

## Letters to the Editor

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### Precision Method for Obtaining Absolute Values of Atomic Binding Energies

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**W**E have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method is an old one: a magnetic analysis of electrons expelled from a substance exposed to x-radiation. Previous attempts in this direction have, however, given considerably less information about atomic structure than ordinary x-ray spectroscopic experiments, and some twenty years ago the method seems to have been definitely abandoned. We have introduced a number of improvements, both regarding the intensity and, in particular, the accuracy (a factor 100), which now enables us to measure atomic binding energies with an accuracy of one single electron volt from microgram quantities. The definition of the lines is essentially limited by the natural line widths of the atomic levels themselves. There is no shift of the lines due to electron scattering or similar causes, which could introduce systematic errors.

Our present most accurate knowledge of atomic binding energies stems from x-ray absorption spectra. However, the energies obtained there are not the true binding energies but the energy differences between internal atomic shells. The definition of the slopes of the absorption edges and their interpretations do not allow better estimates of the binding energies than within 10 ev; in most cases the uncertainty is much greater. By our method we obtain the true binding energies directly from well-defined and sharp electron lines, the peaks of which can be localized well within 1 ev. Furthermore, we can study the Auger spectra in great detail.

A more complete description of the experimental arrangements will be given in a later paper<sup>1</sup> and they will only be mentioned briefly here. The magnetic spectrometer is of the iron-free, double-focusing type with  $\rho=30$  cm. A compactly designed x-ray tube with exchangeable anode, filament, etc., has been built into the spectrometer tank close to the sample holder

which supports a thin evaporated layer of the substance under investigation. Our present G-M detector window transmits electrons down to  $\sim 4$  kev. The external magnetic fields, including the earth field, is compensated to within less than 0.1%.

In our first measurements we have used a Mo anode with a Zr filter and Cu as the object of study. On a thin ( $0.5\mu$ ) Al backing, 0.5 mm wide and grounded at both ends, an equally wide Cu film ( $\sim 500$  A thick) was evaporated. Further, a layer of ThB was collected on the source for energy calibration.

Figure 1 shows the doublet arising from Cu *K* shell electrons expelled by the  $K\alpha_1$  and  $K\alpha_2$  radiation of Mo. As expected, the intensity ratio is close to 2:1. On the low-energy side of each line one can distinguish a satellite, which we have interpreted as due to *K* photoelectrons, scattered inelastically in the source. These peaks correspond to a discrete energy loss of about 16 ev, which is in good agreement with what has been found in other connections in electron physics.<sup>2</sup> The energies of the lines are  $8493.7 \pm 1$  ev and  $8388.4 \pm 1$  ev, respectively. The energies of the Mo  $K\alpha_1$  and  $K\alpha_2$  x-ray lines are known accurately to be 17 479.0 ev and 17 374.1 ev, respectively. Subtracting the photoline energies from those of the corresponding x-ray lines, we obtain two partly independent values of the total *K* binding energy of Cu:  $8985.3 \pm 1$  ev and  $8985.7 \pm 1$  ev, in excellent agreement with each other. (All atomic constants used in the calculations have been taken from the values given by DuMond and Cohen.<sup>3</sup> Further, the  $B\rho$  value of the *F* line of ThB is here assumed to be<sup>4</sup> exactly 1388.44 gauss-cm.) We have been able to check this value of the binding energy by the observation of other lines in our electron spectrum, which are due to

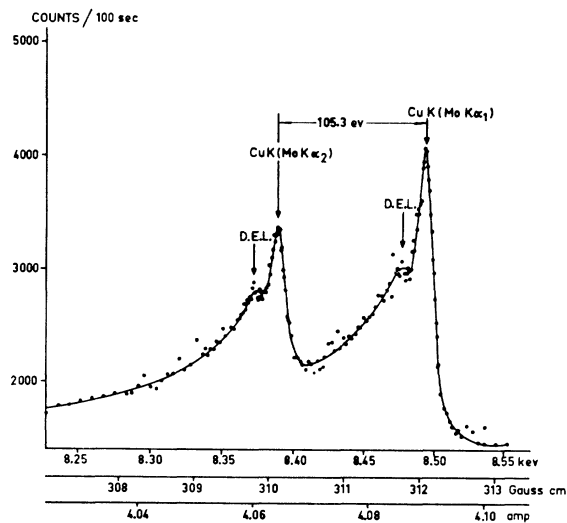


FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo  $K\alpha_1$  and Mo  $K\alpha_2$  x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

the x-radiation of Zr. The binding energy of the Cu  $L_1$  shell has been measured in the same way to be  $1100 \pm 4$  ev. It is satisfactory to note that the energy difference between our  $K$  "doublet" lines, 105.3 ev, is in good agreement with the energy difference of the two  $K\alpha_1$  and  $K\alpha_2$  lines as obtained from ordinary x-ray spectra, namely 104.9 ev.

The  $KLL$  and  $KLM$  Auger spectra from Cu were also obtained. In particular, the former spectrum yields a number of well-resolved lines which have not been observed before.

A close study of the accuracy in determining the exact positions of the electron lines reveals a relative uncertainty in the  $B\rho$  values of  $\sim 1:40\,000$ .

We plan to extend our investigations to other elements over the periodic table. The influence of alloying on the binding energies is also of interest in this connection. A complete description of the experiments will be published shortly,<sup>1</sup> together with a discussion of the Auger spectra and their theoretical interpretation.

<sup>1</sup> Sokolowski, Nordling, and Siegbahn, *Arkiv Fysik* (to be published).

<sup>2</sup> G. Haberstroh, *Z. Physik* **145**, 20 (1956).

<sup>3</sup> J. W. M. DuMond and E. R. Cohen, *Revs. Modern Phys.* **25**, 691 (1953).

<sup>4</sup> K. Siegbahn and K. Edvarson, *Nuclear Phys.* **1**, 137 (1956).

### Anomalous Isotope Effect in Metallic Diffusion\*

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IN most cases of diffusion in metal systems, the temperature dependence of the diffusion coefficient for radioactive tracers diffusing into pure metal crystals is found to obey an Arrhenius equation of the form  $D = D_0 \exp(-H/RT)$ , where the frequency factor  $D_0$  and activation energy  $H$  are temperature-independent. Because of the general consistency of the experimental results, considerable confidence has been placed in the application of the theory of absolute reaction rates<sup>1</sup> to problems of mass transport in solids.<sup>2</sup> In addition to predicting the observed temperature dependence of the diffusion coefficient, the theory predicts that if two different isotopes of the same element diffuse into a solid, the lighter isotope will diffuse faster than the heavier by the ratio of the square root of the isotopic masses, independent of the diffusion mechanism operative.

As a critical check on this theory, we have studied the diffusion of  $Fe^{55}$  and  $Fe^{59}$  in pure monocrystalline silver. The isotopes were obtained in pure form from the Oak Ridge National Laboratory, and the isotopic purity checked by taking gamma-ray spectra, absorption curves, and half-life measurements. The counting

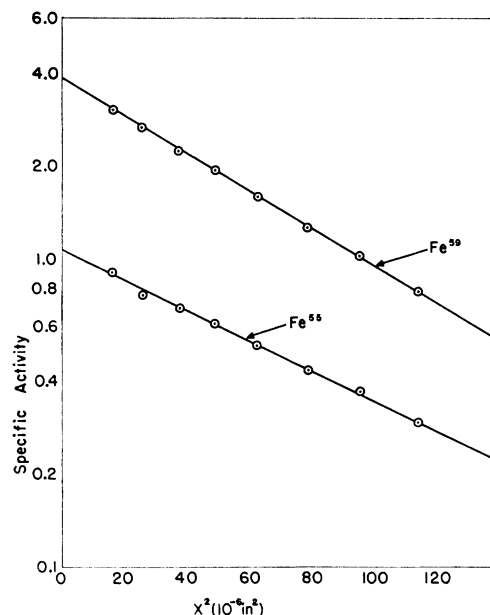


FIG. 1. Diffusion of  $Fe^{59}$  and  $Fe^{55}$  in Ag at  $883^\circ\text{C}$ .

apparatus was initially calibrated with sources made from the pure isotopes. A mixture of the two isotopes was electroplated onto a silver crystal from an oxalate solution made by combining portions of the pure sources. After diffusion in vacuum, the specimen was sectioned. The  $Fe^{59}$  activity was determined by gamma-counting the cuttings, using a calibrated scintillation counter. The individual sections were then dissolved in acid, and the silver precipitated as  $AgCl$ . The residual iron was then precipitated from the solution with 1 mg of carrier iron as iron hydroxide. This procedure was necessary for counting of the very soft x-rays from the  $Fe^{55}$ . The net  $Fe^{55}$  activity in each section was determined by differential counting of the hydroxide precipitate with matched Be and Al absorbers, using an argon-filled end-window counter. In addition, the  $Fe^{59}$  activity of the precipitate was remeasured, so that an accurate determination of the ratio of  $Fe^{55}$  to  $Fe^{59}$  in each section could be made.

The experimental results for diffusion at  $883^\circ\text{C}$  are given in Figs. 1 and 2. It should be noted that the analysis of Fig. 2 gives the ratio of the diffusion coefficients directly, unaffected to first order by uncertainties in the penetration distance, since the distance is identical for the two isotopes. The probable errors shown in Fig. 2 were determined by a separate calibration experiment, using the plating solution as a standard mixture.

By inspection of the figures, it is apparent that the lighter isotope diffuses more rapidly than the heavier, but the relative difference in diffusion coefficients is about 15%, roughly four times larger than predicted by rate theory. This conclusion appears to be completely inconsistent with the theory, and cannot be