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Spectroscopy of the Solid State: Some of the Transition Elements*†

E. M. GYORGY AND G. G. HARVEY
Research Laboratory of Electronics and Department of Physics,
Massachusetts Institute of Technology, Cambridge, Massachusetts

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The $3P_{\frac{3}{2},\frac{1}{2}}$ emission curves of nickel, manganese, and iron have been obtained by using a vacuum recording spectrograph. A plausible interpretation of a number of features of the experimental bands is discussed.

EXPERIMENTAL DATA

We have obtained the $3P_{\frac{3}{2},\frac{1}{2}}$ (valence to M_{23}) emission curves of nickel, manganese, and iron, using the spectrograph previously described.[1–3] A representative nickel emission band is shown in Fig. 1. It was recorded at a bombarding potential of 500 volts and a target current of 4 ma. The range shown is from 50 counts to 200 counts per second. Unfortunately, the long wavelength side of the emission band is near a region of anomalous background. This irregularity (Fig. 2) is the second order of irregularities in the background extending from approximately 100A to 120A that was observed by Skinner.[4] Skinner has shown the source of these anomalies to be connected with the absorption and dispersion of the $2p$ electrons of silicon in SiO_2, the main constituent of the glass of the grating. A comparison of the nickel emission band and the continuous spectrum makes it clear that the anomaly in the background is only appreciable at wavelengths larger than 209A. As a result, we may assume the background radiation is at the level indicated on the experimental curve. Figure 3 illustrates the manner in which satellite intensity increases as the bombarding potential is increased. To obtain these curves the target current was carefully adjusted to make the background emission of the three curves equal. The curves were observed, using the 200 counts-per-second scale of the counting-rate meter and a bombarding potential of 500, 600, and 700 volts. The respective target currents used were 4 ma, 3 ma, and 2.5 ma. The absolute intensity of the emission bands cannot be related to the target current and bombarding voltage, since the position of the focus of the electron beam on the target is not exactly reproducible. The kinks in the $3P_{\frac{3}{2},\frac{1}{2}}$ edges are due to the response time of the counting-rate meter and are not real.[1] The manganese emission band shown in Fig. 4 was recorded at a bombarding potential of 600 volts and a target current of 6 ma. The low intensity made it necessary to use the 100 counts-per-second scale of the counting-rate meter, the larger response time corresponding to the 100 counts-per-

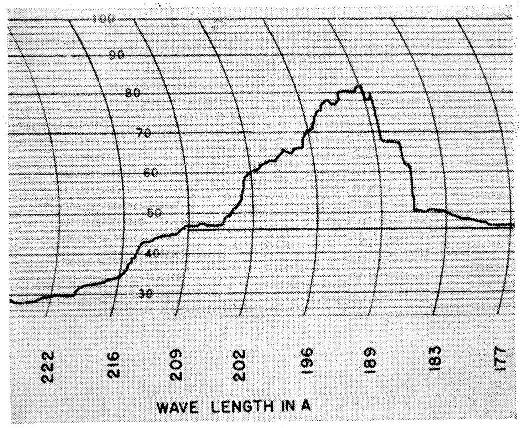

FIG. 1. Band emission curve of nickel. $E_b=500$ volts, $I_b=4$ ma.

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† The work reported here is based in part on a thesis submitted by E. M. Gyorgy to the Department of Physics, Massachusetts Institute of Technology, June, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] E. M. Gyorgy and G. G. Harvey, Phys. Rev. **87**, 861 (1952).

[2] Piore, Harvey, Gyorgy, and Kingston, Rev. Sci. Instr. **23**, 8 (1952).

[3] R. H. Kingston, Phys. Rev. **84**, 944 (1951).

[4] H. W. B. Skinner, Trans. Roy. Soc. (London) **A239**, 95 (1940).

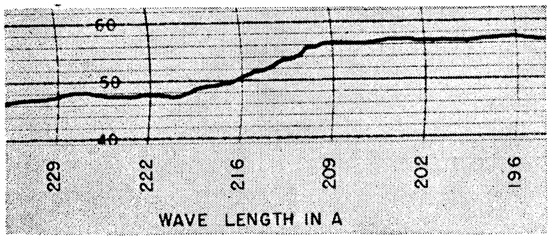

FIG. 2. Background radiation.

second scale, and the more rapid contamination of the sample made it impossible to obtain curves that were reproducible with the accuracy obtained for copper, nickel, and chromium.[1]

It was impossible to obtain a satisfactory iron emission band. The intensity and the ratio of intensity to background are low. The very rapid contamination of the sample made it imperative to record the curves rapidly. However, since the observed curves show more structure than previously obtained, it is probably worthwhile to consider them. The curve shown in Fig. 5 was recorded, using the 100 counts-per-second scale and 6-ma target current at 700 volts bombarding potential.

The experimental curves are modified to represent the distribution of the *s*-type and *d*-type electrons by the method given by Skinner.[4] The background of the experimental curves is eliminated. Then, to minimize the effect of fluctuations, we average the observed intensities. The average intensity with the ordinate divided by a factor proportional to the fourth power of the absolute energy is plotted as a function of energy. This curve is the superposition of the modified $3P_{\frac{3}{2}}$ and $3P_{\frac{1}{2}}$ emission bands. The structure introduced by the response time of the counting-rate meter is, of course, neglected. The distribution curve obtained for nickel is shown in Fig. 6. The modified experimental curve (dotted) shown in Fig. 1 has been added for comparison. In order to disentangle the $3P_{\frac{3}{2}}$ and $3P_{\frac{1}{2}}$ bands, the relative intensities of these bands must be known. We may find the correct intensity ratio if we note that the shape of the experimental curve on the long wavelength side of the $3P_{\frac{1}{2}}$ emission edge is not altered as the satellite intensity is increased. In fact, the majority of the experimental curves used to obtain the average intensity, from which the modified distribution curve given in Fig. 6 is derived, was taken at 600 volts bombarding voltage. These curves showed the expected larger relative satellite intensity (Fig. 3).

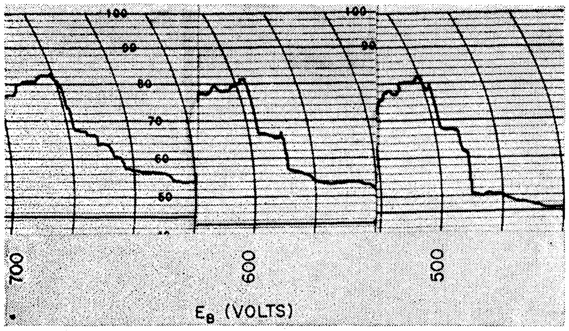

FIG. 3. Emission edges of nickel. (The background level is indicated for each curve.)

On the basis of these observations we may then assume that the shape of the emission curve would be unchanged if the satellite intensity could be reduced to zero. In other words, to find the correct ratio of the $3P_{\frac{3}{2}}$ to the $3P_{\frac{1}{2}}$ intensity, the $3P_{\frac{1}{2}}$ emission edge must be measured from the level of the background. The two bands can then be separated as indicated. The doubtful low-energy parts of the curves are dotted. The experimental observations concerning the shape of the other emission bands that were studied, and the intensity of the satellite emission, were the same as those of nickel. Consequently, we may separate the iron, and the manganese curves, as shown in Fig. 7 and Fig. 8. The modified experimental curves (dotted) have been added. Considering the low accuracy of the experimental iron emission bands, we would not expect the details of the distribution curve to be meaningful. In fact, below 50 volts the method of separation caused the separated curves to be somewhat oscillatory. For

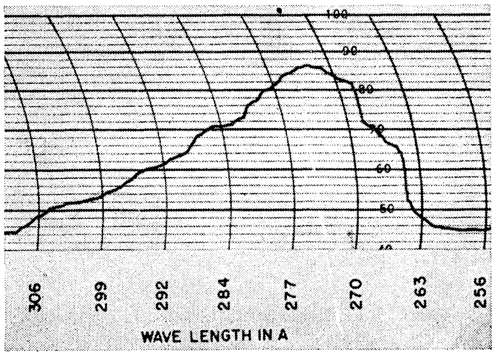

FIG. 4. Band emission curve of manganese. $E_b = 600$ volts, $I_b = 6$ ma.

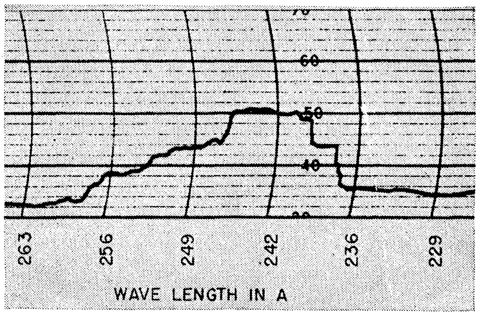

FIG. 5. Band emission curve of iron. $E_b = 700$ volts, $I_b = 6$ ma.

the sake of clarity we have drawn a smooth curve, but in no case was the ordinate changed by more than 10 percent.

The experimental results are summarized in Table I. It should be emphasized that the deviations given are a reasonable limit on the error and are not the probable error. The reasonable limit is determined by considering possible inaccuracies in the calibration of the spectrograph and the inherent low accuracy of the long wavelength side of the experimental curves.

DISCUSSION

The density of states having d-like symmetry around the individual atoms of the lattice is presumably higher than the density of states having s-like symmetry. Also, at least for hydrogen-like wave functions, the $3d$, $3p$ transition has a greater probability than the $4s$, $3p$ transition. Hence, we might expect that the observed emission band represents only the five d bands. However, the experimental emission edges of copper,[1] which has a completely occupied d band, are as sharp as those observed for nickel, which has a partly filled d band. If the experimental emission curves represent only the d band, we would not expect the characteristic sharp edge at the high-energy side of the copper band. This is one of the observations that suggest that s-like states contribute an appreciable part to the experimental bands. In fact, if we assume that transitions from the s-p band to the $3P_{\frac{3}{2},\frac{1}{2}}$ level have a greater probability than transitions from the five d bands, we are able to give a self-consistent interpretation of a number of features of the experimental bands. The copper d and s-p bands would then be roughly represented as shown in Fig. 9. (Part of the s-p band is indicated by the dashed line.) We may note that this curve portrays, except for the relative height of the s-p and d bands, the general features predicted for the energy bands of copper; that is, a narrow, filled d band protruding in the middle of a wider valence band. It should be stressed that the only reason for postulating that the transition probabilities are such as to make the integrated intensity of the d band less than that of the s-p band is that this postulate leads to the most plausible conclusions to put forward at the present time.

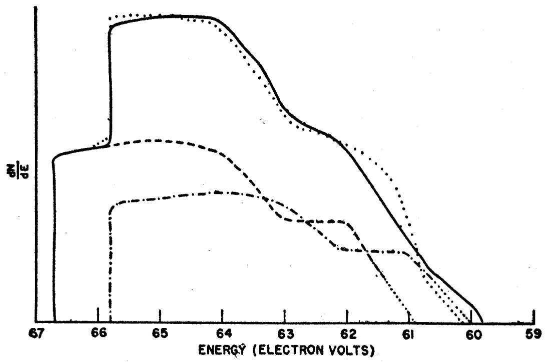

FIG. 6. Electron distribution in nickel.

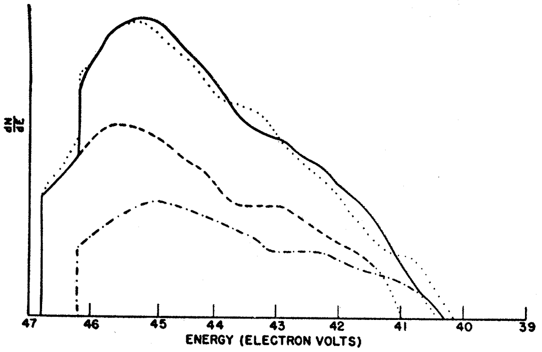

Fig. 7. Electron distribution in manganese.

The width of the conduction bands of the metals of the first two periods of the periodic table are given quite accurately by the Sommerfeld free-electron approximation.[4] On the basis of the calculations of the copper s-p band by Slater[5] and Krutter,[6] we may expect the same to be true for the transition elements because according to these calculations the electrons in the s-p band behave approximately as free electrons, except in the immediate neighborhood of the nuclei of the ions. In Table II we compare the width of the observed emission bands with the width of the s-p band calculated for free electrons. With the assumption that the half of the d band associated with positive electron spin is filled, the number of electrons per atom in the s-p band of nickel, iron, and copper may be obtained from magnetic measurements. The agreement for copper and nickel is good and helps to substantiate the representation of the s-p band shown in Fig. 9. The agreement for iron is not as satisfactory, but the discrepancy could be explained by assuming that the free-electron approximation is not applicable without modification to electrons in the s-p band of iron or that the number of conduction electrons obtained from the magnetic measurements is incorrect. In fact, Seitz,[7] to account for the cohesive energy of iron, suggests that half the d band of iron is not filled, and that consequently the number of conduction, or "free," electrons

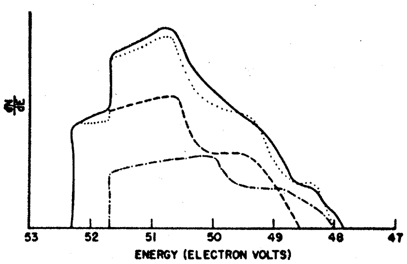

FIG. 8. Electron distribution in iron.

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[5] J. C. Slater, Phys. Rev. **49**, 537 (1936).

[6] H. M. Krutter, Phys. Rev. **48**, 664 (1935).

[7] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 430.

TABLE I. Summary of experimental results (all energies in ev).

	$3P_{\frac{1}{2}}$ emission edge	$3P_{\frac{3}{2},\frac{1}{2}}$ separation	Bandwidth
Mn	46.8±0.2	0.6±0.1	5.8±1.0
Fe	52.3±0.2	0.6±0.1	3.7±1.0
Ni	66.7±0.2	0.9±0.1	5.8±0.5

is larger than 0.22. Since the number of "free" electrons is not known for chromium[1] and manganese, we can only state here that interpreting the observed bandwidths of these metals as the width of the *s-p* band does not lead to any unreasonable conclusions.

Now, in the light of the preceding discussion we might expect the analysis given by Jones, Mott, and Skinner[8] to be applicable to the *s-p* band of copper. Following their procedure we expand ψ_k, the wave function of the electron in the *s-p* band, in the neighborhood of the nuclei in the form

$$\psi_k = a_s(k)\psi_{4s} + a_p(k)\psi_{4p},$$

where ψ_{4s} and ψ_{4p} are the free-atomic wave functions and k is the wave vector. In the case of an energy band derived from an atomic *s*-state and an atomic *p*-state of slightly higher energy they find that

$$a_p(k)^2 = (k/K_1)^2,$$

where $k = K_1$ at the edge of the first Brillouin zone. If we denote the number of electrons per unit energy range by dN/dE, we may regard

$$a_s(k)^2 dN/dE \text{ and } a_p(k)^2 dN/dE$$

as the numbers of *s* and *p* type electrons, respectively, corresponding to k in the *s-p* band. Then we have

$$(dN/dE)_s = a_s(k)^2 dN/dE = [1-(k/K_1)^2] dN/dE.$$

The approximate value of K_1 is given by $\Omega_K = 4/3\pi K_1^3$, where Ω_K is the volume of the zone. We replace k^2 and dN/dE by the corresponding expressions given by the free-electron approximation to obtain $(dN/dE)_s$ as a function of energy. To compare this calculated curve with the observed *s-p* emission band, we must normalize the latter to represent the same number of electrons per atom as the calculated curve. A simple calculation shows that in the case of a half-filled band the calculated curve contains about $\frac{5}{8}$ electrons. The agreement between the two curves (Fig. 9) is remarkably good, considering the crudeness of the assumptions involved. If the postulated separation of the *s-p* and *d* bands is correct, the width of the copper *d* band is approximately 3 volts. It must be remembered, however, that although the analysis described here helps to give qualitatively the general features of the conduction band, it is definitely incorrect in many details. For example, the electronic specific heat of copper predicted by the free-electron distribution is $0.6\times10^{-4}RT$ compared to the experimental value of $0.89\times10^{-4}RT$,[9] where R is the gas constant.

TABLE II. Bandwidths (all energies in ev).

	Observed	Free electron	Number of free electrons
Fe	3.7	2.6	0.22
Ni	5.8	5.3	0.6
Cu	7.1	7.1	1.0

Since the *s-p* band calculated for copper fits the experimental data, we would expect that a similar calculation would give the *s-p* band of nickel. In this case, a comparison of the observed and calculated curves is not possible because there is no natural way to adjust the vertical scale of the observed electron distribution. Fitting the calculated curve to the low-energy part of the nickel curve would not be satisfactory because the exact shape of this part of the curve is in doubt. However, since the crystal structures of copper and nickel are the same, the energy bands for the two metals should be similar. Except, of course, the *d* band of nickel is not filled, and the smaller nuclear charge and smaller lattice spacing might be expected to broaden the bands. We can attempt to separate the nickel *d* and *s-p* bands by analogy to copper, as shown in Fig. 10. This procedure would give an experimental width of the *d* band of approximately 3.6 ev. If we normalize the postulated nickel *d* band to represent 9.4 electrons, we can obtain a numerical value for the density of electrons at the Fermi edge. We then obtain $8.5\times10^{-4}RT$ for the electronic specific heat, which is in good agreement with the measured value 8.72×10^{-4}

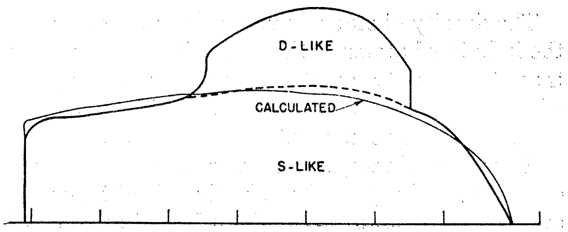

FIG. 9. The electron distribution of copper, showing the postulated *s-p* and *d* bands.

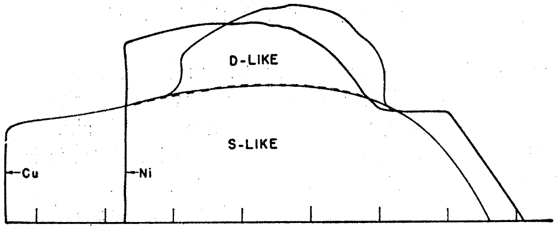

FIG. 10. The electron distribution of copper and nickel, showing the postulated *s-p* and *d* bands.

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[8] Jones, Mott, and Skinner, Phys. Rev. 45, 379 (1934).

[9] J. A. Kok and W. H. Keesom, Physica 3, 1035 (1936).

RT.[10] The contribution of the s-p band to the density of electrons at the Fermi edge has been neglected, since it is an order of magnitude smaller than the contribution of the d band. These results are, of course, only qualitative, since we have also neglected any possible admixture of p-type electrons in the d band and any variation of the transition probability; but they show that the shape of the postulated d band is consistent with the observed electronic specific heat.

The s-p bands of iron, chromium, and manganese might also be expected to be similar to the one calculated for copper, even though the crystal structure of these metals is different. As in the case of nickel, there is no unique way to adjust the vertical scale of the observed curves. Furthermore, a comparison with the copper emission curve can no longer be expected to be valid. Therefore, we arbitrarily adjust the observed manganese curve to fit the calculated s-p band at 2.5 ev (Fig. 11). This procedure results in fair agreement of the low-energy parts of the observed and calculated curves. With less justification, the parabolic rise of the calculated curve is fitted to the bottom of the observed chromium band (Fig. 12). Although these separations of the observed electron distributions into the d and s-p bands are somewhat arbitrary, they form a basis for a discussion of the energy bands. The manganese curve has the expected behavior: a narrow unfilled d band and a wider conduction band. The d band is about 3.0 ev wide. The unfilled d band of manganese would indicate a large electronic specific heat, but certainly not as large as the observed value of $21\times10^{-4}RT$,[11] which is 2.5 times larger than that of nickel. The calculated s-p band of chromium obviously is not correct, since it requires that the d band be filled. However, the low electronic specific heat of chromium indicates that the general features of the separation of the s-p and d bands may be correct. The measured value of the electronic specific heat of chromium is $1.9\times10^{-4}RT$,[12] only about two times larger than that expected from the s-p band alone. The postulated d band, which appears to drop to a low intensity at the emission edge, is consistent with the expected low density of states at the Fermi edge. The low-energy limit of the chromium band is not clearly marked, except perhaps by the inflection in the band, 3.4 ev below the emission edge. The latter interpretation does not fit the calculated s-p band shown, but since the separation of the d and s-p bands of chromium has less justification than the postulated separations discussed for the other metals, we shall not pursue this topic further. We shall not attempt to separate the iron s-p and d bands, since the accuracy of the experimental curves is too low to give us much confidence in the results. However, a comparison of the iron curve and the nickel curve shows that we might say that the d band of iron is about 2.2 ev wide.

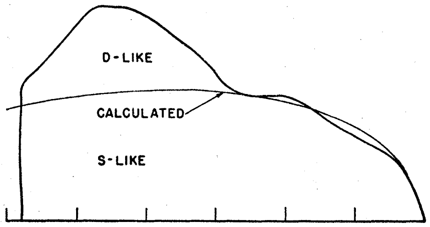

FIG. 11. The electron distribution of manganese, showing the postulated s-p and d bands.

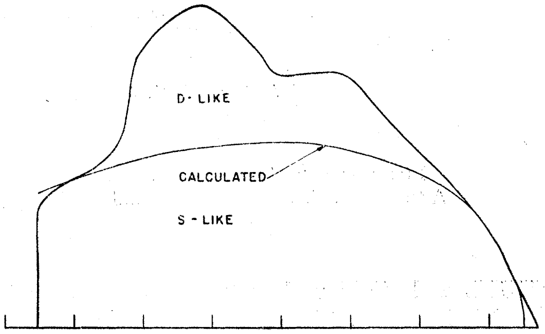

FIG. 12. The electron distribution of chromium, showing the postulated s-p and d bands.

ACKNOWLEDGMENT

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[10] W. H. Keesom and C. W. Clark, Physica **2**, 513 (1935).

[11] Elson, Grayson-Smith, and Wilhelm, Can. J. Research **18**, 82 (1940).

[12] Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952).

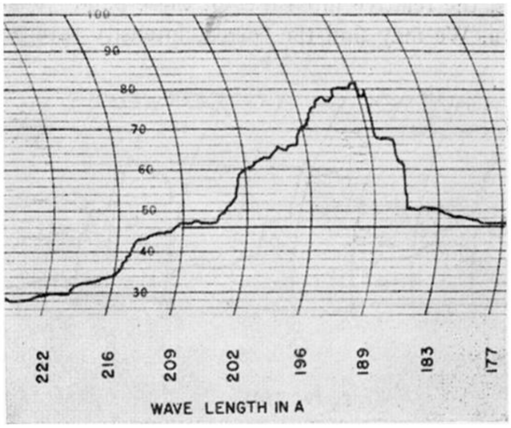

FIG. 1. Band emission curve of nickel. $E_b = 500$ volts, $I_b = 4$ ma.

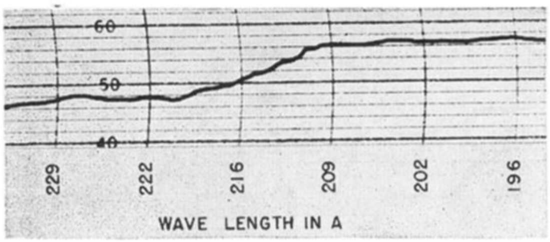

FIG. 2. Background radiation.

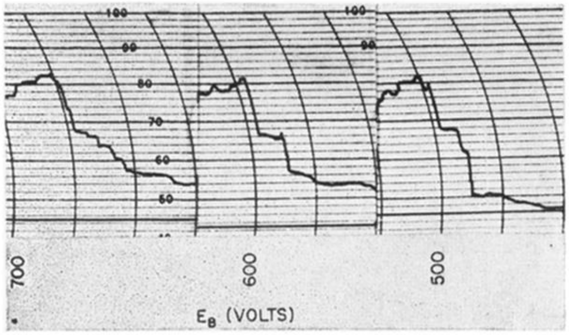

FIG. 3. Emission edges of nickel. (The background level is indicated for each curve.)

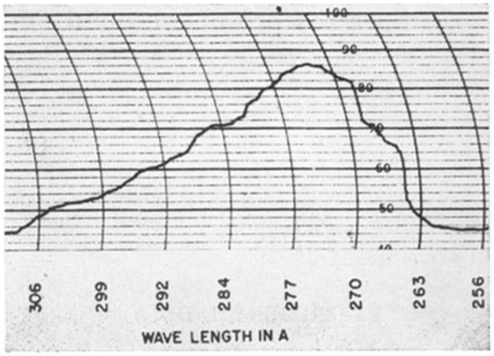

FIG. 4. Band emission curve of manganese.
$E_b = 600$ volts, $I_b = 6$ ma.

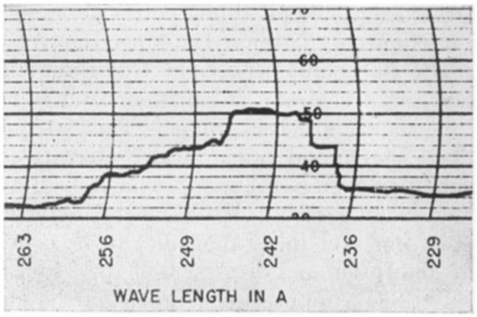

FIG. 5. Band emission curve of iron. $E_b = 700$ volts, $I_b = 6$ ma.