Self-Absorption in the X-Ray Spectroscopy of Valence Electrons

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It is shown that target self-absorption has modified some $K\beta_5$ emission profiles previously observed. The effect has been to produce an exaggerated asymmetry, to depress certain satellites, and to produce an apparent coincidence of the absorption and emission edges.

INTRODUCTION

TARGET self-absorption in x-ray production is a well-known and common phenomenon. Measurements on efficiency and absolute intensities must be corrected and this is done as a matter of course.[1] However, self-absorption has been ignored by x-ray spectroscopists who have examined the emission spectrum from valence electron→empty inner shell transitions.[2] It has been assumed that the electron beam impinging on the target face is stopped so close to the surface that the self-absorption of the x-rays will be negligible. For the valence electron→inner shell transitions, one is in the neighborhood of the absorption edge, and the abrupt change in the absorption coefficient could modify the emission profile if the radiation passes through a significant amount of target material. For studies of the 1–2 A region with which we are primarily concerned, the penetration depth of the cathode electrons into the anode is of the order of a few thousand A. When the radiation is observed at a small take-off angle, the x-ray path in the target is such that significant intensity differences are to be expected on the two sides of the edge.

When care is taken to eliminate self-absorption, the true curves are different from some which are found in the literature which have previously been accepted as correct. The effect of the self-absorption is to produce an exaggerated asymmetry and to suppress the intensity of the satellites having energies greater than the K excitation energy. The reported coincidence in this energy region of the top of the filled bands and the bottom of the empty bands is not borne out in the new curves. It is likely, however, that satellite structure and relatively poor resolving power due to the width of the K state accounts for this, so that the solid state interpretations based on the original curves are not seriously in question.

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[1] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), p. 83.

[2] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935); W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939). See in particular Beeman and Friedman, p. 401.

EXPERIMENTAL

Measurement of the $K\beta_5$ line of Cu and Fe and the $L\beta_5$ of W were made with commercial Philips x-ray tubes. The voltage employed was about 20 kv and the tube was so mounted that the take-off angle was approximately 4.7°. A continuously-pumped x-ray tube was also used for measuring the $K\beta_5$ line of Cr, Fe, Ni, Cu, and Zn, and the $L\beta_5$ line of W. Interchangeable target assemblies were used in which the angle of target take-off was 60°. With this steep angle the usual electrode geometry had to be modified, but it is felt that with this arrangement, the x-ray path in the target was no greater than the penetration depth of the electron. The 60° Fe, Ni, and Cu targets were silver-soldered to a copper cylinder to form the anode. The W and Zn targets were made by vacuum evaporation onto the Fe target. The Cr target was produced by electroplating onto the Cu.

The high voltage and current were obtained from a standard rectified and stabilized x-ray power supply. The data were obtained with a commercial Geiger tube and scaling circuit. The calcite crystals in the two crystal spectrometers had a 1–1 width of about 0.9 volt at the W $L\alpha_1$ line which is good enough to satisfactorily reproduce K edge structures previously observed in this energy range. The question of resolution could play a role in the interpretation of some of the results. In order to get good statistics a relatively high beam was used, but the calculated geometric resolving power was never poorer than 25 000. Our resolution was not quite as good as in the references cited, but the gross features that were obscured by self-absorption are well resolved by our apparatus.

DISCUSSION OF THE CURVES

The W L_{III} edge was measured by using a commercial tungsten target x-ray tube as the source of radiation with a 4.7° take-off angle. This edge structure, shown in Fig. 1(b), is much like that previously given by Bearden and Snyder[3] and the single-crystal work of Coster and Bril.[4] The strong absorption peak, not usually found in metals, arises because of the role of the permitted $2p\rightarrow 5d$ transition. Despite the metallic nature of tungsten, the individual atomic angular

[3] J. A. Bearden and T. M. Snyder, Phys. Rev. **59**, 162 (1941).

[4] D. Coster and A. Bril, Physica **10**, 391 (1943).

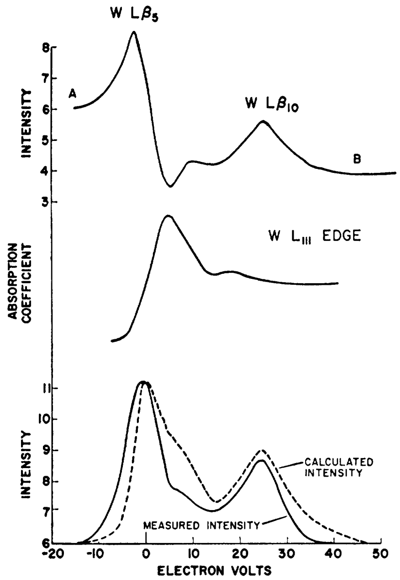

FIG. 1. (a) The observed tungsten emission structure in the neighborhood of the W L_{III} edge for a 4.7° target angle. (b) The W L_{III} edge. (c) The tungsten emission structure near the W L_{III} edge with absorption corrected (dotted line) and absorption eliminated (solid line).

momentum numbers must retain some significance in the partially filled d band.

Of more direct interest for the present discussion is the plot of the emission [Fig. 1(a)] used for measuring the absorption edge. Three things are noteworthy about this curve: (1) The emission in region B is only two thirds as great as that found in region A, (2) the sharp dip in the emission curve occurs at precisely the same point as the maximum in the absorption, and (3) the observed $L\beta_5$ line is apparently very asymmetric and the top of this emission apparently coincides with the inflection point in the leading edge of the absorption curve,[5] which has been taken to be the top of the Fermi distribution.[6]

The first two points make it rather obvious that the emission profile has been profoundly influenced by the target self-absorption of its own radiation. Furthermore, it raises the possibility that the third point is the result of self-absorption rather than any intrinsic characteristic of the W $L\beta_5$ emission line.

Without any further information than the curves of Fig. 1(a) and 1(b) and the assumption that there is an effective depth of penetration of the cathode electrons, it is possible to calculate what the emission contour should be. This is done in the dotted curve Fig. 1(c). One observes that the corrected $L\beta_5$ is not very asymmetric if asymmetry can be measured here, and there is apparently some line structure (presumably a satellite) between $L\beta_5$ and $L\beta_{10}$. The amount of target material traversed by the radiation calculates to be 2.2×10^{-4} cm, which from the geometry yields an effective penetration depth for the cathode electrons of 1.8×10^{-5} cm. This figure is quite reasonable.

In order to remove the uncertainties involved in employing the effective-depth concept, the same emission structure was measured with a 60° target, but even so the intensity on the high-absorption side is several percent less than on the low-absorption side of the edge. The measured structure with this target angle is the full curve of Fig. 1(c). The agreement between the curve for which the absorption is corrected and the curve in which it was essentially eliminated is satisfactory considering the uncertainties involved. The observations made from the dotted curve are substantiated, and it is noted that the presumed top of the Fermi distribution as obtained from the absorption curve is not coincident with that obtained from emission. However, this could well be a result of the width of the K state and the crystal width rather than anything more fundamental.

Since the effect on the $L\beta_5$ emission contour in tungsten for a small take-off angle was quite severe, it becomes necessary to investigate the extent to which self-absorption has modified the $K\beta_5$ curves which are found in the literature. In these curves a high asymmetry is observed as is an apparent coincidence of the emission and absorption edges. These curves were taken with 12° take-off angles and apparently with voltage

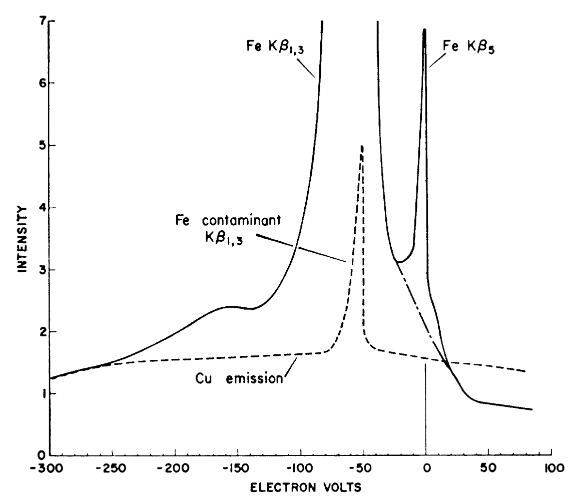

FIG. 2. Iron emission structure for a 4.7° target angle in the vicinity of the Fe K edge with copper emission as the reference level.

[5] The position of this inflection point is somewhat in doubt. The curves of Bearden and Snyder have a slightly different shape on the leading edge and they place the inflection point at about three fourths the height of the main peak. Granting that their data pertaining to this point may be better than ours, the assumptions implicit in the theory of this inflection point do not seem to warrant selecting a point higher than half of the absorption jump as the top of the Fermi level. Furthermore, the recent discovery of Parratt that the asymmetric window of x-ray spectrometers can materially affect the absorption close to the edge must be considered.

[6] Richtmyer, Barnes, and Ramberg, Phys. Rev. 46, 843 (1934).

as high as 35 kv. Considering the various factors involved such as angle, voltage, density, and absorption coefficient difference, it seemed likely that self-absorption did modify their results.

A measurement was again performed on a commercial x-ray tube which had an iron anode (Fig. 2). The take-off angle was 4.7° and the voltage was 24 kv. The dotted curve is a reference curve taken with a Cu tube for purposes of establishing a base line which will account for intensity variations over the wide angular coverage.

The effect of self-absorption in this extreme case is obvious. It should be noted that it is not so much that the structure is reduced to a certain fraction of its proper intensity which produces the erroneous result; rather it is the increasing absorption due to the slope of the absorption edge which makes the tail of the $K\beta_1$ line appear to extend farther than it actually does. This causes one to make an improper correction for the $K\beta_1$ line such as the dashed line shown. A good correction for absorption can be made by making a simultaneous measurement on the absorption edge as was done in the case of tungsten. A similar study on a commercial Cu tube was not useful because we did not anticipate the structure on the low-energy side of the $K\beta_1$ line. The magnitude of the structure and its displacement is consistent with an explanation of this effect as Compton-shifted $K\beta_1$ emission.

Although the calculations based on effective depth are revealing, the measurements on high-angle targets must be made to insure reliable results. Studies were made using the 60° targets previously described, and the results are shown in Fig. 3. For comparison a few of the curves in the literature are plotted to the same scale. The general results are: (1) the $K\beta'''$ structures are relatively more intense than the figures cited in the literature by orders of magnitude. In particular the Cr $K\beta'''$[7] which Bearden and Shaw state is nonexistent is actually a fairly intense structure found at energies corresponding to the high absorption side of the Cr edge. (2) The asymmetries quoted are not correct and, indeed, except in the cases of Cr and Fe they would be meaningless to measure. (3) The theoretical solid-state discussions based on the asymmetries and the apparent coincidence of the top of the emission band and the beginning of the absorption band[8] rest on less firm experimental evidence than was previously thought. Furthermore, some of the effects observed in alloys of various concentrations seem explainable in terms of the amount of absorbing material the radiation had to pass through.

[7] The presence of the Cr $K\beta'''$ is, of course, well established from the work of H. Beuthe, Z. Physik **60**, 603 (1930) and others.

[8] Y. Cauchois, Phil. Mag. **43**, 375 (1952) has commented on one case at least in which such a coincidence is definitely not observed.

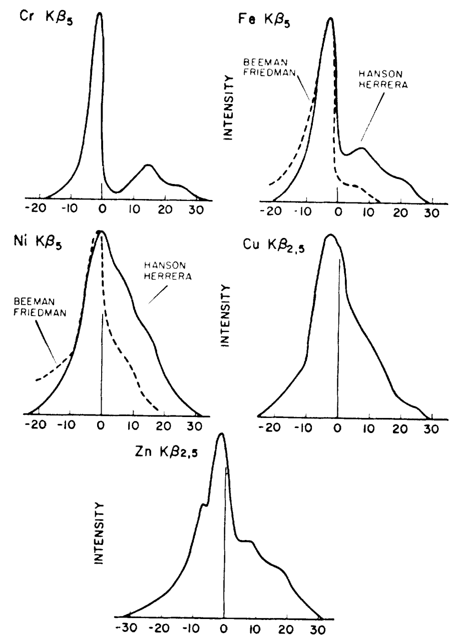

FIG. 3. Emission in the vicinity of K edge with 60° target angles. The units on the abscissas are electron volts.

On the basis of this study, one is entitled at least to raise the question whether self-absorption played a role in the classic experiments on light metals.[9] In general these studies were performed with small target angles and low voltages. Assuming that the cathode electron has a depth of penetration at least equal to the mean free path of a valence electron, the possibility exists that some of these studies were not as conclusive as they appeared to be. Numerous bits of evidence seem to suggest that target self-absorption played a role of some importance and, indeed, it may be possible to understand some of the apparent anomalies in this light. For example, the excessive broadening of the emission edges at elevated temperatures may be partially the result of a concomitant broadening of the absorption edge. It may even be possible to explain the existence of many of the so called "tails" which go off almost indefinitely toward long wavelengths by the characteristic variation of absorption coefficient with wavelength on the long wavelength side of the edge. While one cannot seriously suggest that significant flaws exist in this body of information, it would seem to be advisable that further study show that self-absorption did not play a role.

ACKNOWLEDGMENTS

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[9] H. W. B. Skinner, Repts. Progr. Phys. **5**, 257 (1939).