~~Duplicate~~

AECU-3578

Report No. 5

on

Contract No. AT(11-1)-191

C. H. Shaw

encl.

2161[✓]₀₀₀

March 15, 1956

DO NOT
PHOTOSTAT

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

*Previous
reports*

no 3. AECU-2880

no 4 AECU-3190

1960 TS

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

AECU-3578

RF Project 471
Report 5

ANNUAL
REPORT

by

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

Columbus 10, Ohio

To: U. S. ATOMIC ENERGY COMMISSION
Contract No. AT(11-1)-191

On: SOFT X-RAY SPECTRA OF METALS AND ALLOYS

For the period: March 16, 1955 - March 15, 1956

Submitted by: C. H. Shaw
Department of Physics

Date: March 15, 1956

793 001

SCOPE AND PURPOSE OF THE RESEARCH PROJECT

The purpose of the project is to make measurements and theoretical studies of the characteristic emission and absorption spectra of the four elements, titanium, zirconium, hafnium, and thorium, and their alloys. This work is being coordinated with that in the metallurgy department of ORNL, which is furnishing the pure metals and such alloys as are of significance.

The scope of the work in the experimental direction is to make spectral measurements under the highest resolving power and accuracy of intensity measurement that are feasible in the intermediate wavelength range ($5 < \lambda < 15$ Angstroms), and to plan and construct an instrument in the long wavelength region ($50 < \lambda < 1000$ Angstroms).

The scope of the work in the theoretical direction is to correlate the experimental findings with established theory where possible, in an effort to understand the effect of alloying on the electronic band structure. Conversely, an understanding of the electronic band structure should lead to better understanding of mechanical, thermal, and electrical properties of these alloys.

SOFT X-RAY SPECTRA OF METALS AND ALLOYS

A. SUMMARY OF INVESTIGATION DURING YEAR

The problems receiving attention during the present contract year are described below. Except for the article referred to under item 5, detailed results are not available at the present time.

1. The M-series emission spectrum of thorium is of particular interest from the standpoint of results on zirconium, described in Report No. 4 of this project, dated March 15, 1955. Data previously obtained on zirconium were interpreted to indicate the existence of double exciton states in the excited atom in the metal. Similar data are being taken for the M-series of thorium.
2. Professor J. Korringa has been working further on the theoretical interpretation of the data from zirconium together with results obtained in other experiments on the L-series emission lines of nickel, copper, and zinc. He is preparing an article for publication which examines the experimental results on the assumptions of single and double exciton states in these metals. This bears upon the general problem of identifying the observed spectral structure with the electronic band structure in the metal.
3. The work on zirconium mentioned above suggested that the intensities of the satellites accompanying the $L\gamma_1$ line might depend upon the height to which the Fermi level extends in the metal. To test this point the satellite intensities are being measured in pure zirconium and in an alloy of indium with zirconium prepared for the purpose at the Metallurgy Laboratory of ORNL.
4. The $K\gamma$ emission line of titanium is being measured to determine its contour accurately, and also the contour of the same line in alloys of titanium with vanadium so prepared as to have the bcc structure of vanadium. Both Ti and V emission lines are being studied.
5. An article entitled "The X-Ray Spectroscopy of Solids," is included as a part of this report. It has been prepared and submitted to the American Society for Metals

to be published in June 1956 in the Annual Symposium Volume. This article reviews the significant work in the field during the past 10 years and examines the status of the notion that x-ray emission and absorption spectra can be identified with the density-of-states curve for the valence-conduction band of the metal. Data gathered on this contract were used extensively.

6. Design and construction of the long-wavelength spectrograph (50-1000A) mentioned in previous reports as an objective of this program have not been advanced very far this year. It has been planned that much of this work would be accomplished under University auspices. In previous years several students working for the Master's degree or the Doctorate have helped to advance the project, in addition to those employed on a part-time basis. However, all the doctoral candidates who have been associated with the project have received the Ph.D. and left for permanent employment elsewhere. Dr. Nathan Spielberg left the project in 1953. Dr. J. A. Soules worked during the summer of 1955, resigning in September. No other graduate student was available to assist in the program this year, with or without compensation from the contract. Consequently the Supervisor, Professor C. H. Shaw, has been working alone on the experimental program since the summer of 1955. Some additional details of the spectrograph design have been planned, but no actual construction has been started. A graduate student is expected to be available to assist in this program starting in the fall of 1956; also it is expected that at that time another x-ray spectroscopist will be joining the Physics Department staff and will thereafter participate in this project on a part-time basis.
7. It is expected that during the coming year Professor Korringa will complete a paper on the theoretical interpretation of the data for zirconium; and that Professor Shaw will prepare for publication a report on the experimental work on zirconium, as well as related data on the L-spectra of copper, zinc, and nickel which are being investigated under a contract sponsored by ONR. The expected addition of another faculty member and a graduate student to the staff of the project should permit a significant amount of work on the long-wavelength spectrograph (50-1000A) to be accomplished.

Signature Page

for

Report No. 5

on

Contract No. AT(11-1)-191
RF Project 471

Investigator _____ Date _____

Supervisor C. H. Shaw Date 13 Mar 1956

For The Ohio State University Research Foundation

Executive Director Oran C. Woolpert Date 13 Mar 1956
007

B. THE X-RAY SPECTROSCOPY OF SOLIDS

C. H. Shaw
Department of Physics and
Astronomy

The Ohio State University
Research Foundation
Columbus 10, Ohio

January 1956

FOREWORD

This report is based on a paper presented in October 1955 before the Symposium of the American Society for Metals held at Philadelphia. This is by no means an exhaustive review; selection of the material discussed was made according to the author's interests.

Some of the work reported here was assisted by the Office of Naval Research and the Atomic Energy Commission through contracts with The Ohio State University Research Foundation.

CONTENTS

	Page
I. HISTORICAL INTRODUCTION	1
II. INSTRUMENTATION	8
III. RESULTS AND DISCUSSION	17
K-Series Spectra	22
L-Series Spectra	35
M-Series Spectra	46
BIBLIOGRAPHY	49

I. HISTORICAL INTRODUCTION

Soon after the discovery of x-rays in 1895, Roentgen, in his search for experimental evidence of their nature, passed a beam of the radiation through a crystal of calcite and measured the transmission (18)*. He speculated that the transparency of the crystal might depend upon its orientation, having for example, different transmission characteristics parallel and perpendicular to the optic axis. He failed to detect any effect for equal thicknesses of calcite. A considerably longer exposure might have registered the faint diffraction spots and thereby made Roentgen the discoverer of x-ray diffraction. Much speculation and many inconclusive experiments over the succeeding sixteen years failed to clarify the nature of the radiation. The definitive experiment was performed in 1912. In that year Friedrich and Knipping, acting on a suggestion of M. Laue, obtained a diffraction pattern of zinc blende with heterogeneous radiation (19). The success of this experiment provided convincing evidence that x-rays are electromagnetic radiation of short wavelength.

Von Laue, in his analysis of the zinc blende diffraction pattern, found it difficult to account for all the observed lines on the assumption of a simple cubic structure (20). W. L. Bragg (21) not only accounted for the entire pattern by assuming a face-centered cubic structure but in the process had the inspiration which both placed x-ray diffraction on a firm basis and founded the field of x-ray spectroscopy. He found it convenient and consistent with observation to associate with each line in the pattern a regular array of scattering atoms in the crystal arranged in a multitude of parallel regularly spaced atomic planes, each of which scatters a small fraction of the incident x-ray beam according to Huyghen's principle. This train of thought led Bragg to the idea of the "reflection" of x-rays from a crystal, requiring that two conditions be fulfilled: 1) that the angle of incidence on the atomic planes and the angle of reflection be equal, and 2) that

$$n\lambda = 2d \sin \theta, \quad (1)$$

the so-called Bragg law.

In powder diffraction work a carefully monochromatized beam of x-rays is used, making λ the same for all diffraction lines. This leaves as variables in the Bragg law, n , d , and θ , of which θ can be determined from the lines in the pattern. The analysis of the microcrystalline structure proceeds from this point. In x-ray spectroscopy, on

*See Bibliography at end of report.

the other hand, a large, single crystal is used to analyze the heterogeneous incident beam, and d remains constant throughout the experiment. With n fixed, one has a simple relation between λ and θ , and the experiment consists in determining the spectral intensity, i.e., intensity as a function of wavelength, from the measurements of intensity vs θ .

W. H. Bragg (22), in a terse communication of two sentences, reports his success in observing the reflection of x-rays from a mica crystal with an ionization spectrometer. The approximate design of his equipment is illustrated in Fig. 1. Lead slits A and B directed the x-ray beam over the axis of rotation of the spectrometer. The cleaved mica crystal was mounted with its reflecting face on the axis, about which it rotated. The ionization chamber D likewise rotated about the spectrometer axis. To plot out the x-ray spectrum it was only necessary to position the ionization chamber to receive the reflected ray, according to the first condition above, and then, while preserving this condition, to sweep through the spectrum by varying the angle of incidence θ . The spectral distribution is given as ionization current vs. wavelength obtained through the use of the Bragg law.

Figure 2 is similar to the spectrum Bragg obtained. There are two distinguishable parts: 1) the continuous spectrum, falling off toward greater wavelength, of which we shall have little to say, and 2) superposed on this, the line or characteristic spectrum, which will be our main concern. The latter is termed characteristic because the number, wavelengths, and intensities of the lines are properties of the target material. In 1913 and 1914 Moseley (23) presented a classic experimental study of certain emission lines for elements from aluminum (atomic number 13) to gold ($Z = 79$). His experiments provided striking confirmation of the nuclear structure of the atom as proposed by Rutherford and by Bohr (24)(25). These concepts were extended by Bohr (26) and Stoner (27) to give us our modern picture of the arrangement of electrons in atoms as we pass through the periodic table.

From the measured wavelengths of the characteristic radiations one can quickly compute the frequencies and quantum energies (1). Studies of the quantum energies for the pure elements have led to the concept of the energy level diagram, from which the quantum energy for any given electronic transition* may be obtained by taking the difference in energies of the two levels involved (11). All x-ray lines which can be

* In this paper we shall speak of electronic transitions between levels, though, more properly, one should treat of transitions between energy states of the system. In the excitation of an atom, for example, not only is the ionized level involved, but all levels are shifted more or less in energy. We largely ignore these latter.

Fig. 1. The Bragg spectrometer. The detector D rotates at twice the angular rate of the crystal C. (From Reference 2, courtesy D. Van Nostrand Co.).

Fig. 2. Emission spectrum from a metal, showing the characteristic spectrum superposed on the continuous spectrum. The abscissa is θ in degrees. (From Reference 2, courtesy D. Van Nostrand Co.).

so described are called diagram lines. In addition to the diagram lines many others are observed. They are usually rather faint and usually near diagram lines, but always on the high frequency side. Their positions are not predicted by the energy level diagram. These lines are termed satellites or non-diagram lines and were explained by Wentzel (28)(29) as arising from the fairly rare event in which the radiating atom is ionized initially not in one inner level, but two. Consider, as an example, the schematic energy level diagram for rhodium ($Z = 45$) pictured in Fig. 3. Figure 3a shows one of the possible transitions giving diagram lines when the atom is singly ionized in the L_{III} shell. Figure 3b shows the satellite transitions according to Wentzel (28) in which the atom becomes ionized simultaneously in two inner levels, e.g., L_{III} and M_{IV} , presumably by the initial electron impact. Ionization of the M_{IV} level lowers the energies of all the levels relative to those in Fig. 3a in such a way that the succeeding electron transition $M_V \rightarrow L_{III}$ occurs with somewhat higher radiation quantum energy, accounting for the higher frequency of the satellite as compared to the diagram line.

If one examines quantitatively Wentzel's mode of excitation he finds that the predicted satellites, while in the correct spectral positions, are too weak to account for the observed intensities. Coster and Kronig (28) found the answer (Fig. 3c). They suggested that we fix our attention not on initial excitation of the L_{III} level, which accounts for the diagram radiation $L_{\alpha_{1,2}}$, but rather on the equally probably excitation of the L_I level. The latter can be filled by an electron from an upper level, but not by one from the L_{II} or L_{III} level if the excess energy is to be radiated, for this is forbidden by the selection rules. However, the electron transition $L_{III} \rightarrow L_I$ or $L_{II} \rightarrow L_I$ is allowed if the energy is transferred to another electron, rather than being ejected in the form of radiation. This is called a radiationless or Auger transition. It turns out that for rhodium and for elements of a few atomic numbers above and below rhodium the Auger transition $L_{III} \rightarrow L_I$ has enough energy to eject an $M_{IV,V}$ electron from the atom. The Auger transition probability in these cases is quite high and the satellite intensities are nicely accounted for on this model. The reader must be cautioned, however, that the double inner ionization theory does not account for the number, position, and intensities of all observed satellites by any means.

It is an interesting fact, and instructive for our purposes, that x-ray lines, as well as other spectral lines, are not infinitely narrow, but rather have quite appreciable width. If the line under consideration arises from an electron transition between levels deep inside the atom, it oftentimes may, but not necessarily must, be "simple" in structure. It is said to have a classical or Lorentzian (30) shape, which would result if the radiating source were a damped simple harmonic oscillator. The width of such a line is conventionally measured at half the maximum intensity, usually in electron volts (ev). If, on the other hand, the

Fig. 3. Schematic energy level diagram for rhodium ($Z=45$). Arrows indicate the direction of the electron transition. All levels below the conduction band are normally filled. The energy zero at the top of the diagram represents an electron at rest and entirely removed from the metal. As the electron occupies empty levels nearer the nucleus (N, M, L, K) its energy decreases and it is more tightly "bound" to the nucleus. Thus, an electron must be given energy (e.g., by electron impact) to be lifted to a higher level as in (a) which represents the transitions for the diagram line $L\alpha_1$. Diagrams (b) and (c) give transitions for the $L\alpha_1$ satellites. See text.

outer level from which the electron drops during the radiating process is the valence level in the solid, the line usually (but not always) is much wider than in the first case and may be rather complicated in structure. These features, we should like to say, correspond to the width and structure of the valence electron band of the solid, and from the measurement of such structure we should be able to determine the so-called energy-density-of-electronic-states curve for the solid. (3).

Not only are characteristic spectra observed in emission but also in absorption. The appearance of the latter, however, is in striking contrast with the former. All absorption spectra are characterized by a more or less sharp increase in the absorption coefficient at a critical value of the frequency or wavelength of the incident x-rays, as the frequency (i.e., the quantum energy) is increased (31). This edge, in general, is complicated by the presence of absorption lines (43), which again we should like to associate with structure in the conduction energy band.

We may be quite sure that electron transitions involving the valence and conduction bands are in reality not so simple as indicated in the last paragraphs. If we compare the energy levels of an isolated atom of atomic number $(Z + 1)$ with those of an atom of number Z , we will find that each of the former lies below the corresponding level of the latter on the energy level diagram, because of the greater attraction of the nucleus. When an atom of a solid of atomic number Z is ionized in an inner level the positive ion remaining is quite different from the adjacent ions and must be regarded as an impurity ion of effective nuclear charge $(Z + 1)$. We should expect, then, that the state for the impurity atom corresponding to that for the conduction band for the solid would be the more tightly bound, i.e., would lie below the conduction band for the remainder of the solid. Such atomic-like states are called exciton states (32).

The role played in the x-ray spectra of solids by exciton states seems first to have been pointed out by Mott and Cauchois (111)(178). These authors used such states to explain the existence of the "raies blanches" (white lines) found in some cases in absorption spectra immediately to the high frequency side of the initial absorption. This hypothesis has been elaborated and quite fruitfully applied in the explanation of some puzzling spectral characteristics (213), as we shall see later.

That valence forces in the solid affect x-ray characteristic spectra to a minor, but measureable, degree appears first to have been shown by J. Bergengren (33)(34) in 1920 for the case of absorption. He observed a small difference in the position of the K absorption edge of black phosphorus and of phosphorus in phosphoric acid, whose edge he suggests would probably coincide with that of white phosphorus. Not until 1924 did Lindh and Lundquist (35) find the corresponding effect in emission

spectra. They found a distinct difference in the appearance of the $K\beta$ line of sulphur in the sulfide as compared with that in the sulphate. The many papers on the subject since that time (3) (4) have shown that several effects are detectable upon chemical combination or alloying of various elements. They are: 1) The wavelength change of certain emission lines of light elements; 2) the wavelength change of the absorption edges of light elements; 3) changes in the structure of emission lines; 4) changes in the structure of absorption edges; 5) the appearance of emission lines in the compound, or alloy, not present in the pure element (339)-(3) (36).

It is our task to examine the wavelengths, shapes, and intensities of emission lines or bands and of absorption edges of the pure elements in the various physical states, and of the same elements in their multitudes of chemical combinations and in their varieties of alloys, to learn what such observations can teach us about the behavior of the electrons, especially those electrons which are farthest from the nuclei.

II. INSTRUMENTATION

Valence electron processes occurring during chemical combination and in the alloying of metals involve energies of the order of a few electron volts (37). If we are to study these effects in x-ray spectra with sufficient precision to draw dependable conclusions it is obvious that the instrument employed must be so designed that spectral structure corresponding to such energy differences can be clearly resolved. Actually the spectral modifications observed are often quite subtle; sometimes the structure is merely widened or narrowed or the relative intensities in the structure are changed (339). We should like to use an instrument capable of resolving structure no further apart in energy than 0.5 ev (preferably less than 0.1 ev), and capable of measuring intensities to one percent or less. Let us see what broad implications this has for the experimental approach to the problem.

The spectral range of interest extends from about 0.5 A to 1000 A. The experimentally practicable regions in this interval can be distinguished according to the instrumentation which has been found suitable in each region. These may be termed the short, the medium, and the long wavelength regions.

The short wavelength region (0.5 to 3 A) is characterized by the fact that air absorption, while sometimes appreciable, is usually tolerable and the instruments are for the most part quite open and easily handled. Of the several types of spectrometers which have been designed, three are satisfactory for our purposes: 1) The curved crystal reflection spectrometer, 2) the curved crystal transmission spectrometer, and 3) the double-crystal, or more properly, the two-crystal spectrometer (12).

The x-ray optics are indicated for the three cases in Figures 4, 5, 6. Of the three it is generally recognized that the two-crystal spectrometer inherently has somewhat the highest resolving power. But more important than this is the fact that it is possible to get an estimate (38) of the instrumental resolving power for this instrument. From this measurement one can in some cases correct the observed data to give an idea of what the structure would be with infinite instrumental resolving power (38) (285). Such an estimate of resolving power is obtained by measuring the width at half maximum of the (1,-1) curve as a function of wavelength. The width of the approximate "spectral window" so obtained is shown in Figure 7 for several pairs of crystals. The interest in these curves at the moment is that they all rise at the short wavelengths indicating a deterioration of instrumental resolution in this region. In spite of the simplicity possible in the design and use of x-ray spectrometers in the short wavelength spectral region we must conclude that it is not a very good one for valence and conduction band studies. There is another compelling reason for avoiding the very short wavelength region. High energy electron transitions are associated with the more tightly bound levels in the atom, e.g. the K level. The lifetime of the excited K level is quite short and this level is correspondingly broad, especially for atoms of high atomic number. Lines which involve the K level will have appreciable contributions to their width both from the intrinsic K level width and the instrumental broadening. In spite of these disadvantages a great deal of work has been done in the short wavelength region with most interesting results.

The only test yet devised for spectral resolving power for curved crystal spectrometers is to compare the width of a good representative line with that given by the two-crystal spectrometer using the same kind of crystals with their surfaces prepared in the same way (128). When the measurements are correctly performed the widths are invariably somewhat wider for the curved crystal instrument, indicating lower resolving power (321) (341).

Two methods have been widely used in recording the spectrally analyzed beam, the photographic and the electronic. The photographic method has many advantages, among which is the very desirable simplicity, not only of the detector itself but of the controls necessary for the regulation of the voltage and current of the x-ray tube. Furthermore, photography is ideally suited to survey work of all kinds, for a substantial part of the spectrum may be registered in a single exposure. It is also well suited for the study of faint structure which has no fine detail (39). It is not very satisfactory, however, for the purposes we have in mind, unless extraordinary precautions are taken (83), because of the large and very sharp changes of intensity, and therefore of photographic density, along the plate in many cases. Grain size, scattering in the emulsion and other effects obscure such changes, together with any faint spectral structure in the region.

Fig. 4. Optics of the reflection curved crystal spectrometer. The crystal C, with its atomic planes parallel to the face, is bent to radius $2R$ and placed tangent to the Rowland circle of radius R , upon which the photographic film P, or the slit of the electronic detector, is placed. Radiation of the proper wavelength from any point S on the circle will be brought (almost) to a line focus on the circle. The x-ray target usually is placed at T. S then becomes the virtual source and, because of the properties of the three-dimensional grating, the sharpness of the focus is undisturbed.

Fig. 5. Optics of the transmission curved crystal spectrometer. The reflecting planes are perpendicular to the crystal face, which again is curved so that the planes all point toward O' . The source is an extended one, as indicated. P indicates the photographic film.

Fig. 6. Optics of the two-crystal spectrometer. Both crystals are plane. The axes of rotation are indicated by the dots. X-rays from a broad region of the target T and over a very small spectral range $\lambda = \lambda_2 - \lambda_1$ (where $\lambda_2 > \lambda_1$) are reflected by the first crystal A in a fan of bundles of parallel rays. In the $(1, -1)$ position all rays are reflected by the second crystal B to the detector D with the intensity a maximum when the second crystal is parallel to the first. In the $(1, +1)$ position λ_1 and λ_2 are reflected in succession as crystal B is rotated about its axis in a clockwise direction to plot out the spectrum. The first crystal acts, then, as the collimator, the second as the analyzer.

Fig. 7. Two-crystal spectrometer (1, -1) width at half maximum as a function of wavelength for several kinds of crystals. These curves give some idea of the "spectral window" to be expected.

The Geiger counter, the proportional counter, and the scintillation counter (347) are perhaps the most satisfactory electronic detectors for the short wavelength region. Of these the Geiger counter requires the simplest circuitry but is quite unacceptable for the most precise work because of the unknown and variable spurious count characteristic (177). For much work, however, it is moderately good. The development of fast, high gain pulse amplifiers has made the proportional counter the most satisfactory detector. The proportional counter, very similar in its construction to the Geiger counter, is so named because the voltage pulse size is proportional to the quantum energy. This detector gives no spurious pulses, is in every way very stable in operation, and shows excellent intensity linearity. It has the added advantage that if the pulse amplifier is fed into a channel pulse height discriminator adjusted to pass pulses corresponding to the spectral region being investigated, most counter background pulses will be rejected, together with those caused by radiation reflected in the second order from the crystal and scattered radiation which is widely different in quantum energy from that desired. By this means it is possible to reduce the counter background to 3 counts per minute (cpm) and to measure intensities of 20 cpm to one percent accuracy. The final register can be either a fast scaler or rate meter and pen recorder. The maximum intensity measurable with acceptable accuracy by such pulse counting techniques is about 5×10^5 cpm.

Scintillation detectors likewise have the characteristic that their output potential pulse is proportional to the quantum energy. The remainder of the instrumentation is the same as for the proportional counter. The chief advantage of the scintillation detector is that it preserves its sensitivity at short wavelengths where the gas of the proportional counter becomes quite transparent ($\leq 0.7\text{\AA}$). The chief disadvantage is that the pulse size at the longer wavelengths become comparable to the thermal emission pulses from the cathode of the photomultiplier and the signal-to-noise ratio suffers correspondingly. This can be remedied by cooling the photomultiplier to dry ice or liquid air temperature, an expensive and inconvenient expedient in most cases.

Equipment for the intermediate wavelength range (3 to 30 $\text{\AA}$) is in principle quite similar to that for the short wavelengths. All substances become so opaque, however, that the transmission grating spectrometer is no longer useful. The main difference now is that air is so absorbent that it must be removed from the path of the beam as it traverses the spectrometer and all windows must be designed to pass the more easily absorbed radiation. The former is usually accomplished by mounting the spectrometer in an evacuated tank. There are many variations on the specific design but all spectrometers for this region are either of the curved crystal reflection or the two-crystal type.

Until rather recently this spectral region was reserved almost exclusively for the curved crystal instrument with photographic registration (13). But in recent years two curved (147)(238) and two two-crystal

instruments (124) (353) have been put in operation, all using electronic detectors. As the dispersing medium the curved crystal instruments have used mica in the first order at the longer wavelengths and in the third and fifth orders at the short wavelength end of the interval* (341). Inspection of Figure 7 shows that, of the crystals indicated for the two-crystal spectrometer, calcite and quartz should be used at the shorter wavelength end of the interval, while, of course, beryl must be used at the longer.

The intermediate wavelength region is limited on the long wavelength side to some 20 Å for curved crystal instruments by the grating space of mica, the only near-perfect crystal with a satisfactorily long grating space, high reflectivity, and the physical properties which make it acceptable. The long wavelength limit of the two-crystal spectrometer is at present about 15 Å, a limit imposed by the beryl crystals.**

At wavelengths immediately greater than 20 angstroms a gap exists for which no really acceptable experimental technique has yet been worked out. Both crystal and ruled grating techniques have been used. Useful crystals have been those of organic salts either crystallized from solution or formed from the melt on flat plates by slow cooling (40). These crystals have grating spaces ranging from 30 to 90 angstroms. The concave grating at grazing incidence has likewise been used (315). In this region, however, the energy resolving power is none too great. Perhaps the combination of an organic crystal laid down on a concave support together with a direct photomultiplier (77) as detector would prove useful. The grating, perhaps would have to be cooled because of the rather appreciable vapor pressure of the organic material at room temperature.

The long wavelength region (50 to 1000 Å) promises to be the most fruitful. Here the only available technique satisfying the basic requirements is that of the concave ruled grating used at grazing incidence (41). The x-ray optics are illustrated schematically in Figure 8. The spectral window obtainable in this region is of the order of 0.01 electron volt (42). Both emission spectra and absorption spectra have been recorded in this region, though absorption work is hampered by the difficulty of obtaining suitable continuous spectrum sources (354). Both photographic and electronic registration have been used (263) (308),

* Fairly careful reading of Sandström's three papers so far published on the bent crystal spectrometer has not revealed the kind of crystal he is using. One supposes it is quartz or mica.

**Mica crystals are entirely unsuitable for the two-crystal spectrometer. Stephenson and Martin (152) could find no 1,-1 reflection from mica whatsoever.

Fig. 8. Optics of the concave grating spectrometer used at grazing incidence. The optics of the one-dimensional concave grating requires that the source slit S, the grating G and the detector P all be accurately on the Rowland circle of diameter equal to the radius of curvature of the grating. The grazing angle of the incident beam on the grating must be less than the critical angle for reflection in the wavelength region of interest. Grazing angles of 2 to 6 degrees have been used in the region 50 to 1000 Å. The whole spectrograph must, of course, be housed in a high vacuum.

the latter, however, to a very limited extent and under somewhat questionable conditions (315). The detector in this case was the direct photomultiplier (77) and perhaps the most significant fact learned to the present time is that a given emission band can be recorded with about one thousandth the exposure necessary with the best photographic emulsion especially designed for the purpose (236). This has great significance for the practicability of further extensive investigations in this region.

All workers in the long wavelength field have been acutely conscious of the need for the best possible vacuum in the x-ray tube to preserve the cleanliness of the target. Contamination of the target is manifested in a change of line contour and even of line position because of the chemical effect. Vacuum of 10^{-6} torr is just marginal; one cannot put full confidence in the band shapes measured. To be safe it would seem that the vacuum should be of the order of 10^{-8} to 10^{-9} torr. Recent developments in vacuum measurement and pumping at low pressure (246) with the ion gauge indicate that such vacuum is by no means unreasonable. However, the time-honored pump-trap combination gives good promise of a somewhat more straightforward solution. No more than 2.5 watts of target power are required for satisfactory registration of emission bands in this region (236). It would seem quite feasible to cool the x-ray tube, including the target, with liquid hydrogen and to use a liquid hydrogen trap in the x-ray tube pumping line. Vacuum of 10^{-9} torr might be obtained in this manner.

The remaining auxiliary equipment, such as electronic stabilizers for the x-ray tube potential (105) and current (71), have been well worked out. X-ray intensity can be regulated to 0.1 percent with relatively simple circuits. X-ray tube potential has been regulated to 0.01 percent with somewhat more involved circuitry (130).

In the discussions which follow, for the most part those experimental studies have been emphasized which adhere to the standards of resolving power and accuracy of intensity measurement described above. It is difficult to evaluate single crystal work in which the instrument has not been standardized by comparing a satisfactory line contour with that obtained using an instrument of high and known resolving power and accuracy, such as the two-crystal spectrometer.

III. RESULTS AND DISCUSSION

One distinguishing characteristic of x-ray spectra is their relative simplicity. In the visible and ultraviolet emission spectrum of iron from the iron arc one can count some thousands of lines; the x-ray L-emission series of metallic iron is composed of approximately five lines, while the K-series has only ten (6) (142). But the simplicity

of x-ray spectra is not their most important characteristic. When a piece of solid iron is heated to incandescence one sees only a continuous spectrum, from which little can be deduced about the conduction electronic band structure. On the other hand, the x-ray spectrum preserves its line nature even though the electron transitions occur in atoms tightly bound by valence forces in the solid. Furthermore, since the transitions of most interest to us occur between the valance band, or levels associated with it (178), and a relatively sharp inner level, we are afforded an opportunity of gaining some knowledge of the structure of the valence level of the solid, if it is an insulator, or of the occupied portion of the conduction band, if it is a metal, by studying the emission spectrum. Conversely, studies of the absorption spectrum should furnish information on the conduction band of the insulator or of the unoccupied portion of the conduction band of the metal (5).

The simplest spectrum imaginable should be that of a monatomic gas. It is a rather difficult experimental problem to excite a gas to radiate in the x-ray region (114). Consequently, monatomic gases have been studied with adequate precision only in absorption (43) (93). Figure 9 shows the K-absorption limit of gaseous argon as measured by Parratt. Absorption "lines" are clearly distinguished which arise from electron transitions from the K-shell to those optical levels allowed by the quantum selection rules. These are among the levels involved in the optical excitation and radiation of argon gas. To the high frequency side of this structure the absorption coefficient becomes constant, corresponding to the structureless continuum of energy levels associated with complete ejection of the electron from the atom.

The corresponding spectrum for solid argon*, likewise taken with the two-crystal spectrometer equipped with calcite crystals, is indicated in Figs. 10 and 11, where it is apparent that although the discrete nature of the spectrum persists, it is considerably modified in the solid. It is interesting that only a minor shift in the position of the edge takes place between the gas and the solid; it is even more interesting, in view of the profound modification of the optical levels as indicated by the widened structure, that the initial rise remains almost as steep in the solid as in the gas. These data merely confirm what has been well known all along, namely that condensation or chemical combination perturbs the outer electronic states. At frequencies higher than those shown in Fig. 11 the absorption coefficient continues to oscillate

*Soules and Shaw, to be published.

Fig. 9. K-absorption edge of argon gas. (After Parratt, Reference 43).

Fig. 10. K-absorption edge of argon gas compared to that for argon solid. The crosses represent an arc tangent curve fitted to the initial absorption rise. (See Reference 52).

Fig. 11. K-absorption edge of solid argon.

about a mean value in a way characteristic of the crystalline structure. Kronig (44) gave the explanation in 1932. He suggested that it arises from Bragg reflections of the ejected photoelectron in the crystalline lattice. There is ample experimental confirmation of this idea (331).

It would be most instructive to study the complete emission and absorption spectra of all the elements in both the gaseous and solid states, and then to study the same spectra in various chemical combinations. This, unfortunately, is not possible at the present time. We must be content to work with the spectra, the elements and the compounds which are amenable to our experimental approach. In emission studies with electron excitation this limits us to elements and compounds of relatively high melting point, chemical stability under electron bombardment, and good heat conductivity. In absorption studies the sample must be prepared in the form of thin, uniform foils, free from holes. All samples, of course, should be as pure as possible and precautions should be taken that they remain pure during the measurements. The easiest materials to work with are the refractory metals and alloys, though a very considerable amount of work has been done with chemical compounds such as metallic oxides, sulfides, and salts, and in absorption even with solutions (229), with most interesting results.

Although fluorescence excitation has been used in a very limited number of investigations (45), this method certainly has not been exploited as it should be. Here, of course, damage to the sample by radiation is far less than that produced by electron bombardment. Compounds, as well as metals with relatively low melting points and high vapor pressures, can be investigated.

The following discussions will review material published mainly since 1945, together with some material not yet in print. Mlle. Cauchois, in her 1948 review article (3), gives a bibliography of work from about 1930 to 1948. The references also are grouped at the conclusion of the paper in an auxiliary list according to the chemical element. In his book, published in 1931, Professor M. Siegbahn (6) gives an extraordinarily complete and useful bibliography of the older work.

K-SERIES SPECTRA

Studies of the contours as well as the wavelength of the K-series emission lines have been carried out for a fairly large number of pure elements beginning with lithium (atomic number 3) and for a few alloys and compounds. Absorption spectra have not been so thoroughly studied, doubtless because experimentally they are more difficult to measure, especially in the longer wavelengths.

Most of the work in the short wavelength region was done before World War II. The thorough appreciation of the limitations in this

region, discussed previously in this report, together with the improvement in experimental techniques, especially electronics, during and immediately after the war have led to a new emphasis on the intermediate and long wavelength regions.

Space does not permit a review of the older work in the short wavelength region, but representative references are included in the bibliography.

The most complete and interesting work on insulators is that of Parratt and Jossem on crystalline KCl (341). In a paper remarkable for its clarity and precision of expression they give a thorough discussion of the emission and absorption contours for potassium and for chlorine taken both with a curved crystal and with a two-crystal instrument (Fig. 12). One sees that the emission structure is well separated from the absorption spectrum, as expected for an insulator (5).

It is quite clear from the known electronic configurations of atomic potassium and chlorine (7) that the β_1 line in either case involves electron transitions associated with the 3p levels in the crystal (Fig. 13). The β_1 line is found to have quite accurately a Lorentzian shape, indicating that the transition occurs between singlet atomic states. On this assumption the widths of the β_1 final states will be given by the width at half maximum of the corresponding observed β_1 line, corrected for the resolving power of the instrument and the width of the initial state. The widths of the final states at half maximum turn out to have the remarkably small values of 0.33 ev for chlorine and 0.22 ev for potassium.

The 3p band width at half maximum is estimated theoretically to be about 2 ev for chlorine and 1.5 ev for potassium (14). If it is assumed that the width of the β_1 final state as calculated above is also the width of the corresponding 3p band, we must conclude that the band is much narrower than one would expect.* The faint structure β_x and β'' (Fig. 12) might be assumed to be satellite lines, arising from double inner ionization of the excited atom.

The situation is not clarified when the absorption spectrum is considered. No easy explanation for the relatively narrow peaks A and B (Fig. 12) presents itself. These would simply be a part of the density-of-states curve (multiplied by the transition probability) above the bottom of the conduction band, represented by the initial rise in absorption.

* O'Bryan, however, in studies of the L-absorption spectra of sodium in sodium halides (46) found absorption lines no wider than 0.5 ev, and some as narrow as 0.2 ev.

Fig. 12. Experimental emission and absorption spectra in KCl, involving the valence and conduction bands as shown in Fig. 13. The complexity of the spectra requires additional states which are not shown in Fig. 13. See text. (After Parratt, Reference 341).

Fig. 13. Conventional x-ray energy level diagram (schematic) for crystalline KCl. The arrows point from the initial to the final states. This diagram is incomplete, see text. (After Parratt, Reference 341).

The picture changes somewhat for the better if we admit the hypothesis of exciton states and discard the one-electron approximation. A and B, then, become absorption lines into the atomic-like exciton states below the conduction bands, while the β_1 emission line is pictured as arising from exciton states below the respective 3p band, thus accounting nicely for the narrow width and the Lorentzian shape. The lines β_x and β'' perhaps likewise may be associated with exciton states but might also be interpreted as true satellites. We have failed entirely to correlate the emission spectrum with the density-of-states curve in the valence band. In the words of Parratt and Jossem, "... the strong emission line involving the valence band electrons probably does not in general give much information about the normal unperturbed valence band itself. This conclusion, contrary to the most fundamental postulate in x-ray spectroscopy of the solid state, is more or less tentative. If this conclusion is wrong, we seem obliged to believe that the valence band in KCl is only 0.33 ev wide at the half maximum of the density-of-states curve. Resolution of the question awaits a more precise theoretical treatment than has yet been made."

It is of interest to re-examine the K-absorption curve for solid argon ($Z=18$), whose atomic number lies between those of chlorine and potassium (Fig. 10). We should bear in mind the fact that the van der Waals forces which bind this solid are far weaker than the polar forces binding the KCl crystal. However, there is no reason to assume that exciton levels should not form below the conduction band in this case as in that of the polar crystal, for this is essentially an atomic property, modified, to be sure, by the general crystalline field.

The value for the high frequency dielectric constant as calculated with the Lorentz-Lorenz formula and the polarizability of the argon atom as given by Mott and Gurney (8) is about 1.6. Assuming the hydrogenic approximation for the exciton states, this leads to a separation of the A peak from the bottom of the conduction band of 5.4 ev* while the separation of the B level is only 1.3 ev. Figure 10 fails to show the well-defined double peak so prominent in both the chlorine and potassium absorption curves for KCl. The initial absorption rise for argon, however, is singularly sharp, almost as sharp as the true absorption line of gaseous argon, while the high frequency side of the absorption peak is noticeably less steep. We suggest that the initial absorption rise represents transitions into exciton states so close together that even the first two are not resolved. That such an explanation is entirely at variance with the hypothesis of hydrogenic exciton states cannot be taken very seriously. No explanation is offered as to

*Reference (341), Equation (3).

Fig. 14. K-absorption edge of gaseous and solid krypton..

why the first two exciton peaks should be so well separated in the chlorine and potassium spectra and not in the argon.

Figure 14 shows the K-absorption curves for gaseous and solid krypton ($Z=36$) at 0.86 Å. The gaseous structure here is so fine that it is obscured by the large K-level width and the comparatively wide spectral window of the spectrometer (47). Structure for the solid, however, shows two well-defined peaks, the first of which has probably been lowered considerably by the poor resolution at this wavelength. The separation is about 10 eV, making the association of the second peak with an exciton level doubtful. We might conclude, then, that the arguments offered for argon might be applied as well to krypton.

Moore and Chalklin (336) report recent measurements on the K-emission spectrum of gaseous neon excited by electrodeless discharge in a vacuum tube. The $K\alpha_{1,2}$ and $K\alpha_{3,4}$ lines were obtained with good intensity, but the β_1 emission, as expected, is quite weak. The spectrometer is of the curved mica crystal type with photographic recording. Unfortunately, no two-crystal data were available in this region of the spectrum (14Å) to make possible a good study of the resolution of the instrument. Width and structure data must be taken with some reservation. A corresponding study of argon to be correlated with the absorption studies on argon and the emission and absorption studies on KCl discussed above would be of considerable interest, as also, of course, would the emission spectrum of solid argon.

We turn now to the metals Mg ($Z=12$) and Al ($Z=13$). Recent measurements* on the K-emission and absorption structure made with the two-crystal spectrometer equipped with beryl crystals** are shown in Figs. 15, 16, and 17. The emission lines are to be compared to those of Farineau (50) and Cauchois (257) for aluminum and to Farineau (50) for magnesium. These lines are of particular interest because they do not exhibit a common aberration which so often limits the usefulness of emission lines for band structure studies. We refer to the "satellite" lines on the high frequency side of the emission edge, such as those

* Soules and Shaw, to be published.

**Cauchois (203) and Sandstrom (48) rightly criticized older measurements by Munier, Bearden and Shaw (49) on the absorption spectrum of aluminum because no correction for variations of spectral reflectivity of the beryl crystals (which contain aluminum) had been made. Unfortunately, such correction could not be made with the experimental arrangement used at that time. In the present data the correction has been made both for the emission and the absorption spectra.

Fig. 15. Conduction band K-emission of aluminum, not corrected for instrumental broadening.

Fig. 16. Conduction band K-emission of magnesium, not corrected for instrumental broadening.

Fig. 17. K-emission and absorption of aluminum.

observed by Beeman and Friedman (51) for the K γ lines of elements in the first transition group. The emission edge for magnesium and aluminum are quite clear-cut and by using the method of Richtmyer, Barnes and Ramberg (52) we find 0.7 ev and 0.9 ev respectively for the widths of the K levels at half maximum.

The shapes of the K β lines for Mg and Al are of more than passing interest. In 1934 Jones, Mott and Skinner (53) showed that for a free electron metal, the transition probability to the inner level varies through the conduction band in such a way that a K-emission line should rise as $(E-E_0)^{3/2}$ on its low frequency side (where $(E-E_0)$ is the energy above the low frequency limit of the line, E_0 representing the bottom of the conduction band), and as $(E-E_0)^{1/2}$ for an L_{III}, III line. Farineau's (50) result for aluminum favored the latter form, while Cauchois' curve (257) indicates the former. Figure 15 for Al and Fig. 16 for Mg agree quite well with the Jones-Mott-Skinner prediction of the shape for a K line.

Much later Matyas (103) made approximate calculations on the conduction band structure of aluminum and compared the results with the L-emission measurements of O'Bryan and Skinner (55) and the K-emission according to Farineau (54). The agreement was quite satisfactory within the limitations of the calculations, but unfortunately Farineau's observed K-line contour seems to have been in error.

Figure 17 shows both the K β emission and the K-absorption spectral structures for aluminum. No readjustment in instrumental settings was made between the two sets of data. It is interesting that not only does the position of the emission edge correspond to that of the absorption edge (15) within the experimental error of 0.1 ev, but the slopes of the curves at the inflection point are identical, as one should expect for simple edges in a metal. K-level widths calculated from the form of the absorption edges (52) correspond with those calculated above from the emission edges.

That the emission and absorption edges correspond in position for a metal is not at all inconsistent with the hypothesis of exciton states below the conduction band for the excited ion in the metallic crystal. In 1952 Friedel made a theoretical investigation of the distribution of electrons around a positively charged impurity atom in a monovalent metal (213). Because of the high electron mobility we should expect that in any case the positive charge would be screened. Friedel showed that this can also occur by the formation of exciton or bound states below the conduction band. With this assumption the absorption and emission schemata are shown in Fig. 18. The absorption process is pictured (Fig. 18a) as follows: One of the 1s electrons A is lifted into a p state B above the Fermi level upon absorption of the incident quantum, creating the exciton level Ex and the 1s' bound state (A'D'). Two additional transitions occur, one by an electron from the top of

Fig. 18. Absorption and emission for a metal according to Friedel (Reference 213).

the Fermi level into the exciton level ($C \rightarrow C'$), the other by the remaining electron in the $1s$ level to the bound $1s'$ level ($D \rightarrow D'$), an effect of the enhanced effective nuclear charge. The electron in the localized exciton level C' effectively screens the positive charge A' left by the ejected electron. The total quantum energy required is

$$E = E_{AB} - E_{DD'} - E_{CC'} \quad (2)$$

The energy for the absorption edge is given by formula (2) when B is at the Fermi level (16). The emission process is the exact inverse (Fig. 18b) of the absorption; the structure will lie to the low energy or long wavelength side of the emission edge, whose energy is given when B again is at the Fermi level. Thus, the emission and absorption edges will correspond in energy. It is interesting that in the case of the metal, as with the insulator, we must discard the one-electron approximation to allow the polyelectronic transitions.

It must be remarked that the postulation of exciton levels is not necessary for the explanation of the correspondence of emission and absorption edges in metals. The older view (5) that the conduction band remains unperturbed and that absorption occurs with transition of an inner electron to unoccupied levels in the conduction band, while emission takes place with an electron transition from the occupied portion to the inner level, is quite sufficient. However, we infer the existence of exciton levels in insulators from the characteristics of the emission and absorption spectra; Friedel demonstrates that a like inference for metals is not inconsistent with the observed x-ray spectra or other pertinent properties. As a matter of fact, recent spectral data on zirconium ($Z=40$) lend further support to the exciton postulate for metals, as we shall see presently.

Few K-series spectra have been studied in the long wavelength region in recent years. Chalklin (98) in 1948 reported measurements on the emission spectrum of carbon at 44 Å made with a curved crystal grating at grazing incidence with photographic recording. The blackening curve was obtained for each photographic plate and the microphotometer curves were transformed to intensity curves. The resolution, estimated from structure observed in the bands, is of the order of 0.2 eV. Carbon is interesting because it exists both as a semiconductor (graphite) and as an insulator (diamond). The curves for carbon in graphite, diamond, and SiC are quite unsymmetrical and all are several electron volts wide. More, and perhaps more accurate, data will be needed on carbon before comparisons with theory will become profitable (206).

No new measurements on the K spectrum of lithium have been made since O'Bryan and Skinner reported on the emission (55) in 1934, and Skinner and Johnston presented absorption measurements (56) in 1937.

Friedel (213), however, applied the process illustrated in Fig. 18 to calculate the position of the absorption edge of lithium, as well as the position of structure observed on the high frequency side of the edge (56). He assumed to a first approximation that the lithium atom is ionized in the unperturbed crystal. The main term in the absorption energy, then, is the excitation energy E_I of Li^+ ($1s^2 \rightarrow 1s2s$). This energy is given from the term values in Bacher and Goudsmit (9) as 58.7 ev. From this must be subtracted 3.1 ev for the exchange energy between the $2s'$ electron and the $2s$ conduction band and a further 0.1 ev for the polarization of the $2s'$ electron by the surrounding atomic polyhedra. The resulting 55.5 ev for the quantum energy corresponding to the absorption edge (or the emission edge) compares very favorably to the measured value of 54.5 ev (228 Å) in absorption (56) and 54.8 ev (225 Å) in emission (55). Similar calculations are made for LiI,III of sodium, which gave the absorption edge energy as 30.1 ev compared with the observed energy of 30.6 ev (46). In a subsequent paper (214) Friedel showed that the exciton hypothesis also yields the correct value for the increase in absorption coefficient for Li through the absorption edge.

L-SERIES SPECTRA

Only a few L-series spectra have been thoroughly investigated. In the short wavelength region Richtmyer, Barnes and Ramberg (52) made careful measurements on both the emission and absorption structures for gold ($Z=79$) with the calcite two-crystal spectrometer. They made the first comparisons between observed absorption edges and their predicted arctangent form. On the assumption that the width of a line is given by the sum of the widths of the levels involved and using the observed width of the L_{III} level and the widths of the various lines, a table is prepared giving the widths of almost all the x-ray energy levels for gold.

In 1938 Parratt (57) made comparable measurements, again with the calcite two-crystal spectrometer, for silver ($Z=47$) in the wavelength region 3.2Å to 4.7Å. A table is likewise prepared for the energy level widths of silver. Of particular interest to us when we discuss the L spectrum of zirconium ($Z=40$) will be the satellites accompanying the lines $\text{L}\alpha_1$ ($\text{L}_{III}\text{M}_{IV}$), $\text{L}\beta_2$ ($\text{L}_{III}\text{N}_{IV,V}$), $\text{L}\beta_1$ ($\text{L}_{II}\text{M}_{IV}$) and $\text{L}\gamma_1$ ($\text{L}_{II}\text{N}_{IV}$). $\text{L}\gamma_1$ itself, so far as the measurements show, is single. Hirsh (28) has discussed the application of Coster and Kronig's theory (58) to these transitions and points out that the satellite lines of $\text{L}\alpha_1$ and $\text{L}\beta_2$ should be relatively strong for silver, while those of $\text{L}\beta_1$ and $\text{L}\gamma_1$ should be quite weak. These predictions are substantiated by Parratt.

Recently measurements have been completed on the L-series emission spectrum of zirconium ($Z=40$)*. Four of the lines, corresponding to

*Spielberg and Shaw, to be published.

those mentioned for silver, turn out to be of especial interest. They are shown in Figs. 19, 20, 21, and 22. While $L\beta_2$ in silver was accompanied by prominent satellites, none could be found for zirconium. On the contrary, the Ly_1 line, which is quite without structure in silver (the satellites are well separated from the parent line), is found in zirconium to have prominent structure on its high frequency side, which we might presume is a satellite structure. This structure has several noteworthy features. The observed contour indicates that a) there are two lines; b) the lines are very close to the "parent" line Ly_1 - much closer than the satellites of $L\beta_1$, for example; c) the lines are narrower than the parent line, rather than wider, as one expects for satellites on the simple Coster-Kronig theory*. It is to be noted that the $L\alpha_1$ and $L\beta_2$ lines have the same initial state (L_{III}), while the final states differ in that for $L\alpha_1$ it is an atomic state ($M_{IV,V}$), but $L\beta_2$ is associated with the conduction band. The same description applies to $L\beta_1$ and Ly_1 , except that here the initial state is L_{II} and the final state for $L\beta_1$ is M_{IV} (17).

J. Korringa** has suggested that the observed structure of the Ly_1 line indeed is satellites, but that the satellite process combines double ionization of the excited atom with transitions from exciton states below the conduction band.

The satellite transitions are pictured in the following way. Zirconium has atomic number 40, its electron configuration differing from that of rhodium ($Z=45$) only in the conduction level. Double ionization in the L_{II} level will proceed, then, for zirconium as for rhodium (Fig. 3c), the atom finally being ionized doubly in the levels $L_{II} M_{IV,V}$. But now each of these ionizations will form an exciton level below the conduction band more strongly bound than the exciton level for single ionization, and both of these levels will very quickly be filled with an electron. In the final satellite transition one of the electrons in the exciton level will pass to the L_{II} level with good transition probability (Fig. 23), since this transition is favored by the selection rules. Note that the transition, in contrast with that for the single ionization case (see the discussion in connection with Fig. 18), occurs directly from the exciton level to the L_{II} level without benefit of the conduction band. This occurs because of the shielding effect of the remaining exciton electron with the result that the transition has an atomic-like character.

* On the Wentzel double inner ionization model we should expect satellite lines to be wider than the parent line. This follows from the short lifetime of the $M_{IV,V}$ excited state. Experiment, in general, agrees with this prediction (59).

**Korringa, to be published.

Fig. 19. $L\alpha$ emission for zirconium metal ($Z=40$).

Fig. 20. $L\beta_2$ emission for zirconium.

Fig. 21. $L\beta_1$ emission for zirconium.

Fig. 22. $L\gamma_1$ emission for zirconium.

Fig. 23. Satellite emission in zirconium

Let us examine how well the above-mentioned observed characteristics of the lines are correlated with the proposed model. (a) Two lines are to be expected, one corresponding to the $L_{II}M_{IV}$ state, the other to the $L_{II}M_{V}$ state; (b) the calculated position, on the basis of the Coster-Kronig theory and spectroscopic data (9), is within 1 ev of the observed position; (c) the narrow widths of the line follow from the quasi-atomic nature of the transition.

Measurements recently have been made of the contours of the prominent L-series emission lines of nickel, copper and zinc (12 to 14.5A)* The instrument again was the two-crystal spectrometer with beryl crystals. The noteworthy feature of the curves for all three elements is their peaked nature, exemplified by the curves for copper, shown in Figs. 24 and 25. The question immediately arises, in view of results to be discussed presently on the M-series emission spectra of the first group of transition elements, as to what one should expect for a line shape. If the predominant influence determining the line shape is the density-of-states curve for the conduction band one might expect, for example, a rather irregular shape for the $L\alpha$ and $L\beta$ lines of copper which would correspond to the double-peaked structure indicated by theory (316), or some modification determined by selection rules. Unfortunately the shapes of the L absorption edges for copper are not known, so no direct estimate of the widths of the L levels is available. However, Beeman and Friedman (51) estimate the L_{III} level to have a width at half maximum of 1.4 ev from measurements of the K absorption edge and the $K\alpha_1$ line width, while the L_{II} level they estimate to be no less than 2.4 ev wide at half maximum. These levels, which would be expected to have a more or less Lorentzian shape, have widths which are by no means a negligible fraction of the total width to be expected for the L lines. In addition, it may be that the effect of exciton states in modifying the transition probability as one passes upward from the bottom of the conduction band cannot be ignored (16). This combination of circumstances lends considerable uncertainty to any prediction at the present time of the expected L-series line structures in this spectral region.

As indicated in the section on instrumentation, the most exciting experimental development in the x-ray spectroscopy of the solid state in recent years is probably the work of Harvey, Piore, et al., at MIT in the long wavelength region. For L-series emission only results for sodium ($Z=11$), magnesium ($Z=12$), and aluminum ($Z=13$) have been reported in the literature (236). Kingston (174) transformed the experimental curve for aluminum into a pseudodensity-of-states curve, reproduced in Fig. 26. It is of interest to compare this curve with the $K\beta$ emission line (Fig. 15). The L shape, in agreement with Jones, et al. (53), is quite different from the K on the low energy side, rising as

* Spielberg, Soules and Shaw, to be published.

Fig. 24. $L\alpha$ emission of copper. The upper curve is from Cauchois (Reference 258); the lower was obtained with the two-crystal spectrometer. The experimental points are indicated. The dotted portion of the curve is estimated background for the satellites. L marks the position of the L_{III} absorption limit as measured by Mlle. Cauchois. The spectral window for the lower curve is of the order of 0.4 e.v.

Fig. 25. $L\beta_1$ emission of copper.

Fig. 26. Density of electronic states (s and d) for the conduction band in aluminum. (After Kingston, reference 174).

$(E - E_0)^{1/2}$, if the low frequency "tail" is subtracted off.*

L-absorption spectra of several elements have been observed recently, all with photographic registration. These are very difficult experiments indeed, because of the lack of a suitable source of continuous radiation, as mentioned before. Tomboulian and Pell (185) point out the precautions with which the absorbing sample must be prepared for this spectral region by giving curves for aluminum when the metal is evaporated in a film on a zapon backing and again with an unbacked film. The curves are quite different on the high frequency side of the edge.

M-SERIES SPECTRA

Although a rather considerable amount of work has been done on M-series spectra in the intermediate wavelength region, by far the larger share has been concerned with wavelength determinations and is not of much interest for our purposes. This work is necessarily on elements of high atomic number. One must go to the long wavelength region to explore the M-series spectra of the lighter elements. Some interesting work has been done on metals of the first transition group in this region, mainly by two groups, one in England with Skinner, the other at MIT with Harvey, Piore, et al. (174) (218) (292). It is unfortunate that, at the present time, definitive experimental results are not available, for these two groups do not agree on the probable contours of the emission bands (315).

The experimental techniques used by these groups have differed for the most part in two respects, in the x-ray tubes and the detectors. Skinner has been most careful to prepare the x-ray tube for operation in such a way that contamination of the target is kept as low as possible. A glass x-ray tube is used, which can be degassed by flaming, and the target is heated red-hot before the target material is evaporated onto it. During the run of a few hours the target is renewed several times an hour by evaporation of new material. His detector is a photographic plate, from which microphotometer records are made. The target input power is of the order of a few hundred watts. Harvey, on the other hand, used a "metal" x-ray tube, which, of course, cannot be baked out. There is little doubt that this arrangement is inferior to the well baked out glass tube. However, the target power and exposure

* Landsberg (120) calculated the shape of the $L_{II,III}$ emission of sodium, taking into account the broadening of the individual energy levels of the conduction band by electron collisions. His prediction agrees quite well with the experimental curve, including the tail. See reference (10), p. 439, and reference (103) for further discussion.

times are far smaller than those of Skinner, about 2.5 watts and five minutes, respectively. This is made possible, of course, by the use of the direct photomultiplier as the detector.

One striking fact is that the data obtained by the MIT group for the L-emissions of sodium, magnesium, and aluminum agree convincingly well with that published long ago by the British group (54). For the M-series emission spectra, mostly of elements of the first transition group, there is little agreement (315)(292). Gyorgy and Harvey report emission lines for several elements having beautifully sharp emission edges and flattened tops, while Skinner et al. can find little, if any, evidence of emission edges. Their lines, in general, appear to be somewhat more peaked than those of the MIT group. In the MIT work it was found for several of the elements (e.g., Ca, Mn, Fe) that the emission edges quickly disappeared when the target became contaminated and reappeared only when fresh material was evaporated onto the target. This, of course, agrees with experience at the shorter wavelengths, where one observes that the emission spectrum of a metal may show a sharp edge, whereas its oxide does not (60). Whether either data represent the emission band contour will not become clear until the experiment is better done.

The MIT curve for copper is reproduced in Fig. 27. The original curve has been corrected by dividing its ordinates by a factor proportional to the fourth power of the absolute energy. If this curve is temporarily accepted, we may assume that it represents the density of electronic states in the conduction band after the two overlapping M_{II} and M_{III} bands are disentangled. These are shown by the broken curves, which are similar in form, as expected. The lower, broad portion of the curve has been identified with the s-p band in the metal and the narrower hump on top of this with the narrow d band (292).

The M-series emission curve for copper bears little resemblance in its shape to the L-series emission (Figs. 24 and 25) even though the transitions are to L levels in both cases.

In summary, we might say it appears we are being forced toward the conclusion that in the region below, say, 100Å, even though the inherent resolution of the method is adequate, the structure in the emission and absorption spectra cannot be uniquely identified with the density-of-electronic-states curve for the valence-conduction band. Whether such identification at longer wavelengths is valid is a question yet to be settled.

The author is much in debt to Professor Jan Korringa for many pleasant discussions and to Professor Rudolph Speiser for criticism of the manuscript.

Fig. 27. Density of electronic states (s and d) for the conduction band in copper. (After Gyorgy and Harvey, Reference 218).

BIBLIOGRAPHY

1. Barrett, Structure of Metals, McGraw-Hill, New York, Second Edition, 1952, p. 47.
2. Compton and Allison, X-Rays in Theory and Experiment, D. Van Nostrand Co., New York, 1935.
3. Cauchois, Les Spectres de Rayons X et la Structure Electronique de la Matiere, Gauthier-Villars, Paris, 1938.
4. Lindh, Rontgenspektroskopie, Vol. XXIV, 2. Handb. der Exp. Physik, Leipzig, 1930.
5. Skinner, Reports on Progress in Physics. "The soft X-ray spectroscopy of the solid state." The Physical Soc., London, 5, 257 (1936).
6. Siegbahn, Spektroskopie der Rontgenstrahlen, second edition, Julius Springer, Berlin, 1931.
7. White, Introduction to Atomic Spectra, McGraw-Hill, New York, 1934.
8. Mott and Gurney, Electronic Processes in Ionic Crystals, Oxford Press, second edition, 1948, pp. 14.
9. Bacher and Goudsmit, Atomic Energy States, McGraw-Hill, 1932, pp. 266.
10. Seitz, Modern Theory of Solids, McGraw-Hill, New York, 1940.
11. Reference 2, pp. 590 ff.
12. Reference 2, pp. 687, 709, 751, 753.
13. Complete references to this work are given in the excellent review article by Mlle. Y. Cauchois, (Reference 3).
14. Reference 341, footnote 4.
15. This correspondence has been observed for many metals. See reference 3 for bibliography.
16. Reference 341, footnote 29.
17. Reference 2, p. 830.

PRIOR TO 1945

18. Jauncey, "The birth and early infancy of X-rays." Am. J. Physics, 13, 362 (1945).
19. Friedrich, Knipping and Laue, Sitzungaberichte der Koniglich Bayerischen Akademie der Wissenschaften, p. 303, June (1912).
20. Friedrich, Knipping and Laue, "Interference phenomena for X-rays." (Reprint of reference 19). Ann. Physik, IV, 41, 971 (1913).
21. Bragg, "The diffraction of short electromagnetic waves by a crystal. Proc. Cambridge Phil. Soc. 17, 43 (1912).
22. Bragg, "X-rays and crystals." Nature 90, 572 (1913).
23. Moseley, "The high frequency spectra of the elements." Phil. Mag. 26, 703 (1914).
24. Rutherford, "The scattering of α and β particles by matter and the structure of the atom." Phil. Mag., 21, 669 (1911).
25. Bohr, "On the constitution of atoms and molecules." Phil. Mag. 26, 1, 476, 857 (1913).
26. Bohr, "The structure of the atom and the chemical properties of the elements." Z. Physik., 9, 1 (1922).
27. Stoner, "The distribution of electrons among atomic levels." Phil. Mag., (6), 48, 719 (1924).
28. Hirsh, "A summary of X-ray satellites." Rev. Mod. Phys., 14, 45 (1942).
29. Richtmyer, Rev. Mod. Phys. 9, 391 (1937).
30. Hoyt, "The shape of an X-ray line." Phys. Rev., 40, 477 (1932).
31. De Broglie, "On obtaining x-ray spectra by the passage of the rays through thin foils." C. R. Acad. Sci. (Paris) 158, 333 (1914).
32. Wannier, "Structure of electronic excitation levels in insulating crystals." Phys. Rev., 52, 191 (1937).
33. Bergengren, "On the absorption spectrum of phosphorous for X-rays." C. R. Acad. Sci. (Paris), 171, 624 (1920).
34. Bergengren, "On the X-ray absorption of phosphorous." Z. Physik., 3, 247 (1920).

35. Lindh and Lundquist, "Structure of the $K\beta_1$, line of sulfur." Ark. Mat. Astron. Fysik, 18, No. 14, 3 (1924).
36. Parratt, "Effects of chemical binding on the X-ray $K\alpha_{1,2}$ doublet lines of sulfur studied with the two-crystal spectrometer." Phys. Rev., 49, 14 (1936).
37. Fricke, "The K-characteristic absorption frequencies for the chemical elements magnesium to chromium." Phys. Rev., 16, 202 (1920).
38. Parratt, "Resolving power of the two-crystal X-ray spectrometer." Rev. Sci. Instr., 6, 387 (1935).
39. Coster and Veldkamp, "Determination of the X-ray absorption coefficients of copper and zinc in the neighborhood of the K-absorption edges." Z. Physik, 70, 306 (1931).
40. Karlsson, "Grating constants of high molecular weight, saturated fatty acids together with the K- and L-series. X-ray spectra of several light elements." Ark. Mat. Astron. Fysik., 22A, No. 9 (1930).
41. Mack, Stehn and Edlen, "Theory of the concave grating spectrograph, especially at large angles of incidence." Jour. Opt. Soc. Amer., 22, 245 (1932).
42. Ericson and Edlen, "Series spectra of the lightest elements." Z. Physik., 59, 656 (1929-30).
43. Parratt, "X-ray resonance absorption lines in the argon K-spectrum." Phys. Rev., 56, 295 (1939).
44. Kronig, "Theory of fine structure in X-ray absorption spectra." Z. Physik., 75, 191, 468 (1932).
45. Obert and Bearden, "The effect of chemical combination on K fluorescent X-ray emission lines." Phys. Rev. 54, 1000 (1938).
46. O'Bryan, "Structure of the L-absorption of sodium metal and its halides," Phys. Rev., 57, 995 (1940).
47. Shaw, "The K-absorption edges of Br (Z 35) and Kr (Z 36)." Phys. Rev. 57, 877 (1940).
48. Sandstrom, "The K-absorption spectra of Al and Mg." Ark. Mat. Astron. Fysik., 28A, No. 12 (1941).

49. Munier, Bearden and Shaw, "Principle M-series emission lines of tungsten and the K-absorption of magnesium and aluminum." Phys. Rev. 58, 537 (1940).
50. Farineau, "Contribution to the spectrographic study of the electronic structure of metals." Ann. de. Phys., (11), 10, 20 (1938).
51. Beeman and Friedman, "The X-ray K-absorption edges of the elements Fe (Z 26) to Ge (Z 32)." Phys. Rev., 56, 392 (1939).
52. Richtmyer, Barnes and Ramberg, "The widths of the L-Series lines and of the energy levels of Au(Z=79)," Phys. Rev., 46, 843 (1934).
53. Jones, Mott and Skinner, "A theory of the form of the X-ray emission bands of metals." Phys. Rev., 45, 379 (1934).
54. Skinner, "The soft X-ray spectroscopy of solids." Trans. Roy. Soc. (London), 239, 95 (1940).
55. O'Bryan and Skinner, "Characteristic X-ray from metals in the extreme ultraviolet." Phys. Rev., 45, 370 (1934).
56. Skinner and Johnston, "Fine structure of soft X-ray absorption edges. I. Li, Mg, Ni, Cu metals." Proc. Roy. Soc., A161, 420 (1937).
57. Paratt, "The silver L-series spectrum: Line widths, wavelengths, relative intensities, satellites and widths of energy levels." Phys. Rev., 54, 99 (1938).
58. Coster and Kronig, "A new type of auger effect and its influence on the X-ray spectrum." Physica, 2, 13 (1935).
59. Randall and Parratt, "L α satellite lines for elements Mo (Z 42) to Ba (Z 56)." Phys. Rev., 57, 786 (1940).
60. Kunzl, "On the K-series of aluminum, magnesium and sodium." Physik, 99, 481 (1936).

1945

61. Beeman, Forss and Humphrey, "The copper K-absorption edges of the cuprous halides." Phys. Rev., 67, 217 (1945).
62. Cauchois, "Universal spectrograph for X-rays, useful to 20A." J. phys. radium 6, 89.
63. Rule, "X-ray line absorption in the M-series for Sm (Z 62)." Phys. Rev., 68, 246 (1945).

64. Trischka, "Structure in the X-ray K-absorption edges of solid potassium chloride." Phys. Rev., 67, 318.

1946

65. Cauchois, Manecu and Le Blau, "L-spectra and characteristic levels for osmium." C. R. Acad. Sci. (Paris) 222, 1383.
66. Cauchois, "New observations on the emission of X-rays from atoms multiply ionized in deep layers." C. R. Acad. Sci. (Paris), 222, 1484.
67. Corson, "The theory of the fine structure of X-ray absorption limits in polyatomic molecules." Phys. Rev., 70, 645.
68. Das Gupta, "Soft X-ray absorption and emission spectra of Mg. Al, Si and their oxides." Indian J. Phys., 20, 226.
69. Krasnikov, "Hydrogen and proton gas in metals." Bull. Acad. Sci. USSR, Dep. Sci. Tech. (1), 133.
70. Kunzl and Svobodova-Joanelli, "The K-spectrum of Neon." Bull. Int. Acad. Techque Sci., 47, 91.
71. LeMieux and Beeman, "Stabilization of X-ray tube current and voltage." Rev. Sci. Instr. 17, 130.
72. Platt, "Structure in the X-ray K-absorption edge of metallic potassium." Phys. Rev., 69, 337.
73. Sarmiento, "Study of the satellites of the $L\alpha$ radiation of gold." Portugaliae Phys. 2, 139.
74. Shaw, "Secondary structure in the K-absorption limit of germanium tetrachloride." Phys. Rev., 70, 643.
75. Sorum, "The L-emission and absorption spectra of copper in pure metal, α brass, cuprous and cupric oxide. Kgl. Norske Videnskab. Selskabs Forh. 19, 44.
76. Sorum, "A high-vacuum X-ray spectrograph with concave crystal for comparison measurements." 19, 48.

1947

77. Allen, "An improved electron multiplier particle counter." Rev. Sci. Instr. 18, 739.
78. Barrere, "L-absorption and emission spectra of dysprosium." J. phys. radium, (8), 8, 72.

79. Barton and Lindsay, "The K X-ray absorption edge of silicon." Phys. Rev., 71, 406.
80. Brill, "Natural widths and relative intensities of some X-ray spectral lines." Physica, 13, 481.
81. Cauchois, "X-ray absorption spectra of some divalent nickel salts and their aqueous solutions." C. R. Acad. Sci. (Paris), 224, 1556.
82. Cauchois and Hulubei, Longueurs d' Onde des Emissions X et des Discontinuites d' Absorption X. (Hermann et Cie, Paris, 1947).
83. Coster and deLang, "On the resolving power of the ordinary X-ray spectrograph and the natural width of the X-ray spectral lines." Physica, 13, 379.
84. Das Gupta, "Second order chlorine K-valence band spectra of chlorides." Indian J. Phys., 21, 129.
85. DuMond, "A high resolving power, curved-crystal focusing spectrometer for short wavelength X-rays and gamma-rays." Rev. Sci. Instr. 18, 626.
86. Groven, "The K-emission spectrum of arsenic vapor, As (Z 33)." C. R. Acad. Sci. (Paris), 225, 572.
87. Hulubei, "Search for element 87." Phys. Rev., 71, 740.
88. Stephenson, "X-ray absorption structure of GeCl_4 and AsCl_3 ."
89. von der Lage and Bethe, "A method for obtaining electronic eigenfunctions and eigenvalues in solids with an application to sodium." Phys. Rev., 71, 612.
90. Woo and Sun, "On the absorption of X-rays." Science Repts. Natl. Tsing Hua Univ., 4, 398.
91. Woodall, "A further discussion of the gold L-spectrum." Phil. Mag., 38, 829.
92. Alexander, "Geometrical factors affecting the contours of X-ray spectrometer maxima, I. Factors causing asymmetry." J. Appl. Phys., 19, 1068.
93. Brogren, "A new method of investigating X-ray absorption spectra in gases." Ark. Mat. Astron. Fysik., 36B, No. 2.
94. Brogren, "The lattice constant of some reflecting planes in quartz." Ark. Mat. Astron. Fysik., 36B, No. 3.

95. Brogren and Friskopp, "Determination of the lattice constant of quartz 1011." Ark. Mat. Astron. Fysik., 36B, No. 4.
96. Burkhart, Peed and Saunders, "X-ray spectrum of element 43." Phys. Rev., 73, 347.
97. Cauchois, "Research on the origin of bands accompanying X-ray absorption edges of certain metals in salt solutions." C. R. Acad. Sci. (Paris), 227, 65.
98. Chalklin, "Intensity measurements in the very soft X-ray region." Proc. Roy. Soc. A194, 42.
99. Coster and Kiestra, "On the empty electron bands of lowest energy of the transition metals Mn and Fe and their oxides." Physica, 14, 175.
100. Friedman and Birks, "A Geiger counter spectrometer for X-ray fluorescence analysis." Rev. Sci. Instr., 19, 323.
101. Hulubei, Cauchois and Manescu, "New emissions in the K β spectra." C. R. Acad. Sci. (Paris) 226, 764.
102. Manescu, "Influence of the valency of rhenium on its X-ray absorption spectrum." C. R. Acad. Sci. (Paris) 226, 1010.
103. Matyas, "The energies of electrons in aluminum." Phil. Mag., 39, 429.
104. McQuillan and Kay, "The preparation of titanium and vanadium X-ray targets." J. Sci. Instr. and Phys. in Ind., 25, 423.
105. Pepinsky and Jarmotz, "An inductively coupled series tube D.C. high voltage regulator." Rev. Sci. Instr., 19, 247.
106. Tombouliau, "Radiative X-ray transition within the L-shell of sulfur." Phys. Rev., 74, 1887.
107. Valadares and Mendes, "Influence of voltage on the L α satellites of gold." C. R. Acad. Sci. (Paris), 226, 1185.
108. Weill, "Discontinuity of K-absorption of copper X-rays in aluminum-copper alloys at different stages of precipitation." C. R. Acad. Sci. (Paris), 227, 202.
109. Burkhart, Peed and Spitzer, "The K spectra of element 61." Phys. Rev., 75, 86.

110. Cauchois, "Notes on the K and L white absorption lines." C. R. Acad. Sci. (Paris), 228, 1720.
111. Cauchois and Mott, "The interpretation of X-ray absorption spectra of solids." Phil. Mag. 40, 1260.
112. Coster and de Lang, "The X-ray absorption edges L_I of tantalum and of tungsten and L_{II} and L_{III} of platinum." Physica, 15, 35.
113. Gokhale, "On the width of lines in X-ray spectra." C. R. Acad. Sci. (Paris), 228, 169.
114. Groven, "Study of X-rays emitted from gases." Ann. de. Phys, (Paris) (12), 4, 62.
115. Groven and Lagasse, "Weak emission lines in the $L\alpha$ spectrum of Hg (Z 80)." C. R. Acad. Sci. (Paris), 228, 1642.
116. Groven and Lagasse, "Study of the L-spectrum emitted by mercury vapor." Bull. Acad. Roy. Belge. Cl. Sci., 35, 1065.
117. Hanson and Beeman, "The Mn K-absorption edge in manganese metal and manganese compounds." Phys. Rev., 76, 118.
118. Konya, "Theoretical calculations of the form and width of the Compton-line." Hungar. Acta Phys. 1, 12.
119. Kostarev, "Interpretation of the 'superfine' structure of the X-ray absorption spectra of solids." J. Exptl Theoret Phys. (USSR), 19, 413.
120. Landsberg, "A contribution to the theory of soft X-ray emission bands of sodium." Proc. Phys. Soc. (London), A62, 806.
121. Morlet, "Study of the K-spectrum of selenium in the gaseous phase." Bull. Acad. Roy. Belge. Cl. Sci., 35, 1059.
122. Peed, Spitzer and Burkhart, "The L-spectrum of element 61." Phys. Rev. 76, 143.
123. Slater, "Electrons in perturbed periodic lattices." Phys. Rev. 76, 1592.
124. Stephenson and Mason, "Continuous X-ray spectrum from 8A to 14A." Phys. Rev., 75, 1711.
125. Taylor, "A 5 KW crystallographic X-ray tube with a rotating anode." J. Sci. Instr. and Phys. in Ind. 26, 225.

126. Vainshtein, "The structure of the X-ray K-absorption edge of nickel in solutions." Dokl. ady Akad. Nauk SSSR, 69, 771.
127. Victoreeen, "The calculation of X-ray mass absorption coefficients." J. Appl. Phys., 20, 1141.
128. Watson, West, Lind and DuMond, "A precision study of the tungsten K-spectrum using the 2-meter focusing curved crystal spectrometer." Phys. Rev., 75, 505.
129. Wohlfarth, "Interchange interaction and collective electron ferromagnetism." Phil. Mag. 40, 703.

1950

130. Bearden and Schwarz, "A precision evaluation of h/e by X-rays." Phys. Rev., 79, 674.
131. Berman, "A method for increasing the safe power input of X-ray tubes." Rev. Sci. Instr., 21, 275.
132. Borovskii, "A method of bending a crystal for a bent crystal X-ray spectrograph." Doklady. Akad. Nauk, SSSR, 72, 485.
133. Borovskii, and Barinskii, "The investigation of the fine structure of absorption spectra." Doklady. Akad. Nauk, SSSR, 72, 31.
134. Brogren and Hæggblom, "The lattice constant of Quartz $11\bar{2}0$."
135. Cauchois, "Applications of X-ray spectroscopy to solid state problems." Madison Conference (1950).
136. Cauchois, "Observations on the K-emission discontinuities of Al and Mg in dilute alloys." C. R. Acad. Sci. (Paris), 231, 574.
137. Cauchois, "X-ray spectrochemistry with bent crystals." Trans. Instrum. Meas. Conf., Stockholm (1949), 46 (1950).
138. Cauchois, "Some examples of applications of bent-crystal spectroscopy." Trans. Instrum. Meas. Conf., Stockholm (1949), 55 (1950).
139. Cauchois and Manescu, J. Chem. Phys., 47, 892.
140. Coster and Kiestra, "On the fine structure near the Fe K-absorption edges in the various oxides of Fe." Phil. Mag. 41, 144.
141. Das Gupta, "The soft X-ray valence band spectra and the heat of formation of chemical compounds and alloys." Phys. Rev., 80, 281.

142. Edamoto, "The fine structure of K-series X-ray emission spectra of the elements Mn (Z 25) - Zn (Z 30) and Ge (Z 32)." Rep. Res. Inst. Tohoku Univ., A2, 561.
143. Gilvarg, "Application of the pure bending of a crystal plate in a crystal holder to focusing X-ray spectrographs," Doklady Akad. Nauk SSSR, 72, 489.
144. Goens, "The X-rays emitted by arsenic vapor excited in an electromagnetic field of very high frequency." Bull. Acad. Roy. Belg. Cl. Sci., 36, 937.
145. Gokhale, "On the effect of the width of the microphotometer slit on the recorded width of the lines of X-ray spectra." C. R. Acad. Sci. (Paris), 230, 636.
146. Hirsh, "The satellites of the X-ray line M β ." Physica 16, 377.
147. Jossem and Parratt, "A versatile precision bent crystal focusing vacuum X-ray spectrometer." Phys. Rev., 79, 210.
148. Kostarev, "Theory of the temperature dependence of the fine structure of X-ray absorption spectra of solids." J. Exptl Theorer. Phys. (USSR) 20, 811.
149. Kurylenko, "White rays on the long wavelength side of the K-discontinuity for X-rays of oxides of the corumdum type." Cahiers phys. (No. 34), 37.
150. Morlet, "Note on the study of the K-spectrum of gaseous Br (Z 35)." C. R. Acad. Sci. (Paris) 230, 942.
151. Pell and Tombouliau, "Interface absorption by evaporated aluminum films at 130 A," Phys. Rev. 79, 210.
152. Stephenson and Martin, "Note on crystals suitable for double crystal X-ray spectroscopy in the region 3-15A." Rev. Sci. Instr., 21, 1023.
153. Stewardson and Zandy, "The L-M and K-M discrepancies in the rare earths." Proc. Phys. Soc. (London), A63, 670.
154. Vainshtein, "On the form of the K $\alpha_{1,2}$ lines of the X-ray spectra of the atoms of nickel in simplest chemical compounds. III." J. Exptl Theoret. Phys. (USSR), 20, 442.
155. Vainshtein, "Form of the K $\alpha_{1,2}$ X-ray lines of the atoms of copper and nickel in alloys of the Ni-Cu system." J. Exptl Theoret. Phys. (USSR), 20, 446.

156. Vainshtein, "On the structure of the fundamental K-absorption edge of atoms of transition elements in metals." Doklady Akad. Nauk. SSSR, 70, 21.

1951

157. Barinskii, Narbutt and Vainshtein, "Correlation between the theory of the fundamental X-ray absorption edge and the fine-structure theory. Doklady Akad. Nauk. SSSR, 79, 49.
158. Barton, Robinson and Perlman, "The L X-ray spectra from radioactive decay of transuranium elements." Phys. Rev., 81, 208.
159. Borovskii and Rydrik, "X-ray absorption lines." Doklady Akad. Nauk, SSSR 80, 41.
160. Brogren, "A simple two-crystal spectrometer made for investigating crystal lattices." Arkiv Fysik 3, 507.
161. Brogren, "A new type of crystal holder for focusing X-ray spectrometers." Arkiv Fysik 3, 315.
162. Curie, "On the line-widths and hyperfine structure in X-ray spectra." C. R. Acad. Sci. (Paris), 233, 1351.
163. Das Gupta and Bhattacharjee, "Soft X-ray L spectra of Fe, Co, Ni, Cu and their oxides." Indian J. Phys., 25, 555.
164. Deodhar and Mande, "Spin doublets in the α -spectrum of platinum." J. Sci. Ind. Research (India) 10B, 45.
165. Deodhar and Mande, "A new non-quadrupolar radiation in the platinum L-spectrum." J. Sci. Ind. Research (India) 10B, 260.
166. Drenck and Pepinsky, "New X-ray diffraction tubes of high brilliance." Rev. Sci. Instr., 22, 539.
167. Frilley, Gokhale and Valadares, "On the influence of the nuclear magnetic moment on the width of X-ray lines." C. R. Acad. Sci. (Paris), 233, 1183.
168. Fujimoto and Chiba, "X-ray K-absorption edge energies of elements Li, Be, B, and C." Sci. Rep. Tohoku Univ. First Ser., 35, 154.
- 168a. Fletcher and Wohlfarth, "Calculation of the density-of-states curve for the 3d electrons in nickel." Phil. Mag., 42, 106.
169. Glaser, "The absolute absorption coefficient of germanium and the fine structure in the K-edge of some of its components." Phys. Rev., 82, 616.

170. Gokhale, "A curved crystal X-ray spectrograph of high resolving power." C. R. Acad. Sci. (Paris) 232, 1086.
171. Gokhale, "On the widths of $K\alpha$ lines of elements Rb (Z 37) to Sn (Z 50)." C. R. Acad. Sci. (Paris), 233, 937.
172. Groven and Morlet, "Weak rays in the K X-ray emission spectra of the elements between Zn (Z 30) and Kr (Z 36)." Bull. Acad. Roy. Belg. Cl. Sci., 37, 630.
173. Kichenassamy, "On the width of $K\alpha$, lines." C. R. Acad. Sci. (Paris), 232, 1074.
174. Kingston, "Spectroscopy of the solid state: Potassium and calcium." Phys. Rev., 84, 944.
175. Kostarev, "On the temperature limits for the vanishing of fine and hyperfine structure in the X-ray absorption spectra of different elements." Zhur. Eksptl i Trort.
- 175a. Leigh, "A calculation of the elastic constants of aluminum." Phil. Mag. (7), 42, 139.
176. Nilsson, "The K-absorption limit of antimony." Arkiv Fysik, 3, 167.
177. Parratt and Hempstead, "On the reliability of Geiger-counter response at moderately high rates." J. Appl. Phys., 22, 1502.
178. Parratt and Jossem, "S-ray spectroscopy of the solid state." Phys. Rev., 84, 362.
179. Rogers and Chalklin, "A Geiger counter spectrometer for soft X-rays." Proc. Phys. Soc. (London), A64, 935.
180. Salgueiro and de Sousa, "Influence of the applied potential on the satellites of the X-ray lines of gold, lead and bismuth." Portugaliae Phys., 3, 95.
181. Salgueiro and Ferreira, "Study of the form and intensity of the satellite band accompanying the $L\beta_2$ -ray of gold." Portugaliae Phys. 3, 117.
182. Stephenson, Krogstad and Nelson, "The K X-ray absorption structure of Cl_2 and HCl." Phys. Rev., 84, 806.
183. Stewardson and Lee, "The M_{IV} and M_V absorption edges of Er (Z 68). Proc. Phys. Soc. (London), A64, 318.

184. Taylor, "Intense gallium X-rays for microradiography and diffraction investigations." *Nature (London)*, 168, 471.
185. Tombouliau and Pell, "Absorption by aluminum in the soft X-ray region." *Phys. Rev.*, 83, 1196.
186. Vainshtein, Barinskii and Narbutt, "Contribution to the theory of the fundamental X-ray absorption edge of atoms in molecules." *Doklady Akad. Nauk, SSSR*, 77, 1003.
187. Vainshtein, Barinskii and Narbutt, "Structure of the X-ray fundamental absorption edge of atoms in molecules." *Doklady Akad. Nauk, SSSR*, 78, 39.
188. Vainshtein, Barinskii and Narbutt, *Doklady Akad. Nauk, SSSR*, 79, 225.

1952

189. Abeles, "On the effective number of free electrons in aluminum." *J. phys. radium*, 13, 240.
190. Adams, "Motion of an electron in a perturbed periodic potential." *Phys. Rev.*, 85, 41; 86, 427.
191. Agarwal, "Nomenclature of X-ray diagram lines." *Sci. Cult.*, 17, 479.
192. Alexopoulos and Brogren, "Spectrum of the Compton Radiation from Solids." *Nature*, 170, 886.
193. Arndt and Riley, "Comparison of Geiger and proportional counters for intensity measurements in X-ray diffraction." *Proc. Phys. Soc. (London)*, A65, 74.
194. Barinskii, "X-ray absorption spectra of molybdenum in the compounds $(\text{NH}_4)_2 \text{MoO}_4$, $\text{K}_4 \text{Mo}(\text{CN})_8$ and MoS_2 ." *Doklady Akad. Nauk SSSR*, 83, 381.
195. Barinskii, Vainshtein and Narbutt, "Use of the magnitude of the jump in the coefficient of X-ray absorption for the calculation of the fine structure of the fundamental edge." *Doklady Akad. Nauk SSSR*, 82, 355.
196. Barinskii, Vainshtein and Narbutt, "The structure of the X-ray absorption edge of atoms of transition elements in chemical compounds." *Doklady Akad. Nauk SSSR*, 83, 199.
197. Bhattacharjee, "The low-energy satellite of the valence band spectra of some insulators." *J. Sci. Ind. Research (India)* 11B, 199.

198. Brogren and Rylander, "Scintillation counters for X-rays." Arkiv Fysik 4, 495.
199. Cauchois, "Preliminary remarks on the L-spectrum, the conductivity band and the color of silver." C. R. Acad. Sci. (Paris), 235, 613.
200. Cauchois, "The L-absorption spectrum of nickel. An anomaly." Phil. Mag. 43, 375.
201. Cauchois, "Energy levels of heavy atoms." J. phys., 13, 113.
202. Cauchois, "Notes on the technique for studying K-spectra of aluminum." Acta Cryst., 5, 348.
203. Cauchois, "Comparative study of the K-absorption spectrum of metallic aluminum." Acta Cryst., 5, 351.
204. Coles, "Electronic structures and physical properties in the alloy systems Ni-Cu and Pd-Ag." Proc. Phys. Soc. (London), B65, 221.
205. Cosslett, "Intensity limitations in a point source of X-rays." Proc. Phys. Soc. (Lon.) B65, 782.
206. Coulson and Taylor, "Studies in graphite and related compounds. I. Electronic band structure in graphite." Proc. Phys. Soc., (London), A65, 815.
207. Curie, "The breadth of spectral lines and hyperfine structure in X-ray spectra." J. Phys. radium, 13, 505.
208. Deodhar and Mande, "Non-quadrupole lines in X-ray spectra." Nature (London) 169, 889.
209. Deodhar and Mande, "New forbidden lines in the L-spectrum of mercury." J. Sci. Ind. Research (India) 11B, 1.
210. Doughty and McGrath, "The M_5 and M_4 X-ray absorption edges of tantalum." Phys. Rev., 85, 1040.
211. Faessler and Goehring, "X-ray spectrum and chemical bonds." Naturwissenschaften, 39, 169.
212. Fletcher, "Density-of-states curve for the 3d electrons in nickel." Proc. Phys. Soc. (London), A65, 192.
213. Friedel, "The distribution of electrons round impurities in monovalent metals." Phil. Mag., 43, 153.

214. Friedel, "X-ray transition probabilities with special reference to K-absorption in lithium." Phil. Mag., 43, 1115.
215. Friedel, "The absorption of light by noble metals and its relation to the van der Waals contribution to the cohesive energy." Phys. Soc. (London), B65, 759.
216. Givens and Siegmund, "The absorption of selenium in the soft X-ray region." Phys. Rev., 85, 313.
217. Gokhale, "Contribution to the study of the widths of X-ray spectral lines." Ann. de phys. (Paris), 7, 852.
218. Gyorgy and Harvey, "The spectroscopy of the solid state: copper and chromium." Phys. Rev. 87, 861.
219. Hayasi, "The satellites of the $K\beta_1$, β_5 lines and the fine structure of the K-absorption edge of copper." Sci. Rep. Tohoku Univ. First Ser., 36, 225.
220. Hirsh, "Auger enhancement of the $M\alpha$ X-ray satellite lines," Phys. Rev. 85, 685.
221. Howorth and Jones, "The cellular method of determining electronic wave functions and eigenvalues in crystals, with applications to sodium." Proc. Phys. Soc. (London) A65, 355.
222. Kiyono, "X-ray K-absorption spectra of potassium in KF, KCl, KBr, and KI." Sci. Rep. Tohoku Univ. First Ser., 36, 1.
223. Kiyono, "X-ray K-absorption spectra of potassium in various compounds." Sci. Rep. Tohoku Univ., First Ser., 36, 236.
224. Kockel, "Energy bands and localized states in the perturbed Kronig potential." Z. Naturforsch., 7a, 10.
225. Kostarev, "Theory of the X-ray absorption and emission spectra in ionic crystals." Zhur. Eksptl : Teort.
226. Lee, Stewardson and Wilson, "The M_V absorption edges of Tm and Er and the origin of the Er M_V absorption lines," Proc. Phy. Soc. (London), A65, 668.
227. Lee-Whiting, "X-ray absorption line-width and electron stopping power," Proc. Roy. Soc., A212, 362.
228. Mande, "The 's-t' doublet in the mercury L X-ray spectrum," Proc. Nat. Acad. Sci. India, A21, 11.

229. Mitchell and Beeman, "The X-ray K absorption edges of covalently bonded Cr, Mn, Fe and Ni." J. Chem. Phys. 20, 1298.
230. Morita, "On structure of X-ray K absorption edge of potassium in potassium halide." Sci. Rep. Tohoku Univ., First Ser., 36, 256.
231. Mott, "Recent advances in the electron theory of metals. A review." Progress in Metal Phys. 3, 76.
232. Narbutt, Barinskii and Vainshtein, "The structure of the fundamental X-ray absorption edge for ions in solution." Doklady Akad. Nauk SSSR, 82, 567.
233. Narbutt, Vainshtein and Barinskii, "The relation of the structure of the fundamental X-ray absorption edge to the X-ray emission spectra for atoms in molecules and polar crystals." Doklady Akad. Nauk SSSR 87, 381.
234. Parratt, Hempstead and Jossem, "Plain and beaded wire Geiger counters for X-rays." Rev. Sci. Instr., 23, 1.
235. Parratt and Jossem, "Backstreaming in oil diffusion pumps," Rev. Sci. Instr., 23, 188.
236. Plore, Harvey, Gyorgy and Kingston, "A high vacuum recording spectrograph for the study of radiation from solids in the 100-800A range." Rev. Sci. Instr., 23, 8.
237. Riou, "Study of L-spectra excited by internal conversion." J. Phys. radium, 13, 593.
238. Sandstrom, "A large bent crystal vacuum spectrograph." Arkiv, Fysik 4, 517.
239. Schawlow and Townes, "Charge distribution in nuclei from X-ray fine structure." Science, 115, 284.
240. Slatis and Lindstrom, "The inherent half-width of K conversion lines." Phys. Rev., 88, 1429.
241. Vainshtein, Barinskii and Narbutt, "Calculation of the structure of the main X-ray absorption edge of atoms in molecules." Zhur. Eksptl; Teort. Fiz., 23, 593.
242. Vainshtein, Narbutt and Barinskii, "The structure of the fundamental X-ray absorption edge of atoms in polar crystals and in connection with the ultraviolet absorption." Doklady Akad. Nauk SSSR, 82, 701.
243. Zandy, "The M_{IV} and M_V absorption edges of Pr (Z 59), Nd (60), Sm (62) and Eu (Z 63)." Proc. Phys. Soc. (London), A65, 1015.

244. Adell, Brogren and Haeggbloom, "The X-ray diffraction from quartz," Arkiv Fysik, 7, 197.
245. Alexopoulos and Brogren, "Evidence of a band structure in the Compton radiation from solids," Arkiv. Fysik., 6, 213.
246. Alpert, "New developments in the production and measurement of ultra high vacuum," Appl. Phys., 24, 860.
247. Arndt, "The use of Geiger and proportional counters in X-ray diffraction studies," Atomics (London) 4, 217.
248. Backovsky, "The regularity of the X-ray spectra of light elements," Czech. J. Phys., 3, 137.
249. Birks, J. B., Scintillation Counters, Pergammon Press, London, 148 pp.
250. Borovskii and Golovner, "Multiplicity in X-ray emission spectra," Doklady Akad. Nauk SSSR, 87, 233.
251. Brenner and Brown, "Calculations of K-absorption edges in some heavy atoms," Proc. Roy. Soc., A218, 422.
252. Brogren, "The X-ray diffraction from quartz and the influence of surface treatment," Arkiv Fysik, 6, 321.
253. Brogren, "Concerning the possibility of using ground calcite crystals as X-ray gratings," Arkiv Fysik, 6, 479.
254. Brogren, "A determination of Avogadro number," Arkiv Fysik, 7, 47.
255. Brogren and Adell, "The transmission and absorption of X-rays in calcite near the Bragg angle," Arkiv Fysik, 7, 1.
256. Brogren and Haeggbloom, "Some atomic planes in quartz suitable for X-ray spectroscopy," Arkiv Fysik 6, 171.
257. Cauchois, "The K-emission spectrum of aluminum in the conductivity band region," Acta. Cryst., 6, 352.
258. Cauchois, "The L-spectra of nickel and copper," Phil. Mag. 44, 173.
259. Deodhar and Agarwal, "Nomenclature of X-ray lines," J. Sci. Research (India) 12 B, 639.
260. Friedel, "Anomaly of the M_{IV} , V absorption in heavy elements," Proc. Phys. Soc. (London), A66, 333.

261. Gillam and Cole, "On monitoring a Geiger-counter spectrometer beam," J. Sci. Instr., 30, 429.
262. Hartman and Tomboulion, "Far ultraviolet radiation from the Cornell synchrotron," Phys. Rev., 91, 1577.
263. Herglotz, "Secondary emission of chromium $K\alpha_3$ satellites," Osterr. Akad. Wiss. II a, 162, 235.
264. Krogstad, Nelson and Stephenson, "X-ray absorption fine structure with polarized X-rays," Phys. Rev., 92, 1394.
265. Laskar, "Semi-direct determination of the fluorescence yield of the K-level of certain atoms from measurements of X-ray line widths," C. R. Acad. Sci. (Paris), 236, 2149.
266. Morlet, "Construction of a spectrograph for soft X-rays of wavelength 2 to 20A. L-emission spectra of wavelength 9 to 14A," Bull. Acad. Roy. Belgique Cl. Sci., 39, 205.
267. Mott, "Note on the Electronic Structure of the Transition metals," Phil. Mag. 44, 187.
268. Narbutt, "X-ray absorption spectra of zinc in molecules of $ZnCl_2$, $ZnBr_2$, and ZnS ," (Translation: NSF-tr-187, Jan. 1954), Doklady Akad. Nauk SSSR, 92, 273.
269. Nilsson, "A precision determination of the K excitation potential of some 3d elements," Arkiv Fysik, 6, 513.
270. Pines, "A collective description of electron interactions: IV. Electron interactions in metals," Phys. Rev., 92, 626.
271. Rowland, "Analysis of fluorescent X-radiation by means of proportional counters," J. Appl. Phys., 24, 811.
272. Sakellaridis, "Emission and absorption L-spectra of holmium (Z 67)," C. R. Acad. Sci. (Paris), 236, 1014.
273. Sakellaridis, "Emission and absorption L-spectra of gadolinium (Z 64) and thulium (Z 69)," C. R. Acad. Sci. (Paris), 236, 1244.
274. Sakellarides, "L-emission and absorption spectra of europium (Z 63) and terbium (Z 65)," C. R. Acad. Sci. (Paris). 236, 1547.
275. Sakellaridis, "Energy levels and weak emissions of the elements: Tm (Z 69), Ho (Z 67), Tb (Z 65), Gd (Z 64), Eu (Z 63)," C. R. Acad. Sci. (Paris), 236, 1767.

276. Townsend, "Solid-state absorption spectra of Mg and MgO," Phys. Rev., 92, 556.
277. Vainshtein, "On the theory of the fine structure of the X-ray absorption spectra of ions in solution." Doklady Akad. Nauk SSR, 91, 1059.
278. Vainshtein and Kavetskii, "X-ray absorption spectra of Ni, Cu and Zn ions in aqueous and non-aqueous solutions." Doklady Akad. Nauk SSSR, 91, 775.
279. Wainwright and Parzen, "Electronic energy bands in crystals." Phys. Rev., 92, 1129.

1954

280. Agarwal, "A formula for the K- and L-absorption discontinuities." Curr. Sci., 23, 357.
281. Backovsky, "X-ray emission and absorption spectra of carbon." Czech. J. Phys. 4, 300.
282. Backovsky and Drahokoupl, "Non-diagram lines in the K-spectrum of neon." Czech. J. Phys., 4, 507 (German).
283. Bedo and Tombouljian, "L-absorption spectrum of Si and SiO₂." Phys. Rev., 95, 621.
284. Brogren, "Relation between the width of an X-ray line and the resolving power of the double-crystal spectrometer." Phys. Rev., 96, 589.
285. Brogren, "A note on the widths of X-ray emission lines." Arkiv Fysik 8, 391.
286. Cauchois, Manescu and Le Berquier, "L-spectrum of Plutonium." C.R. Acad. Sci. (Paris), 239, 1780.
287. Eckhardt and Seifert, "A fine-focusing X-ray tube with electrostatic focusing." Optik 11, 195.
288. Faessler and Schmid, "On the structure of the K β X-ray spectrum of sulfur," Z. f. Phys., 138, 71.
289. Ferreira, "Contribution to the study of the satellite band intensity of the L α lines for elements of atomic number 73 to 92." Rev. fac. cienc. Univ. Lisboa B, 3, 65.
290. Friedel, "Electronic structure of primary solid solutions in metals." Adv. in Phys., 3, 446.

291. Gold, "Direct cellular evaluation of the density of states in phase and space and the accurate calculation of Fermi levels." J. Appl. Phys., 25, 1278.
292. Gyorgy and Harvey, "Spectroscopy of the solid state: Some of the transition elements." Phys. Rev., 93, 365.
293. Hanson and Schrader, "A linear motion X-ray spectrometer." Rev. Sci. Instr., 25, 422.
294. Hume-Rothery and Coles, "Transition metals and their alloys." Advances in Physics, 3, 149.
295. Jaffe, "The M X-ray from radium D and the M X-ray fluorescence yield of bismuth." Bull. Res. Coun. Israel, 3, 316.
296. Johnston and Tombouliau, "Absorption spectrum of beryllium in the neighborhood of the K-edge." Phys. Rev., 94, 1585.
297. Jones, "Soft X-ray emission bands in metals." Phys. Rev., 94, 1072.
298. Jones and Schiff, "Nuclear magnetic resonance in lithium and sodium." Proc. Phys. Soc. (London) A65, 217.
299. Kircher, "An X-ray tube for spectroscopy." Optik, 11, 196.
300. Kostarev and Borovskii, "Theory of X-ray absorption spectra." Zhur. Eksptl Teort. Fiz., 26, 377.
301. Leder and Marton, "Effect of chemical combination on the characteristic energy loss of electrons," Phys. Rev., 95, 1345.
302. Maurin, "Are electric octupole lines observable in X-ray spectra?" Bull. Acad. Polon. Sci. Cl., 3, 2, 69.
303. Narbutt, "A study of the X-ray absorption spectra of zinc in solutions." Zhur. Eksptl Teort. Fiz., 26, 208.
304. Nigam, "Fine structure of X-ray absorption spectra in homopolar crystals." Curr. Sci., 23, 117.
305. Parratt and Hempstead, "Anomalous dispersion and scattering of X-rays." Phys. Rev., 94, 1593.
306. Parratt and Jossem, "X-ray spectroscopy of valence and conduction bands of potassium chloride," Physica 20, 1134.
307. Raimes, "Energy band shapes and band widths in metals." Phil. Mag. (7) 45, 727.

308. Rogers and Chalklin, "A Geiger counter vacuum spectrometer and its use for the study of soft X-ray lines." Proc. Phys. Soc. (London), B67, 348.
309. Roos, "A new method for measuring Auger transitions." Phys. Rev., 93, 40.
310. Sakellaridis, "L-absorption and emission spectra of erbium (Z 68) and its energy levels." C. R. Acad. Sci. (Paris), 238, 2296.
311. Sandstrom, "The resolving power of a large bent crystal spectrograph." Arkiv Fysik 8, 129.
312. Sandstrom and Nordfors, "The transparency of cellulose acetate, cellophane, nylon, mylar and teflon in the region 3 to 10A," Arkiv Fysik, 8, 147.
313. Schiff, "A calculation of the eigenvalues of electronic states in metallic lithium by the cellular method." Proc. Phys. Soc. (London) A67, 1.
314. Shinoda, Suzuki and Kato, "Two types of band emission curves of copper in the soft X-ray region." Phys. Rev., 95, 840.
315. Skinner, Bullen and Johnston, "Notes on soft X-ray spectra, particularly of the Fe group elements." Phil. Mag., 45, 1070.
316. Slater and Koster, "Simplified LCAO method for the periodic potential problem." Phys. Rev., 94, 1498.
317. Snelgrove, El-Hussaini and DuMond, "Corrected values of tungsten K-series X-ray wavelengths with the 2-meter curved crystal diffraction spectrometer." Phys. Rev., 95, 1203.
318. Vainshtein, Barinskii and Narbutt, "On the theory of X-ray absorption spectra." Zhur. Eksptl Teort. Fiz., 27, 521.

1955

319. Alfred and March, "Fields around impurity atoms in metals." Phil. Mag. 46, 759.
320. Beckman, "Relative intensities of the X-ray K-lines of the heavier elements." Arkiv Fysik, 9, 495.
321. Brogren, "On line width determinations with bent crystal spectrometers." Arkiv Fysik, 9, 287.

322. Brogren and Nording, "The anomalous X-ray transmission through a crystal on both sides of the K-absorption edge of an element in the crystal." Arkiv. Fysik, 9, 349.
323. Callon, "L absorption spectra and energy levels of neodymium (60) and samarium (62)." C. R. Acad. Sci. (Paris), 240, 615.
324. Callon, "A new determination of the K absorption frequencies of caesium (55) and barium (56)," C. R. Acad. Sci. (Paris), 240, 854.
325. Candlin, "On the identification of X-ray satellites." Proc. Phys. Soc. (London), A68, 322.
326. Cauchois, "Preliminary investigations on the X-ray spectra from alloys irradiated with fast neutrons." C. R. Acad. Sci. (Paris), 241, 942.
327. Das Gupta, Sen and Bhattacharjee, "Study of the carbon K α and aluminum L_{2,3} bands by a newly constructed soft X-ray ruled grating spectrograph." J. Sci. Ind. Research (India) 14B, 129.
328. Das Gupta and Wood, "Soft X-ray spectra of magnesium-aluminum, magnesium-silicon, and aluminum-silicon alloys." Phil. Mag., 46, 77.
329. Fine and Hendee, "X-ray critical absorption and emission energies in Kev: Table of values." Nucleonics, 13, 36.
330. Karnatak, "Effect of chemical combination on the X-ray K-absorption edge of zirconium in its compounds." J. Sci. Ind. Research (India) 14B, 33.
331. Kurylenko, "Brillouin zones, electrical conductivity of metals and X-ray K-absorption spectra." Cahiers phys. No. 54, 1.
332. Lewis, Green, Mulder, Milner and Kolchin, "Computed transition probabilities for X-ray continua of potassium." Phys. Rev. 98, 1020.
333. Mande, "On the L-absorption spectra of gold in the pure metal and in gold-palladium alloys," C. R. Acad. Sci. (Paris), 240, 1205.
334. Mande, "The L-absorption spectra of gold in gold-silver alloys," C. R. Acad. Sci. (Paris), 240, 2222.
335. Moore, "A bent crystal X-ray spectrometer with roller bearing rotation mechanism." Jour. Sci. Instr., 32, 324.
336. Moore and Chalklin, "The K-series emission of neon." Proc. Phys. Soc. (London) A68, 717.

337. Nelson and Ellickson, "Scintillation counter for detection of X-rays." J. Opt. Soc. Amer., 45, 984.
338. Nigam, "The origin of fine structures in X-ray absorption spectra of ionic solutions." Proc. Phys. Soc., (London), B68, 472.
339. Nordfors, "A note on the Al $K\alpha_3\alpha_4$ lines in metal and oxide." Proc. Phys. Soc. (London), A68, 654.
340. Parratt, "Energy levels in metallic potassium." Phys. Rev., 98, 1150.
341. Parratt and Jossem, "X-ray spectroscopy of the solid state: KCl." Phys. Rev., 97, 916.
342. Sakellaridis, "Emissions in the neighborhood of absorption discontinuities in the L region of the X-ray spectra of the rare earths." J. Phys. radium, 16, 271.
343. Sakellaridis, "Multiplets characteristic of the rare earths in their X-emission spectra." J. Phys. radium; 16, 422.
344. Sawada, Tsutsumi, Shiraiwa, "On the structure of the X-ray non-diagram lines $K\beta$ for elements from Cr (Z 24) to Zn (Z 30)." J. Phys. Soc. (Japan) 10, 647.
345. Sawada, Tsutsumi, Shiraiwa and Obashi, "On the fine structures of X-ray absorption spectra of amorphous substances." J. Phys. Soc. (Japan), 10, 464.
346. Sprague, Tomboulion and Bedo, "Calculations of grating efficiency in the soft X-ray region." J. Opt. Soc. Amer., 45, 756.
347. Taylor and Parrish, "Absorption and counting efficiency data for X-ray detectors." Rev. Sci. Instr., 26, 367.
348. Tomboulion and Bedo, "Metal foils as filters in the soft X-ray region." Rev. Sci. Instr., 26, 747.
349. van den Berg and Brinkman, "High luminosity spectrometry in the soft X-ray region. I. The cylinder spectrometer." Physica, 21, 85.
350. Wertheim and Igo, "Isotope shift in the X-ray spectra of heavy elements." Phys. Rev., 98, 1.
351. Wolfsberg and Perlman, "Multiple electron excitation in Auger processes." Phys. Rev., 99, 1833.

- 352. Woodruff and Givens, "Soft X-ray absorption of evaporated thin films of tellurium." Phys. Rev., 97, 52.
- 353. Shaw, Spielberg and Soules, to be published.
- 354. Recently Hartmen and Tombouliau (reference 262) have recorded the continuous spectrum given by the Cornell synchrotron with excellent results.

DISTRIBUTION LIST

Annual Report, March 1956

U.S. Atomic Energy Commission Chicago Operations Office P.O. Box 59 Lemont, Illinois	6	Dr. L. G. Parratt* Department of Physics Cornell University Ithaca, New York	1
California Research and Development Company Livermore Research Lab. P.O. Box 751 Livermore, Calif.	1	Dr. J. W. M. DuMond* Department of Physics Calif. Inst. of Technology Pasadena, California	1
Oak Ridge National Lab. Metallurgy Division P.O. Box P Oak Ridge, Tenn.		Dr. W. W. Beeman* Department of Physics University of Wisconsin Madison, Wisconsin	1
Attn: J. H. Frye	1	Dr. J. A. Bearden* Department of Physics Johns Hopkins University Baltimore, Maryland	1
Attn: J. O. Betterton	1		
Attn: L. K. Jetter	1		
Prof. R de L. Kronig Laboratory for Technical Physics Mijnbouwplein 11 Delft, Holland	1	Dr. Gunter Schwarz* Department of Physics Florida State University Tallahassee, Florida	1
Prof. N. J. Grant Metallurgy Department Massachusetts Institute of Technology Cambridge, Mass.	1	Dr. N. F. Mott* Cavendish Laboratory Cambridge University Cambridge, England	1
Prof. Yvette Cauchois* Laboratoire de Chimie Physique 11 Rue Pierre-Curie Paris, Ve, France	1	Dr. C. S. Barrett* Institute for the Study of Metals University of Chicago 5640 Ellis Avenue Chicago 37, Illinois	1
Dr. J. Friedel* Ecole des Mines Paris, France	1	Dr. Jack A. Soules* Department of Physics New Mexico College of Ag. and Mech. Arts State College New Mexico	1
Dr. Arne Sandstrom* University of Uppsala Uppsala, Sweden	1	Dr. K. Das Gupta* Department of Physics 92 Upper Circular Road Calcutta 9, India	1

*Distribution of "The X-Ray Spectroscopy of Solids" by C. H. Shaw being
made under ONR Contract N6onr-22521 NR 017-606

DO NOT
PHOTOSTAT