agreement in the case of 42 Mo,
(2) the non-agreement between the measurements of Gyorgey and Harvey and those of Skinner et al. of the $M_{\mathrm{II,III}}$ emission bands of the iron-group metals.
(3) the susceptibility versus temperature curve for pure copper,
(4) the shift with temperature of the optical absorption of pure copper,
(5) the small discrepancy between theoretical and observed saturation magnetization curves,
(6) the hitherto very puzzling Cu $L\alpha$ and Ni $L\alpha$ line shapes for CuNi alloys of different composition,
(7) the number of Bohr-magnetons per atom versus composition curve for CuNi alloys,
(8) the susceptibility versus temperature curves for CuNi alloys of different composition which show a hitherto unexplained rise of the susceptibility with temperature.