plane waves in the usual way:

$$f_n{}^o = f_n - \sum_{\mathbf{K}_i} \tilde{f}_n(\mathbf{K}_i) e^{i(\mathbf{K}_i+\mathbf{k})\cdot\mathbf{r}}. \tag{A2.1}$$

We normalize each $f_n{}^o$ to average value unity. This is equivalent to adjusting f_n so that

$$\Omega^{-1}\int_\Omega |f_n|^2 d\tau - \sum_{\mathbf{K}_i} |\tilde{f}_n(\mathbf{K}_i)|^2 = 1. \tag{A2.2}$$

Calling the first normalized function $\phi_1{}^o$, we proceed to orthogonalize $f_2{}^o$ to this. We obtain, after several obvious steps,

$$\phi_2{}^o = (f_2{}^o - C\phi_1{}^o)(1-C^2)^{-\frac{1}{2}}, \tag{A2.3}$$

where

$$C = \Omega^{-1}\int_\Omega f_2{}^* f_1 d\tau - \sum_{\mathbf{K}_i} \tilde{f}_2{}^*(\mathbf{K}_i)\tilde{f}_1(\mathbf{K}_i), \tag{A2.4}$$

and f_1, f_2 have been adjusted in accord with (A2.2).

We can carry through the remaining orthonormalization by repeated application of the procedure used in (A2.3). For example, $f_3{}^o$ may be orthogonalized to $\phi_1{}^o$ by replacing $f_2{}^o$ by $f_3{}^o$. If the resulting function is then resubstituted for $f_2{}^o$ and if $\phi_2{}^o$ is substituted for $\phi_1{}^o$, the function $\phi_3{}^o$ results. The coefficient C must be calculated for each case.

The matrix elements can be computed in the same manner as before.

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K-Emission Spectrum of Metallic Lithium[*]

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The emission spectrum of an evaporated lithium target has been investigated in the spectral region extending from 60 to 600 A. The intensity distribution of the characteristic *K* emission band has been determined photometrically. Some features of the distribution $I(E)/\nu^2$ are as follows: the band has a maximum at 54.02 ev (229.50 A); the distribution drops to one-half of its maximum value on the high-energy side at 54.58 ev; and the decay in intensity from the peak to the high-energy limit of the band occurs in an energy interval of 1.18 ev. In agreement with the results of earlier investigators, the band does not show a sharp high-energy cutoff. A second band, similar in shape and having a maximum at 82.83 ev, has been observed and is presently identified as a *K* satellite.

INTRODUCTION

THE present investigation was undertaken with a view to re-examine the intensity distribution of the lithium *K* emission band which lies in the soft x-ray region. The spectrum is observed when the metal is bombarded by electrons possessing energies of a few hundred electron volts. The *K* emission spectrum is a result of electronic transitions from valence levels (2*s* band) into vacancies created in the *K* shell. The radiation was first detected photoelectrically by Skinner,[1] the band was observed previously by O'Bryan and Skinner,[2] and its shape was examined by Skinner.[3] These observations first pointed to a somewhat surprising lack of sharpness prevailing over the high-energy region of the band.

Unlike the case of the band spectra emitted by metals such as magnesium or aluminum which possess a more complex electronic structure, the *K* emission band of the lightest alkali metal is expected to be more susceptible of theoretical interpretation. It was therefore considered worthwhile to determine the spectral characteristics of the lithium *K* band with attentive concern for operational details in conducting the experiment and with adoption of a more critical attitude in the reduction of the experimental record.

In the radiative process referred to above, the core level is sharp, energy-wise, and has well-defined symmetry properties. Hence the spectral distribution of the observed radiation emitted in these transitions should provide some information of the nature of the level structure of the valence band for those transitions which are allowed.

If one writes the usual radiation formulas in a form appropriate for transitions from a group of closely spaced levels to a sharp inner level, the power radiated by the source in the frequency range $d\nu$ is found[4] to be

$$I(\nu)d\nu = \frac{8}{3}\frac{ne^2\hbar^3\Omega}{m^2c^3}\nu^2 \int_S \frac{\sum_i \left|\left(0\left|\frac{\partial}{\partial x_i}\right|k\right)\right|^2}{|\mathrm{grad}_k E|} dS d\nu, \tag{1}$$

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[*] Supported in part by the Office of Ordnance Research, U. S. Army.

[†] Corning Glass Foundation Fellow.

[1] H. W. B. Skinner, Proc. Roy. Soc. (London) **A135**, 84 (1932).

[2] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

[3] H. W. B. Skinner, Trans. Roy. Soc. (London) **239**, 95 (1940).

[4] D. H. Tomboulian, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 30, p. 259.

where n is the number of radiators per unit volume, Ω is the volume of the unit cell of the crystal, ν is the radiated frequency, and $(0|\partial/\partial x_i|k)$ is the matrix element between inner and valence states. Here the density of states function, $N(E)$, is defined by

$$N(E)dE=\frac{\Omega}{4\pi^3}\int_S \frac{1}{|\mathrm{grad}_k E|}dSdE, \quad (2)$$

where S is a surface of constant energy in k space. Formal simplification can be achieved by replacing the matrix element by an appropriate average value which may be considered as constant over the surface S. In this case the radiated power becomes

$$I(\nu)d\nu=\frac{32\pi^3}{3}\frac{ne^2\hbar^3}{m^2c^3}\nu^2\left\langle\sum_i\left|\left(0\left|\frac{\partial}{\partial x_i}\right|k\right)\right|^2\right\rangle N(E)d\nu. \quad (3)$$

This result may be written in the still simpler form

$$I(E)/\nu^2\sim F(E)N(E). \quad (4)$$

Thus an observation of the radiation emitted by a solid when transitions between the valence band and an inner level take place leads to information about the product of the averaged matrix element and the density of states function for the populated portion of the band. In general little can be done to extricate the function $N(E)$ from this product since information about the wave functions is meager.

Because of the selection rules, the observed intensity distribution will depend upon the symmetry character of the inner level. For states of lowest energy in the valence band it may be sufficient to treat the electrons as free. With this stipulation, the matrix element when evaluated for transitions to an inner level of s symmetry yields the well-known result for the low-energy intensity distribution in a K band, namely

$$I(E)/\nu^2\sim E^{\frac{1}{2}}. \quad (5)$$

EXPERIMENTAL

The general techniques of emission spectroscopy are well described in the literature[3–5] and only details pertinent to the present investigation will be described here. The vacuum spectrograph used in these measurements was designed to operate at grazing incidence. The dispersing element was a concave glass grating mounted at 5.5° with respect to the incident beam. Wavelength positions were determined in each case by the superposition of a known spark spectrum over a portion of the recorded lithium band.

The x-ray tube was constructed of glass with side arms available for the insertion of the x-ray filament, target and an evaporation furnace designed for frequent distillations of lithium onto a four-sided stainless steel target. Although the melting point of lithium is 186°C, it is necessary to heat the metal to about 500°C to reach a vapor pressure adequate for distillation. An enclosed furnace constructed of sheet tantalum was used for the evaporation. Tantalum is one of the few materials which resist corrosion by molten lithium. However other parts of the x-ray tube were in danger of being attacked. Hence, to prevent molten lithium from coming in contact with the walls of the tube, the furnace required essentially vacuum tight construction. This was achieved by spot welding a number of interlocking sections together with a small exit port directly in front of the x-ray target. The design of the evaporator was such that the lithium which finally reached the target was doubly distilled—a circumstance which aided materially in removing trace impurities possibly present in the source.

Generous amounts of the metal were deposited at each evaporation such that after ten successive distillations, the accumulated layer of lithium was nearly a half millimeter in thickness. Each evaporation prepared four target surfaces for subsequent electron bombardment, and no freshly coated surface was exposed to the electron beam for a period of longer than twelve minutes. The target surfaces did not show visible signs of deterioration after this time interval. The evaporation was repeated after the successive bombardment of the four faces.

The target and tube were carefully outgassed before the lithium was deposited. Outgassing of the target was achieved by heating it to a temperature of 400°C under electron bombardment in the absence of water cooling. The system was considered ready for evaporation of lithium when the tube pressure had dropped to 1 to 2×10^{-6} mm of Hg. These and better pressures were maintained throughout the exposures.

For the purpose of photographic calibration, two registrations of the band in a known time ratio were obtained on the same plate with intimate mixing of the exposures to minimize the effects of intensity fluctuations. For example, in one run the exposures were mixed 160 times and fresh lithium was evaporated eleven times. This procedure made it fairly certain that the ratio of intensities evaluated at corresponding wavelengths of the two contiguous registrations was given by the predetermined ratio of exposure times.

In general the accelerating voltage was maintained at either 600 volts or 750 volts and the electron current at 100 milliamperes. With this input power the band was detectable photographically in one hour but longer exposures were required to attain densities adequate for reliable photometric reduction. Because of the low melting point of lithium, it was not feasible to increase the power input significantly beyond the specified value.

A spectrogram resulting from the longest attempted exposure of eight hours served as a severe test of the optical adjustments and the degree of freedom attained

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[5] W. M. Cady and D. H. Tomboulian, Phys. Rev. 59, 381 (1941).

from the effects of such common contaminants as carbon compounds. The plate showed no visible fogging from light scattered diffusely from the grating or other parts of the spectrogram. Unless extreme precautions are taken to eliminate grease vapors, experience indicates that the K_α band of carbon can be photographed in many orders with exposure times less than one hour. On the plates taken in these measurements there was only a slight indication of the first order carbon image, and no traces of the characteristic tungsten, oxygen, or nitrogen lines which make their appearance when the target surface contains compounds of the above elements.

From the preceding remarks it may be inferred that the target surface was apparently free from appreciable amounts of contaminants and that the observed radiation had not been altered materially in appearance by absorption arising from extraneous materials on the target. The radiation was emergent from the target at about 45° from the surface. This circumstance, combined with the shallow penetration by the low-energy electron beam, makes it possible to disregard effects arising from self-absorption.

A supplementary experiment was carried out in an attempt to determine average target temperatures under electron bombardment with various coolants in the target interior. A small thermocouple junction was spot-welded to the target surface in the vicinity of the focal spot, with the lead wires so placed as to minimize the danger of disturbing the distribution of the accelerating electric fields existing prior to the insertion of the couple. Measurements were made with three different coolants; water at tap temperature (13°C), a mixture of alcohol and dry ice and circulated at −70°C, and liquid nitrogen. In all cases, the thermocouple indicated a large increase in temperature with any of the liquids used as coolants. Water cooling was found to result in the *lowest* average surface temperature (162°C) when the power input (60 watts) was sufficient for adequate photographic densities. Under typical excitation conditions, 600 volts and 100 milliamperes, the thermocouple indicated a reading which was only 26° below the melting point of lithium. Since x-rays produced by electron bombardment are generated in the first few hundred angstroms of the lithium deposit with the major portion of the input power being dissipated as heat in this layer, it becomes apparent that a well-defined and controllable value may not be assigned to the so-called temperature of the focal spot. Such observations indicate that one should not presume the attainment of a low focal-spot temperature simply because of the presence of a low-temperature refrigerant in the target interior. Fluorescent excitation utilizing the very intense radiation from high-energy electron accelerators would appear to present better opportunities for emission studies in which the target temperature may be controlled.

RESULTS

The raw data obtained in these measurements consist of two adjacent photographic images, exposed in a known time ratio with intimate mixing of exposures, and a condensed spark spectrum which overlaps a portion of one of the images produced by the lithium radiation. By utilizing microphotometer recordings of the plate, the wavelength and energy scales can be determined accurately from the spark spectrum. Photometric procedures applicable to this spectral region are described in the literature[4–6] and will not be included here. The shape of the lithium band as deduced from different plates was reproducible to about one percent with the exception of the extremities of the band where fluctuations of the order of three percent were observable.

Unlike the situation in absorption measurements, where essentially a comparison of the incident and emergent intensities is involved, emission measurements necessitate the consideration of all factors which may play a part in modifying the source distribution. A few of the more significant factors will be mentioned here. The shape of the lithium band as deduced from a microphotometer record and photometric reduction will contain inherent modifications introduced by the spectral response of the dispersing instrument and the detector. There is experimental evidence[7] that the photographic response of the Ilford *QI* emulsion used is flat in energy in this region of the spectrum. In any case, variations in response would certainly be small over the limited spectral extent of the lithium band. The photometric reduction has been based on this property of the detector. Furthermore, in the wavelength region of interest, there are no absorption edges characteristic of the elements present in the emulsion.

The first order reflecting power of the grating is a function of wavelength. This reflecting power has not been determined for the particular grating used in these measurements, however, detailed experience with a similar grating indicates[7,8] that the reflecting power varies by less than one percent over the wavelength spread of the lithium band and such variation is less than the photometric errors.

A further modification is introduced by the combined effect of the spectrograph slit and grating, that is, the instrument will in effect spread a very narrow band of frequencies into what appears as a finite distribution (such an instrumental characteristic is often referred to as the instrumental window). The net effect of such a modification will be a softening of features present in the spectral distribution of the source which features vary sharply over a frequency interval comparable

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[6] Tomboulian, Bedo, and Neupert, J. Phys. Chem. Solids (to be published).

[7] D. H. Tomboulian and P. L. Hartman, Phys. Rev. **102**, 1423 (1956).

[8] Sprague, Tomboulian, and Bedo, J. Opt. Soc. Am. **45**, 756 (1955).

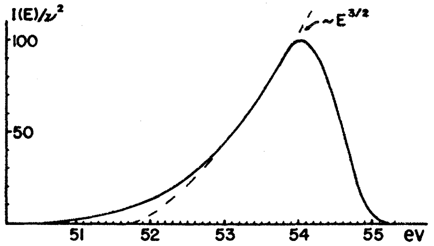

FIG. 1. The K emission band of lithium. The solid curve shows the observed intensity distribution as a function of the emitted photon energy, E. The dotted curve is a plot of $E^{\frac{3}{2}}$, representing the best fit on the low-energy side.

with the extent of the window. The problem may be formulated mathematically as a folding operation. If $I(E)$ represents the observed distribution, $\chi(E)$ the source distribution, and $S(E,E')$ the instrumental window function, the various quantities are related by

$$I(E)=\int\chi(E')S(E,E')dE'. \tag{6}$$

In this connection an attempt was made to determine the window function by observing the intensity distribution of an atomic spectrum line free from multiplet structure. An important feature of the window function, namely the form of the function far removed from the peak, is difficult to ascertain; but it is found that the instrumental line shape is reproduced quite well by a Gaussian distribution.

Various graphical and numerical methods have been developed to solve the integral equation in (6) above. Application of the graphical methods[9] to the observed lithium band indicates there are no first-order corrections which are larger than the photometric errors. Such a result is not surprising since the width of the window function at half maximum is 0.06 ev and no feature of the observed band shape has a comparable width.

The curve shown in Fig. 1 represents the intensity distribution (divided by the square of the radiated frequency) as a function of the radiated photon energy. (See Table I for numerical information.) According to Eq. (4), the ordinate (here expressed on an arbitrary scale) should be proportional to the product of transition probability and density of states functions.

Some characteristic features of the intensity distribution appearing in Fig. 1 are as follows: (1) the peak occurs at 54.02 ev; (2) on the high-energy side of the peak the intensity falls to one-half of peak value at 54.58 ev; (3) the recorded radiation extends from 50.5 ev to 55.2 ev yielding a band spread of 4.7 ev; the full width at half maximum being 1.46 ev. The peak is located 1.18 ev from the high-energy termination of the band and 0.56 ev from the midpoint of the high-energy edge. Also shown in Fig. 1 is a curve varying as the $\frac{3}{2}$ power of the energy which gives the best fit with the observed distribution. The fit was arrived at by plotting $[I(E)/\nu^2]^{\frac{2}{3}}$ as a function of E and observing the linear portion of the plot. The "reduced width," defined as the energy interval terminating at the zero of the $E^{\frac{3}{2}}$ curve and the steepest tangent which can be drawn at the high-energy edge, is 3.22 ev.

The curve presented in Fig. 1 agrees fairly well in shape with that published by Skinner.[3] The latter's results indicate a somewhat greater width at half maximum but neither curve shows a sharply dropping high-energy edge. It would be of interest to compare the present results for lithium with the K emission bands of other alkali metals. Unfortunately, corresponding data are not available in the literature as yet.

A number of theoretical calculations of the electronic band structure of lithium have been reported. The earliest of such calculations involving details of the valence wave functions seems to be that of Millman[10] whose results indicate that lithium should exhibit a behavior which is quite different from that deduced from a free electron model. Among more recent calculations, Parmenter[11] has applied the method of orthogonalized plane waves to a determination of the band structure. He has obtained the energy as a function of the wave vector for three different directions in the crystal. In the lowest approximation the energy is found to be independent of the direction of $\mathbf{k}$, and such independence appears to be essentially maintained as higher approximations are computed. Parmenter's value for the width of the valence band is 4.06 ev which may be compared with the present experimental result of 4.7 ev for the full band spread and 3.22 ev for the reduced width. (The free-electron band width for lithium is 4.8 ev.[3]) Utilizing the wave functions obtained in these calculations, Parmenter has also attempted to determine the intensity distribution of the K emission spectrum. The computed values of the intensity are roughly proportional to the $\frac{3}{2}$ power of the energy, and Parmenter points out that the reason for the slow decay in intensity near the high-energy end of the experimentally observed band is not known. He also predicts the upper limit of the band to be at 57.8 ev, a value to be compared with the experimental mean edge at 54.6 ev.

Schiff[12] has utilized the cellular method to investigate the electronic states of lithium. Eigenvalues were computed at the center of the zone face, the midpoint of the zone, and at the intersection of four zone faces. (These are the points designated as Γ_s, $N_p{}^1$, N_s, H_p, $H_d{}^1$, and H_s in the notation of Howarth and Jones.[13]) In contrast to the analogous calculation for sodium,[13]

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[9] See, for example, R. N. Bracewell, J. Opt. Soc. Am. **45**, 873 (1955).

[10] J. Millman, Phys. Rev. **47**, 286 (1935).

[11] R. H. Parameter, Phys. Rev. **86**, 552 (1952).

[12] B. Schiff, Proc. Phys. Soc. (London) **A67**, 2 (1954).

[13] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

Schiff finds that the state of lowest energy at the zone boundary has *p*-type symmetry. On this basis, namely the mixing in of *p* symmetry at points away from the zone center until the symmetry is predominantly *p*-type at the boundary, one is led to expect a fairly rapid decay in the observed x-ray *K* emission band near the Fermi surface since the *p* to *s* transition probability is high. Such a deduction is contrary to the observations in that the measured distribution falls to zero at the high-energy end in an interval corresponding to about one-quarter of the over-all extent of the valence band spectrum.

More, recently, a study of the electronic level scheme has been undertaken by Glasser and Callaway[14] who again employed the method of orthogonalized plane waves. Their results also indicate that the states closest to the Fermi surface are of *p* character.

By means of nuclear magnetic resonance experiments, Jones and Schiff[15] have investigated the symmetry properties of states near the Fermi surface. They interpret their results to be in accordance with the theoretical predictions of Schiff mentioned above. They comment that the emission band shape, as reported by Skinner,[3] appears to be incompatible with the calculated electronic states of the valence band. The present measurements are essentially in harmony with those of Skinner, indicating again that the spectroscopic x-ray evidence is not in agreement with the calculations of Schiff.

Since a discrepancy appears to exist between calculated and observed band shapes, it seems worthwhile to consider as many features as possible of an observational nature which might contribute to producing an experimental shape which would differ from the shape as computed theoretically. Various instrumental factors have been mentioned above, and it appears that none of these could have materially or significantly altered the band shape. Jones and Schiff[15] have suggested that the source of the discrepancy may lie in the excitation process associated with the production of x-ray spectra, namely that the emission takes place at an atom with an inner electron vacancy and the resulting spectra give information only about states which are strongly perturbed. This view is applicable to all x-ray spectra. However, in other cases of soft x-ray spectra, e.g., sodium *L* emission, it has not seemed necessary to appeal to a mechanism of this nature since there already exists fair agreement between observation and calculation.

Table I. Values of the relative intensity distribution as a function of the wavelength of the emitted radiation and the associated energy distribution (divided by the square of the radiated frequency). The energy in ev of the emitted photon was obtained from $E=12397.43/\lambda$, (λ in A).

λ(A)	$I(\lambda)$	E(ev)	$I(E)/\nu^2$
224.1	0.0	55.25	0.0
224.65	1.35	55.18	1.26
225.27	5.00	55.02	4.70
225.63	10.0	54.94	9.48
226.07	20.0	54.83	18.7
226.43	30.0	54.74	28.8
226.67	40.0	54.69	38.5
226.95	50.0	54.62	48.5
227.25	60.0	54.55	58.5
227.59	70.0	54.47	68.4
227.98	80.0	54.38	78.8
228.45	90.0	54.27	89.6
228.85	95.0	54.17	95.1
229.33	99.0	54.06	100
229.98	95.0	53.91	97.4
230.35	90.0	53.82	92.6
230.87	80.0	53.70	83.1
231.50	70.0	53.55	73.5
232.20	60.0	53.38	64.1
233.00	50.0	53.20	54.0
233.92	40.0	52.98	43.9
235.00	30.0	52.75	33.5
236.45	20.0	52.43	22.9
238.77	10.0	51.92	11.9
240.82	5.00	51.48	6.11
244.30	1.35	50.75	1.75
245.0	0.0	50.50	0.0

Throughout the preceding discussion we have considered the observed spectral distribution of the lithium band to be representative of the level density and associated transition probabilities of the valence band. However, in fact the final states also possess an energy distribution (spread of about 0.02 ev)[16] and strictly the observed intensity variation should be compared not with Eq. (3) but with the result of a formulation which includes the band-like nature of the inner level. Further, the observed spectrum should reflect an inherent modification associated with the radiative process and determined by the transition probabilities establishing the lifetime of the excited states. If in a given case the natural width of the inner level is a large fraction of the spectral breadth of the valence band, it is difficult to see how one can compare an experimentally observed band shape with that deduced from a theoretical model which does not take into account the role played by the radiative process.

From theoretical considerations[16] and from application of the method of Richtmyer, Ramberg, and Barnes[17] to the lithium *K* absorption curve of Skinner and Johnston,[18] there is evidence that the width to be associated with the *K* level in lithium is less than 0.1 ev. This is a relatively small spread and the observed behavior over the high-energy region of the lithium emission band can hardly be attributed to the lack of sharpness of the inner level. However, since the various theoretical determinations of the lithium emission band shape are not in agreement with the

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[14] M. L. Glasser and J. Callaway, Bull. Am. Phys. Soc. Ser. II, 2, 314 (1957).

[15] H. Jones and B. Schiff, Proc. Phys. Soc. (London) **A67**, 217 (1954).

[16] A. W. Overhauser (private communication).

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

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

observed spectrum, we have attempted to investigate the nature and extent of the modification which must be attributed to the inner level if the observations are to be essentially in accord with the computed band shape (to the extent that such a modification may be treated mathematically as a folding operation). In this connection the integral in Eq. (6) was evaluated by taking $\chi(E)$ proportional to $E^{\frac{3}{2}}$ and by regarding $S(E,E')$ to be either Lorentizian or Gaussian in form. The process of matching the observed distribution $I(E)$ was subject to the choice of two parameters; namely the width adopted in characterizing the spectral window and the value of E taken to designate the high-energy limit of the domain over which the $E^{\frac{3}{2}}$ behavior was assumed to hold.

The results of these integrations indicate that folding with the Lorentzian distribution will not reproduce the experimental curve for the emission band. The long "tails" characteristic of this distribution are emphasized in the integrated result and do not have their counterpart in the experimental shape. Much better agreement is obtained when the modifying function is taken as Gaussian. For a Gaussian distribution with a half-width of 0.35 ev and for an energy range of 2.8 ev for the function $\chi(E)\sim E^{\frac{3}{2}}$, it is possible to reproduce quite well the observed band shape.

In addition to the band shown in Fig. 1, examination of the spectrograms reveals a second band, less intense than the band at 227 A, with a high-energy edge at 148.4 A (a displacement toward higher energies of 29 ev from the band edge of Fig. 1). This band has a rather broad maximum centered at 82.83 ev, a drop in intensity to one-half of peak value on the high-energy side at 83.54 ev, a full width at half-maximum of 1.90 ev, and a full band spread of 5.0 ev. In appearance it resembles closely the lithium K band portrayed in Fig. 1. It does not seem possible to identify this second band with the characteristic spectrum of any impurity likely to be present at the target. The band in question has been observed on all plates exposed to the lithium radiation, and in each case the peak intensity of the weaker band at 148.8 A bears the same ratio (1/10) to the peak intensity of the lithium band at 227 A. This second band has tentatively been identified as a lithium K satellite and its origin is attributed to double excitation of the K shell.

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Loss of Exchange Coupling in the Surface Layers of Ferromagnetic Particles

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Experiments with spherical iron particles 28 A to 265 A in diameter demonstrate that the proposed nonferromagnetic surface layer on an iron particle must be less than 1 A thick. This conclusion is based upon a comparison of the ferromagnetic iron indicated by magnetic saturation, and the total amount of iron as determined by chemical analysis.

It has been proposed[1] that the saturation magnetization of thin layers at temperatures above absolute zero should decrease with thickness because of a decrease in Curie temperature caused by a weakened exchange coupling. For films or particles in the angstrom size range the atomic layers involved would account for a large fraction of the volume thus reducing the saturation induction greatly. Such behavior has been reported, for example, in the case of thin nickel films.[2]

The magnetic properties of ultrasmall particles are of interest because of their excellent permanent magnet characteristics. Magnets composed of elongated fine particles of iron and iron-cobalt have been made with energies up to 5×10^6 gauss-oersteds.[3,4] However, the theoretical upper limit of energy for magnets composed of ideally elongated particles of iron is 40×10^6 gauss-oersteds. The difference between experiment and theory has been accounted for mainly by nonideal particle shape, particle misalignment, particle size and shape distribution, and imperfect packing of the particles.[4,5] The magnitude of the loss in induction due to the loss in exchange coupling at the surface is an additional factor to be considered.

Becker[6] has shown that cobalt precipitated in solid copper has a nonmagnetic layer less than 1 A in thickness at room temperature. An analysis of measurements

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[1] M. J. Klein and R. S. Smith, Phys. Rev. **81**, 378 (1951).

[2] R. Coren and H. J. Juretschke, J. Appl. Phys. **28**, 806 (1957); E. C. Crittenden and R. W. Hoffman, Revs. Modern Phys. **25**, 310 (1953); H. H. Jensen and A. Nielsen, Trans. Danish Acad. Tech. Sci. **2**, 3 (1953).

[3] Mendelsohn, Luborsky, and Paine, J. Appl. Phys. **26**, 1274 (1955).

[4] Luborsky, Mendelsohn, and Paine, J. Appl. Phys. **28**, 344 (1957).

[5] I. S. Jacobs and C. P. Bean, Phys. Rev. **100**, 1060 (1955).

[6] J. J. Becker, J. Metals **209**, 59 (1957).