tained at room temperature agrees well with the value 4.77 and 4.72 electron volts obtained by Glasoe[11] and Cardwell,[1] respectively, at room temperature. Wahlin's[4] values 4.21 and 4.48 ev, determined thermionically for β and γ iron, respectively, do not agree with the corresponding values 4.62 and 4.68 ev reported in this work. No satisfactory explanation of this disagreement is evident.

As in the case of nickel,[5] it should be noted that the magnitudes of the vertical shifts required to bring the experimental curves into coincidence with the theoretical curve are not the same for all temperatures. The photocurrent in each case was measured in the same units. In a normal case with no allotropic change involved, no vertical shift occurs. According to Fowler's theory, such a shift indicates a change in the probability factor. Hence, the vertical shift in the case of iron indicates a change in both the number density of free electrons and the transition probability factor for these electrons. Whether the latter is characteristic of the metal itself or is produced by a changed equilibrium condition of a gaseous layer on the surface is a question which can be answered only when marked advances in present vacuum techniques are developed.

The writer wishes to express his indebtedness to Mr. Robert St. John whose services were valuable during the first year of the experimental work.

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[11] G. N. Glasoe, Phys. Rev. 38, 1490 (1931).

PHYSICAL REVIEW VOLUME 92, NUMBER 3 NOVEMBER 1, 1953

Solid-State Absorption Spectra of Mg and MgO †

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(Received June 24, 1953)

Linear absorption coefficients have been determined for Mg and MgO for wavelengths from 80A to 350A. The results for Mg have indicated values range from 1.8×10^4 to 12×10^4 cm^{-1}. These values are in reasonable agreement with those extrapolated from the region of the K absorption edge. Surface effects were eliminated by plotting transmission against foil thickness. MgO exhibits three absorption bands in this spectral region. These bands have been tentatively identified and discussed in relation to earlier emission data of O'Bryan and Skinner. A gap of about 4 ev is found to exist between the top filled level and the proposed conduction band.

INTRODUCTION

USING a method similar to that described by Tomboulian and Pell,[1] the photon absorption by magnesium and magnesium oxide has been studied experimentally in the wavelength region near the magnesium $L_{2,3}$ edges. The electronic configuration of Mg, which results in two $3s$ electrons, makes the distribution of electronic energy states in the metal of particular interest. This arises from the prediction based on a nonoverlapping band structure that this metal should be an insulator. Since the energy band arising from the $3s$ atomic states is filled, no electronic conduction would be expected.

The absorption by the metal in this wavelength region (from 80A to 350A) has been measured by O'Bryan and Skinner.[2] Apparent trouble with surface contaminants, however, made absolute measurement of the absorption coefficients very difficult. The present work on Mg was therefore undertaken to eliminate or correct for surface effects and to seek absolute values for the absorption coefficients. The work on MgO absorption was intended as a supplement to emission work done by O'Bryan and Skinner.[3] Also it enabled a comparison to be made between the absorption spectrum for Mg when in a conductor and in an insulator. Since MgO contamination of the Mg films was anticipated, it was hoped a means of correcting for this would also come from the MgO study.

EXPERIMENTAL

The source of radiation was of the condensed spark discharge type described by Tomboulian and Pell.[1] A concave glass grating with a 1.5-meter radius of curvature was used at an angle of incidence of about 85°. Slit widths of 0.05 to 0.10 mm were used.

Absorber foils of Mg were formed by evaporation in a vacuum of less than 10^{-5} mm Hg as determined by a McLeod gauge. A liquid N_2 trap was used between the gauge and evaporation bell jar. A small disk of Mg was heated in an open graphite crucible on which was wound a tungsten heater coil. The evaporated Mg was condensed on a microscope slide coated with zapon plastic. To minimize the absorption effects of the zapon, the slide then was immersed in amyl acetate to free

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† Based on the authors thesis presented in partial fulfillment of the requirements for the Ph.D. degree at Cornell University, September, 1951.

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[1] D. H. Tomboulian and E. M. Pell, Phys. Rev. 83, 1196 (1951).

[2] H. M. O'Bryan and H. W. B. Skinner, Proc. Roy. Soc. (London) A162, 49 (1937).

[3] H. M. O'Bryan and H. W. B. Skinner, Proc. Roy. Soc. (London) A176, 229 (1940).

the evaporated film from its backing. The resulting films were bright and metallic showing no discolorations. The unbacked Mg foils were then mounted on fine-wire open-mesh nickel screening.

Absorber thicknesses were determined by assuming the foil density to be that of bulk Mg. Determination of weight/cm^2 of foils for a given amount of evaporated Mg gave the foil thickness per gram of evaporated Mg. When this ratio was measured for films of thickness 3×10^{-4} cm or more, values agreed to within 5 percent. When attempted for foils thinner than this, weighing from 50 to 100 micrograms, the scatter was greater but the average value was consistent with that obtained from the thick foils. This indicated that the use of a single ratio for all thicknesses was justified, provided the evaporation geometry remained fixed. The measured foil thicknesses were in agreement with values calculated for a point source evaporating over a solid angle determined by the crucible depth and diameter.

MgO foils were prepared by heating the unbacked Mg foils supported on the nickel screen to 600°C for 5 minutes in a hydrogen furnace with a small amount of water vapor. If the furnace was left on for several hours prior to treatment, the residual water vapor was removed and the Mg foil passed the treatment apparently unchanged. If then a few drops of water were introduced along with the sample, the foil was rapidly converted to a transparent, brittle material. Since heats of combustion predict that Mg will replace the hydrogen in water with a large evolution of heat, this film is undoubtedly MgO. The formation of the hydroxide is prevented by the high temperature. Use of a desiccator and prompt mounting in the vacuum spectrometer, at pressures of 10^{-4} mm Hg or less, also served to prevent formation of the hydroxide.

The photographic methods were similar to those of the earlier paper[1] with the exception that each plate consisted of three spectra. Two of these were taken with no absorber and were used to calibrate the plate as described by Skinner and Johnston.[4] Each plate was internally calibrated and a third spectrum was that transmitted by the absorber. Appreciable changes in the calibration curves were recorded and seem to indicate the presence of the Eberhard effect.[5] These plates were not utilized for the data given in the following.

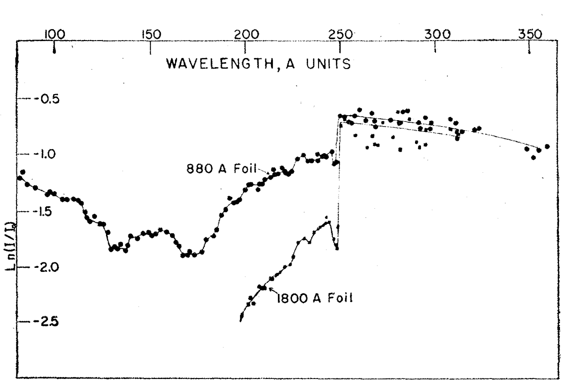

FIG. 1. $\ln(I/I_0)$ as a function of wavelength for two Mg foils of thickness 880A and 1800A.

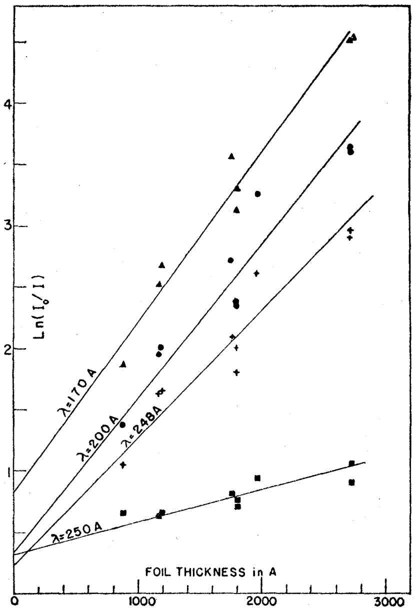

FIG. 2. $\ln(I_0/I)$ as a function of Mg foil thickness at several wavelengths.

The location of the L absorption edges in Mg can be predicted in the following way. The $L_{2,3}$ edges can be found from the relation: $\nu_K=\nu_{K\alpha}+\nu_L$, where ν_K is the K absorption-edge frequency, $\nu_{K\alpha}$ is the K_α emission frequency, and ν_L is the $L_{2,3}$ absorption-edge frequency. Data obtained by Wetterblad and Ase[6] for Mg give the result $\lambda_L=251$A. The separation of L_2 and L_3 absorption edges can be found from the usual spin doublet formula. This gives $\lambda_{L3}-\lambda_{L2}=1.19$A. The position of the L_1 edge can be predicted on the basis of observations made on the $L_{2,3}\rightarrow L_1$ transition in Mg.[7] This data places the L_1 absorption edge at 140A.

RESULTS

Magnesium

Figure 1 gives the $\ln(I/I_0)$ curves for two typical samples with thicknesses of 880A and 1800A. I_0 is the incident intensity and I is the intensity transmitted by the absorber. One such curve is obtained from each photographic plate; the curves shown are averages of two and four plates for the 880A- and the 1800A-foil, respectively. To check on the consistency of such curves

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[4] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).

[5] Harrison, Lord, and Loofbourow, *Practical Spectroscopy* (Prentice-Hall, Inc., New York, 1948).

[6] T. Wetterblad (Mg. K emission), Z. Physik. **42**, 603 (1927); Ase (Mg K absorption edge), Reported in Siegbahn, *Spektroskopie der Röntgenstrahlen* (1931).

[7] D. H. Tomboulian and W. M. Cady, Phys. Rev. **59**, 422 (1941).

for various thicknesses and to eliminate surface effects, the curves shown in Fig. 2 were plotted giving $\ln(I_0/I)$ *versus* thickness for several wavelengths. If a fraction C of the incident radiation is absorbed or reflected by the surface layers, then the data should follow the relation $\ln(I_0/I)=\mu x-\ln C$. This linear relation is borne out to within the rather appreciable experimental error. The ordinates are averages of from two to four plates while the foil thicknesses were determined but once. As individual ordinate determinations were good to within 5 percent while foil thickness was determined to within 10 percent, the ordinate values were used as the independent variable in determining the least square lines for the various wavelengths.

Figure 3 shows values of μ calculated from the slopes of curves similar to those in Fig. 2 for 12 different wavelengths.

As a further check on the data's consistency, the magnitude of the change in $\ln(I_0/I)$ at the $L_{2,3}$ edge was plotted against foil thickness as shown in Fig. 4. This change was measured between wavelengths of 250A and 248A. The presence of this sudden increase in the absorption coefficient depends upon the Mg being in a metallic state with a Fermi level having a large density of empty energy levels just above it. If a thickness d of the deposited Mg was converted to a nonmetallic state such as MgO, then the data of Fig. 4 should yield a straight line whose slope is the change in the absorption coefficient between 250A and 248A and whose x axis intercept is equal to d. As for Fig. 2 the ordinate of Fig. 4 should be more reliable than the sample thickness. Thus a least-squares line was drawn using the ordinate values as the independent variable. The slope of the line gives a value for the change in μ of $(8.26\pm0.65)\times10^4$ cm^{-1}, while d was found to be 218 ±134A. The errors quoted are probable errors calculated from the data.

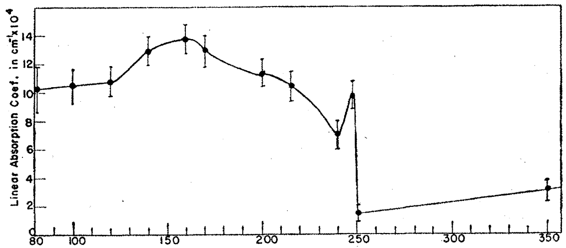

FIG. 3. Linear absorption coefficient for Mg as a function of wavelength.

As a final check on surface contamination, a foil was prepared and left on the zapon backing. Aside from a general increase in absorption, this had the effect of increasing the dip observed in Fig. 1 at a wavelength of 170A.

Magnesium Oxide

Magnesium oxide absorption was measured for three films. These were formed by oxidizing Mg foils whose measured thicknesses were 1450A, 2200A, and 2670A. No evidence of surface effects or surface contamination was found, for $\ln(I_0/I)$ was directly proportional to the thickness in the three cases. Figure 5 gives the values of $\ln(I_0/I)$ for the MgO film formed from the 2200A Mg foil. By assuming the densities of the Mg and MgO foils to be the same as for the bulk materials, one can find the thickness of the MgO film formed by oxidizing a Mg film of known thickness. This gives a thickness of 1710A for the MgO absorber considered in Fig. 5. Values of the linear absorption coefficient can be obtained from Fig. 5 by multiplying the ordinate by 6.15×10^4 cm^{-1}. All prominent features of the curve were found on all three foils. This includes the almost atomic-like absorption at 215A, the details of the band structure, and the absorption band of smaller magnitude near 100A.

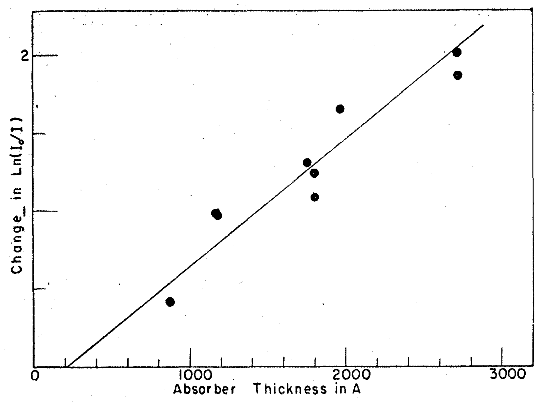

FIG. 4. The change in absorption of Mg foils at the $L_{2,3}$ absorption edge as a function of measured foil thickness.

DISCUSSION

Magnesium

The present study confirms the general properties of Mg absorption observed by O'Bryan and Skinner,[2] but differs in some details. The absorption maximum near 170A exhibits more fine structure and is not so large as reported in the earlier work. There is a clear indication that this maximum arises from some type of zapon-Mg interface as described by Tomboulian and Pell in the case of aluminum. Figure 2 shows the slopes of the curves for the 200A and 170A data to be nearly identical indicating equal Mg absorption coefficients even though the 170A absorption is always greater at any thickness. The 170A absorption must therefore contain an appreciable contribution from a surface layer. Also, leaving the zapon backing on increased the magnitude of this absorption maximum. The earlier report estimated that the change in μ at the $L_{2,3}$ edge was 1.8×10^4 cm^{-1}. This disagrees with the present value of 8.3×10^4 cm^{-1}. The discrepancy could arise if the earlier work was done with absorbers having a larger amount of Mg converted to some nonmetallic state.

The 880A curve in Fig. 1 shows a marked increase in absorption at a wavelength of 140A where the L_1 edge should be observed. The magnitude of the absorption change there is about $\frac{1}{3}$ that of the $L_{2,3}$ edge which is what would be expected on the basis of the statistical weights. Though five foils gave an indication of this edge, it remains doubtful as to whether it is a surface effect, fine structure from the $L_{2,3}$ edge or the L_1 edge.

The x intercept of Fig. 4 represents how much of the measured foil thickness has been converted to some nonmetallic state. As given above, the least square value obtained was 218A but it was found to have a large probable error of 134A. The large uncertainty in the intercept is felt to arise almost entirely from insufficient accuracy in the foil thickness determinations. Using more precise thickness measurements this method should be useful in the study of the formation of nonmetallic compounds on metals. As an example, the change in the absorption edge jump would enable one to study the surface oxidation of a metallic foil as a function of time and temperature.

In Fig. 6 are shown the available data on the K and L absorption coefficients for Mg metal. For wavelengths less than the K edge, Allen's data is plotted.[8] For wavelengths above the K edge Stobbe's theory[9] agreed well with data available for aluminum absorption just above the K edge, so good agreement would be expected here as well. As was the case for aluminum L absorption,[1] the extrapolation of the shorter wavelength curve falls somewhat above the observed L absorption in the case of Mg.

Magnesium Oxide

Magnesium oxide has a crystal structure similar to that of NaCl with a Mg-O separation of 2.10A. From the normal chemical valences of Mg and O one would anticipate that the compound consisted of doubly charged ions. Calculation of the electron affinity of O^{--} in the MgO lattice by the Born ionic model or the Born-Mayer equation for ionic solids assuming the metal ion to be doubly charged yields a value in fair agreement with values calculated similarly from CaO, SrO, and BaO.[10] However, an indication that other than ionic bonding is also present comes from the failure in the Cauchy relation between the elastic constants.[11] Thus the lattice most likely consists of ions nearly doubly charged with a small amount of nonradial interaction.

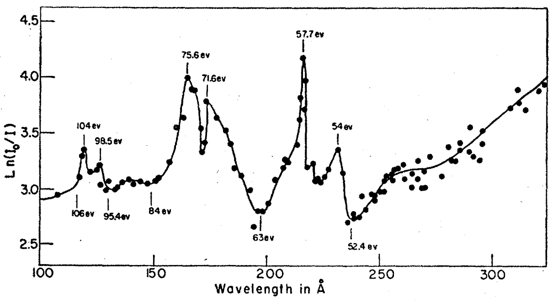

FIG. 5. $\ln(I_0/I)$ as a function of wavelength for a MgO foil formed by oxidizing a 2200A-Mg foil.

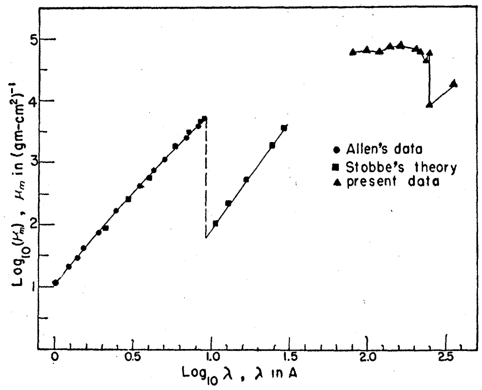

FIG. 6. Mg mass absorption coefficient as a function of wavelength near the K and L absorption edges.

The absorption spectrum of MgO as shown in Fig. 5 consists of three absorption bands for the wavelength region studied. The band with a threshold energy at 52 ev is believed to arise from the electronic transition from the $L_{2,3}$ shell to the conduction band. The band whose threshold is near 95 ev is then identified as arising from an L_1 shell electron being excited to the conduction band. The observed difference in the threshold energies of about 43 ev agrees within the uncertainty of the threshold determinations with the $L_{2,3}-L_1$ energy separation found by Tomboulian and Cady. The band widths appear comparable and absorption magnitudes differ by a factor of about 3 as expected from the statistical weights of the two shells. If one ascribes the structure seen between 52 ev and 82 ev to the density of conduction band energy levels alone, it is seen that a nearly forbidden range of energies is present at 12 ev above the lowest empty level. Also there is an indication of splitting each of the wider bands into two by a depression in the density of states.

These interpretations of the absorption spectrum are in conflict with the emission spectrum as obtained by O'Bryan and Skinner[3] and interpreted by Mott and Gurney.[12] The emission data as interpreted would place the top filled band of levels (the O^{--} $2p$ states) in the energy range from 50 ev to 60 ev above the Mg^{++} $L_{2,3}$ (or $2p$) states. This in turn implies the present absorption band with an average energy of 58 ev results in

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[8] E. U. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), Appendix IX.

[9] H. Hall, Revs. Modern Phys. 8, 358 (1936).

[10] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1942), p. 89.

[11] M. A. Durand, Phys. Rev. 50, 449 (1936).

[12] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 76.

the Mg^{++} $2p$ electrons being excited to levels already occupied by the O^{--} $2p$ electrons. This conflict arises from the double emission bands observed by O'Bryan and Skinner. If their lower energy peak is taken as arising from the direct transition from the filled band to the Mg^{++} $2p$ state, then the filled band occupies the energies from 38 ev to 48 ev above the Mg^{++} $2p$ state leaving a gap of about 4 ev between the filled and empty bands.

This interpretation of the emission data leaves unexplained the high-energy emission band observed by O'Bryan and Skinner. This, however, seems a smaller shortcoming than the overlap between filled and empty levels which results from Mott and Gurney's interpretation when applied to the present absorption data. It may be noted in this regard that the emission studies were carried out under conditions of electron bombardment which resulted in aluminum oxide being decomposed to leave a visible deposit of aluminum metal. If similar partial decomposition of the MgO occurred, the possibility of singly charged Mg ions being present would offer a lower lying energy level which would explain the high-energy emission band.

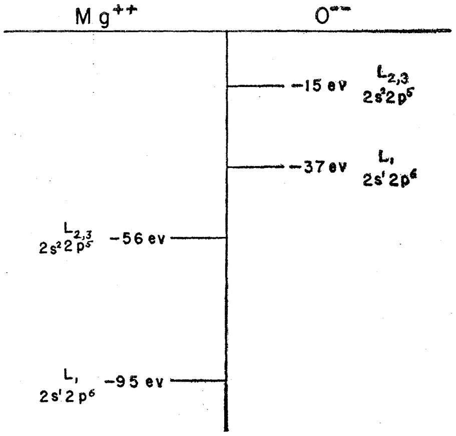

FIG. 7. An approximate electronic energy level scheme for MgO giving the levels of the isolated doubly charged ions after shifting them by an amount equal to the Madelung potential (see F. Seitz, reference 13).

The absorption band interpretation given here gains support from the type of energy level diagram suggested by Seitz.[10] A purely ionic type of lattice is assumed and the energy levels of the Mg^{++} and O^{--} ions are found for the isolated states. Shifting these ionic levels by the Madelung potential, whose magnitude is 24 ev in MgO, we get an estimate of the positions of the energy bands in the solid. The levels are shown in Fig. 7 after shifting the Mg^{++} levels upward and the O^{--} levels downward by the Madelung potential.

The energy level of the O^{--} $2s2p^6$ excited ionic state was not known, so estimates were made which place it between -10.4 ev and -17.7 ev. The first estimate used the neon L_1 absorption edge[13] to determine an effective screening constant for the L shell of a 10 electron atom. The screening of the $2p$ electrons in the case of O^{--} will be smaller than in the case of neon and hence the use of neon's screening constant gives too large an energy. The other estimate utilized the ionization potential of neutral oxygen, *viz.*, 13.6 ev, and the extension of the screening doublet law down to oxygen. This predicts an L_1 ionization potential of 28.6 ev. To then estimate the screening of the two extra $2p$ electrons in O^{--}, a charge of $2e$ was considered as a spherical shell of 1.32A in radius as given by Goldschmidt.[14] This raises the electronic potential energy inside the sphere by 10.9 ev giving for the state in question an ionization potential of 17.7 ev. This is too low an estimate, for the $2p$ electrons will shield somewhat inside the L shell as well as outside it. An average value of -13 ev was thus taken for this level. The O^{--} $2s^22p^5$ level is given by Seitz[10] on the basis of the Born cycle. The Mg^{++} $2s^22p^6$ level is a spectroscopic one[15] and the Mg^{++} $2s^12p^6$ level is taken as 39 ev lower as found by Tomboulian and Cady for Mg metal. The Mg and O K levels are at -1300 ev and -500 ev, respectively, and do not concern us here.

The levels as plotted will be greatly broadened by perturbations from nearby atoms in the solid, but the levels should give approximately the mean energies of the bands involved. If the bottom of the conduction band is taken as the zero of energy, a negligible electron affinity is implied and this has been done. From this tentative level diagram one sees that a mean energy of 56 ev is expected for the Mg $L_{2,3}\rightarrow$conduction band transition and 95 ev for the Mg $L_1\rightarrow$conduction band. These numbers agree quite well with the observed values of 58 ev and 100 ev. Also a mean energy of 41 ev for the emission band O $L_{2,3}\rightarrow$Mg $L_{2,3}$ is seen to agree with the mean energy of 43 ev given by the low-energy emission peak observed by O'Bryan and Skinner. It appears at present that photoconductivity experiments would be fruitful in identifying more clearly the absorption band corresponding to the conduction band and hence identifying which of the emission bands is to be the fundamental one.

The author wishes to express his deep gratitude for the continual guidance and encouragement given him by Professor D. H. Tomboulian who suggested the work on magnesium absorption. Also gratefully acknowledged are discussions with Professor J. A. Krumhansl regarding interpretation of the MgO results and the use of the microphotometer equipment made possible by Dr. G. W. Gartlein.

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[13] R. F. Bacher and S. A. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[14] V. M. Goldschmidt, Chem. Ber. **60**, 1263 (1927).

[15] C. E. Moore, Natl. Bur. Standards (U. S.) Circular 467, U. S. Government Printing Office, Washington, D. C. (1949).