PHYSICAL REVIEW VOLUME 101, NUMBER 5 MARCH 1, 1956

Comparison of the Characteristic Energy Losses of Electrons with the Fine Structure of the X-Ray Absorption Spectra

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(Received November 7, 1955)

Comparison of the characteristic energy losses of electrons in several materials with the fine structure found on the short-wavelength side of the x-ray K-absorption edge indicates that there is a correlation between the two phenomena. This leads us to believe that many of the characteristic energy losses may be due to excitation of the valence electrons to higher allowed energy levels. It is also shown that, in general, the energy-loss spectra are similar for metals which are neighbors in the periodic table, and that there is some dependence on the crystal lattice constant.

INTRODUCTION

IT is the purpose of this paper to show that a striking correlation exists between the characteristic energy losses of electrons in solids and the fine structure found on the short-wavelength side of the x-ray absorption edge. For the sake of simplicity, we consider here only the K-edge fine structure, and compare the characteristic losses with the maxima of absorption of the fine structure as measured from the K-edge. Since the x-ray K-edge corresponds to a transition of a K-electron to the first unoccupied level above the Fermi level, and the maxima of absorption of the fine structure to transitions to higher allowed levels, it is quite plausible to account for the characteristic energy losses as due to excitations of the valence electrons to the same higher energy levels. It is, of course, obvious that the initial states will differ for the two cases, and that, therefore, there will be some differences in the level spectra obtained in regard to the number of levels observed and the probabilities of the transitions. One might also reasonably expect differences in the energy values due to the fact that the fine structure is measured from the Fermi level. There would also be possible differences in the widths of the spectral lines since the initial K-state for the x-ray case is very sharp whereas, off-hand, the initial state for the electron case would appear to be considerably broader. At the present time there are not sufficient data available to allow discussion of the transition probabilities or the half-widths of the spectral lines, and we can only approach the problem from the limited viewpoint allowed by a comparison of energy absorption values.

Before we present the numerical data, we will first discuss the characteristic energy losses and the x-ray fine structure so that the two phenomena in question are understood. These discussions will be brief since there are rather complete reviews of both subjects; in the case of the x-ray fine structure by Hanawalt[1] and by Kurylenko[2] and in the case of the characteristic losses by Marton, Leder, and Mendlowitz.[3]

CHARACTERISTIC ENERGY LOSSES

It has been found that electrons, which interact with a solid, lose rather small, well-defined amounts of energy. The distribution in energy of the electrons after the interaction, measured either in transmission through thin films or in reflection from the solid, gives a spectrum consisting of a strong line, corresponding to those electrons which have not lost energy, and then several other lines corresponding to the characteristic energy losses. The range of energies of observed losses is approximately between 5 and 75 ev and the line shapes vary from very narrow (e.g., aluminum) to very broad (e.g., silicon). These energy losses have been known since 1924,[4] but until 1941, when Ruthemann[5] started investigating them, they were measured only in conjunction with measurements of secondary electron emission. In recent years a number of investigators[6–10] have been interested in this problem, with a subsequent rapid increase in the data available. Kronig and Penney,[11] in an article on the band structure of solids, suggested that the observations of Rudberg[12] might be interpreted in terms of interband transitions. Haworth[13] in 1935 observed the characteristic losses in Mo and also discussed these in terms of interband transitions. In 1936, Rudberg and Slater[14] attempted a theoretical description of the results for copper, based on the quantum theory of the solid state. They considered that the incident primary electrons caused transitions from the occupied $3d$ band to the $4s$ band and others above. To calculate the relative probability of different energy losses, they used the density of states curve and

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[1] J. D. Hanawalt, J. Franklin Inst. **214**, 569 (1932).

[2] C. Kurylenko, Cahiers phys. **54**, 1 (1955).

[3] Marton, Leder, and Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. VII, pp. 183–238.

[4] J. A. Becker, Phys. Rev. **23**, 664 (1924).

[5] G. Ruthemann, Naturwiss. **29**, 648 (1941); **30**, 145 (1942); Ann. Physik **2**, 113 (1948).

[6] G. Mollenstedt, Optik **5**, 499 (1949); **9**, 473 (1952).

[7] L. Marton and L. B. Leder, Phys. Rev. **94**, 203 (1954); L. B. Leder and L. Marton, Phys. Rev. **95**, 1345 (1954).

[8] W. Kleinn, Optik **11**, 226 (1954).

[9] H. Watanabe, J. Phys. Soc. Japan **9**, 920 (1954); **9**, 1035 (1954); Phys. Rev. **95**, 1684 (1954).

[10] D. Gabor and G. W. Jull, Nature **175**, 718 (1955).

[11] R. L. Kronig and W. G. Penney, Proc. Roy. Soc. (London) **130**, 499 (1930–1931).

[12] E. Rudberg, Phys. Rev. **50**, 138 (1936); Proc. Roy. Soc. (London) **A127**, 111 (1930).

[13] L. J. Haworth, Phys. Rev. **48**, 88 (1935).

[14] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).

approximate wave functions corresponding to each of the levels. The velocity distribution curve so obtained was compared with the characteristic energy loss curve measured by Rudberg.[12] They found that the first two maxima agreed quite well, but that the theoretical distribution contained peaks which Rudberg had not observed. More recent measurements[7,15] have shown the existence of these higher energy losses so that the calculated values of Rudberg and Slater fit better than it appeared at that time. Cauchois[16] compared the characteristic energy losses in aluminum with the fine structure of the x-ray *K*-absorption edge. However, she made the comparison with the maxima of transmission, and Watanabe[9] has correctly pointed out that the comparison should be made with the maxima of absorption.

The approaches of Kronig and Penney,[11] Haworth,[13] Rudberg and Slater,[14] and Cauchois[16] are all essentially the same since they all postulate excitation of a single "free" electron to higher energy levels. On the other hand, Bohm and Pines[17] have attempted to explain the characteristic losses on the basis of excitation of collective oscillations in the free-electron gas of a metal. It appears that there may be some agreement with the Bohm-Pines theory for the cases of Al, Be, and Mg.

X-RAY ABSORPTION EDGE FINE STRUCTURE

In this section we will present a summary of the experimental and theoretical background of the x-ray fine structure. Two theories attempting to explain the fine structure have been formulated. While they both are able to interpret certain aspects of the experimental data successfully, they contain inherent difficulties which limit their range of validity. We present these theories in order to give a more complete picture of the available information concerning the x-ray fine structure.

The x-ray absorption edge is obtained by passing x-rays through an absorber and measuring the intensity of the transmitted beam as a function of the wavelength. It is found that, at a wavelength corresponding to the energy required to transfer an inner shell electron to the first empty higher level, there is a sudden increase in absorption of the x-ray beam. This region of high absorption is called the absorption edge. As the wavelength is decreased, the absorption coefficient fluctuates. In some cases these fluctuations have been observed over a range of several hundred electron volts. This fluctuation of the absorption is called the fine structure.

In order to explain this fine structure, Wentzel[18] and Coster[19] suggested that each x-ray quantum could cause a double or even multiple ionization of the atom, thus removing simultaneously a *K*- as well as an *L*- or *M*-electron from the atom. However, experimental results[20] on the isolated atoms which make up the solid show that the fine structure of the *K*-absorption edge extends only 10–20 electron volts from the edge whereas in the solid the fine structure can extend as much as 300 electron volts from the edge. Furthermore, it has been shown that the fine structure in a solid is a function of the temperature, and also[21] that, for solids with the same crystal structure, the spectra can be made to overlap if one employs a scaling parameter which is a function of the lattice constant.

Kronig[22] inferred from these experimental data that the fine structure is a property of the whole aggregate of atoms forming the solid rather than the sum of the individual contributions of the several atoms. He based his interpretation on the quantum theory of the solid state. The electron is excited from the *K*-shell by the photon with sufficient energy to raise it to a position above the uppermost occupied level in the valence or conduction band. If the energy of the electron in its final state corresponds to an allowed energy band, the electron travels around in the solid in a manner which is essentially free. He assumes that the influence of the lattice on the motion of the electron is a small perturbation by a periodic field. The momentum and energy are related by the expressions which specify the translational symmetry of the wave function corresponding to an energy in a particular band. Because of certain symmetry properties of the material it is found, for given values of the momentum $\hbar k$, that the "free" electron cannot travel through the material. This occurs when the momentum satisfies the Bragg relations. In this case, the electron waves are reflected by certain planes in the material in such a manner as to set up an interference pattern which gives a null probability of finding the electron in this momentum state—thus we have a forbidden state.

The energy at the boundary of an allowed band in a cubic structure is given by

$$W=\frac{h^2}{8md^2}(\alpha^2+\beta^2+\gamma^2), \tag{1}$$

where h is Planck's constant, m is the electronic mass, d is the lattice constant, and α, β, and γ are integers. If an electron were to receive from the photon the requisite energy corresponding to the momentum which satisfies the Bragg reflection law, the photon would not be absorbed by the material. In this instance we would find a maximum in transmission (minimum in absorption) in the x-ray fine structure. The probability of no

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[15] P. P. Reichertz and H. E. Farnsworth, Phys. Rev. **75**, 1902 (1949).

[16] Y. Cauchois, Conference on Applications of X-Ray Spectroscopy to Solid State Problems, October 23–25, 1950, Navexos P-1033 (unpublished); Acta Cryst. **5**, 351 (1952).

[17] D. Bohm and D. Pines, Phys. Rev. **85**, 338 (1952); **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

[18] G. Wentzel, Ann. Physik **66**, 437 (1921).

[19] D. Coster, Phil. Mag. **44**, 546 (1922).

[20] D. Coster and J. H. Van der Tuuck, Z. Physik **37**, 367 (1920); J. D. Hanawalt, Phys. Rev. **37**, 715 (1931).

[21] D. Coster and J. Veldkamp, Z. Physik **70**, 306 (1931); **74**, 191 (1932); G. A. Lindsay, Z. Physik **71**, 735 (1931).

[22] R. L. Kronig, Z. Physik **70**, 317 (1931); **75**, 191 (1932); **75**, 468 (1932).

absorption increases with the number of planes able to participate in this type of reflection. In this way one can find the various heights of the transmitted lines in the absorption spectra in terms of these equivalent planes. It should be noted at this point that we are considering dipole excitation of the electron by the photon and should expect the final state of the electron in the *K*-absorption spectrum to be a *p*-state. Kronig considers the distribution of the various angular momentum states in the bands to be dense enough so that for almost any momentum in the band there is a wave function contribution from a *p*-type state.

Since the positions of the absorption minima are a consequence of the Bragg law, we would expect the energy corresponding to the various absorption minima to be a function of the lattice spacing. Therefore, different materials with the same type of structure should exhibit similar types of spectra which can be made to coincide by scaling in terms of the lattice constant. The spacing of the absorption minima should also be temperature-dependent. This is found to be so in many materials.

Hayasi[23] interprets the fine structure in a somewhat different manner. Since the initial electron state in the *K*-shell is an *s*-state, it is necessary that the final state have a *p*-type symmetry. He utilizes the fact that there are deviations from perfect periodicity in the solid because of thermal vibrations and because of other impurity types to allow him to consider the final state of the electron as a "quasi-stationary" state. That is, he considers the electron trapped and localized over a small number of lattice sites. We can think of the electron in the *p*-type state to be reflected from a pair of planes at right angles to the direction of propagation. The electron "bounces" back and forth between these planes and so is localized about the emitting atom. The strength of localization is obtained by finding the number of equivalent planes about the "emitting" atom which can give the same type of localization. For those states having a large number of equivalent planes participating, one would expect a greater probability of trapping than those states which have a smaller number of planes. In this way a number of transitions can be ruled out. In a manner, this is a type of selection rule.

The energy of the final state is given by the knowledge of the planes participating in localizing the electron. This corresponds to the energy of the forbidden states in the Brillouin zone structure of the solid. It is interesting to note that where Kronig finds a forbidden final state, and so a minimum in the absorption, Hayasi finds a "bound" allowed state (in a forbidden zone) and thus a maximum in absorption. Also, Hayasi calculates the width of the various "bound" energy levels by considering the thermal displacement of the various planes which smears out the energy of the electrons being bound by these planes. In addition to this thermal width, there is the natural line width of the forbidden zones known in the usual Brillouin zone theory.

In his theoretical treatment,[24] Hayasi studies a modified one-dimensional Kronig-Penney model where there is a deviation in the periodic potential at the origin. He finds that in this manner the energies of the "quasi-stationary" states correspond quite closely to the Brillouin zone boundary energies. In terms of a one-dimensional model, an impurity localized to one lattice site can give the symmetry of the localized level to correspond to a *p* state. Slater and Koster[25] have shown that in a three-dimensional cubic model, with the perturbing potential exhibiting the same symmetry properties as the lattice, the *p*-type levels will not appear if the perturbation is localized to one lattice site. When the perturbation extends over more than one lattice site with sufficient strength, *s*, *p*, *d*, etc., types of localized levels appear to break off from the band and exist in the forbidden zone.

IMPLICATIONS OF THE THEORIES

On the basis of either the Kronig or Hayasi theory, several properties of the fine structure can be predicted. For instance, metals crystallizing in the same type should have the same type of fine structure. In the case of neighboring metals in the periodic table, the density of states would probably be similar, so that those with the same type of crystal structure will have the same spectrum but scaled by the lattice constant [e.g., for a cubic structure it is given by Eq. (1)]. Where crystals are not of the same kind, e.g., cobalt (hexagonal) and nickel (cubic), we might still expect similar spectra but with some modification because of the differing crystal types. This is because an hexagonal close-packed lattice can be approximated by a cubic lattice with an appropriate lattice constant.[26] Where metals are not neighbors in the periodic table, the densities of states may be quite different. Therefore, although the fluctuations may be correlated with a parameter which is a function of the lattice constant, the line shapes might differ because of the different densities of states.

In the Kronig theory, the liberated electrons were regarded as almost free, so that the forces exercised by the lattice may be regarded as small perturbations.

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[23] T. Hayasi, Sci. Repts. Tohoku Univ. **33**, 123 (1949); **33**, 183 (1949); **34**, 185 (1950). We are indebted to Professor Hayasi for a preprint of an article to appear in Science Reports of Tohoku University in which he considers the relationship between the characteristic energy losses, the x-ray absorption fine structure, and the critical potentials for Ni and Cu. He postulates a level structure for the final states of the excited electrons in a manner similar to that given in our present paper. Certain outer shell levels are assumed to be the initial states for the characteristic loss transitions and are assigned energy values derived from critical potential data. This allows him to calculate the energy differences between the initial and final states which are then compared to the characteristic loss spectra.

[24] T. Hayasi and S. Okada, Sci. Repts. Tohoku Univ. **37**, 331 (1953); T. Sagawa, *ibid.* **37**, 339 (1953).

[25] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

[26] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 16.

This implies that the foregoing conclusions would be valid only at some distance from the zero potential, and from experiment[27] this distance appears to be approximately 50 ev from the absorption edge. The distance from the edge within which the lattice dependence would not hold would, of course, vary for different metals. Using his own theory, Hayasi found good agreement with the measured values for nickel and copper to within 12 ev and for lithium to 6 ev from the edge. Since Hayasi employs quasi-stationary states (localized levels), it would be expected that his theory would probably hold better than the Kronig theory near the *K*-edge.

COMPARISON OF THE X-RAY FINE STRUCTURE WITH THE CHARACTERISTIC LOSSES

While we do not attempt to apply the details of the theories of the fine structure to the characteristic energy losses, some of the more general aspects are helpful for the correlation. Both the theories of the fine structure and the experimental data indicate that the energy dependence of the fine structure goes as the inverse square of the lattice constant. It is to be expected that any theory which assumes a lattice dependence for the energy levels will show that the energies are inverse functions of the square of the lattice constant. This can readily be obtained from dimensional considerations. We will investigate these aspects after we first show the numerical agreement between the characteristic energy loss spectra and the x-ray fine structure. In all cases the fine structure values are the maxima of absorption taken from the *K*-absorption spectra, and are measured in ev from the *K*-edge. The characteristic energy losses are all measured in ev from the zero loss (elastic peak).

TABLE I. Comparison for aluminum. The fine structure values are given in the first column and the characteristic losses in the second, both in ev.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
8.0	7.0
15.0	14.6
24.5	21.6
...	29.2
34.0	36.2
42.0	43.8
52.0	50.8

[a] See reference 28.
[b] These values for the characteristic losses are the combined results of several investigators.

In Table I we show the two sets of values for aluminum. The fine structure values are those given by Johnston and Tomboulian[28] and the characteristic loss values are the average of all the published values. It is obvious that the numerical correlation is quite good except for the absence of the 29.2-ev value (which probably is a multiple of the 14.6-ev loss) in the fine structure. It should be pointed out that aluminum presents one of the best cases for the plasma theory since the theoretical plasma loss fits quite well the measured 14.6-ev loss, and Blackstock, Birkhoff, and Slater[29] have shown that the theoretical mean free paths also fit the experimental values. However, the plasma theory does not account for the 7.0-, 21.6-, 36.2-, and 50.8-ev losses. From our own, unpublished, data we know that the 14.6-ev loss for aluminum has a larger cross section than any of the other characteristic losses, and this leads us to believe that in this case we may be observing a multiple process consisting of a superposition of the plasma loss on the interband transition. It should be noted that, of all the cases for which comparisons have been made, the Be data are completely in disagreement (see Table V). Here too there are indications from other sources[3] that the Be electron losses may be due to plasma excitations, and so might have no counterpart in the x-ray fine structure.

TABLE II. Comparison for iron. The fine structure values are given in the first column and the characteristic losses in the second column, both in ev.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
9.3	7.0
15.8	15.8
22.9	20.4
39.0	36.5
55.1	56.1

[a] See reference 30.
[b] See references 7 and 8.

TABLE III. Comparison of values for potassium.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
1.05	...
2.5	...
3.8	...
6.1	...
8.0	8.3
10.0 12.0	11.4
17.0	15.4
19.2	19.5
21.5	22.6
24.5 26.8	25.5
29.0	29.6
32.8	32.0

[a] See reference 31.
[b] See reference 7.

In Table II are listed the values for iron. The x-ray values are those given by Aoyama and Fukuroi,[30] while the characteristic losses are taken from the measurements of Kleinn[8] and Marton and Leder.[7] The numerical

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[27] G. P. Brewington, Phys. Rev. **46**, 861 (1934); D. Coster, Physica **2**, 606 (1935); V. P. Barton and G. A. Lindsay, Phys. Rev. **46**, 362 (1934).

[28] R. W. Johnston and D. H. Tomboulian, Phys. Rev. **94**, 1585 (1954).

[29] Blackstock, Birkhoff, and Slater, Phys. Rev. **100**, 1078 (1955).

[30] S. Aoyama and T. Fukuroi, Sci. Repts. Tohoku Univ. **28**, 410 (1939–1940).

TABLE IV. Comparison of values for potassium.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
2.7	...
5.2	5.4
10.0	10.9
...	16.6
...	21.9

[a] See reference 32.
[b] See reference 7.

agreement is extremely good. In Table III we give the values for potassium. Four low-lying levels are found in the case of the fine structure given by Platt[31] which were not found for the characteristic losses by Marton and Leder. However, this may simply be due to their low probability plus lack of resolution of the spectrograph close to the zero level. The other levels are in excellent agreement. The 11.4- and 25.5-ev characteristic losses are shown as average values of the bracketed x-ray values. We do this tentatively because they do fall midway between the two sets of values, and also because in the characteristic energy loss spectrum they are broader than the other loss lines.[3]

The comparison for sodium (Table IV) is not as complete as in the other cases, although two values which are common to both sets of measurements are in excellent agreement. It is easy to see why the 2.7-ev x-ray value would not be observed in the characteristic loss spectrum with the present resolution available since it would fall close to the zero-loss line and probably be obscured. It is also probable that the 16.6- and 21.9-ev characteristic losses have not as yet been observed in the x-ray case since Rule[32] could observe with consistency only the first three values.

In Table V, we have given the values for several other metals which we will not discuss individually. The tabulated values represent the combined measurements of several investigators in some cases. We find that there are either fine structure values or characteristic losses without counterpart in the other. It will be interesting, in view of this possible indication of their existence, to see whether they will be found with further measurement.

Equally good correlation is found for the several compounds that have been measured in both cases. In Tables VI, VII, VIII we have given both sets of values for NaCl, KCl, and KBr. We note that for these materials, as for potassium, more losses are observed than are generally found for the metals, indicating many closely spaced, narrow levels.

SIMILARITIES IN THE CHARACTERISTIC LOSS SPECTRA

We have pointed out earlier that it might be expected that neighboring metals in the periodic table have similar spectra, provided the density of states are not radically different, modified by a dependence on the lattice constant [e.g., Eq. (1)] and the crystal structure.

TABLE V. Comparison of the values for several other metals.

Fine structure (ev)	Charact. losses (ev)	Fine structure (ev)	Charact. losses (ev)
Ag[a]	Ag[b]	Be[c]	Be[b]
...	4.1	13.4	6.5
...	7.4	25.9	18.9
17.0	16.7	35.8	38.0
24.0	23.3	43.1	...
33.0	...	56.9	56.0
44.0	45.3		
Ca[d]	Ca[b]	Co[e]	Co[b]
...	3.6	4.0	5.7
7.6	8.4	20.5	18.3
15.0	13.0	24.5	24.0
...	17.9	48.0	47.0
29.3	29.0		
...	36.4		
49.2	46.0		
Cu[f]	Cu[b]	Li[g]	Li[h]
3.5	3.5	4.3	...
7.5	6.8	9.4	9.8
14.0	12.0	11.5	...
23.0	⎰20.3	17.6	17.8
	⎱25.5	23.0	29.0
34.0	34.5		
47.0	...		
Mg[a, i]	Mg[b]	Ni[j, d]	Ni[b]
7.4	4.7	2.4	...
11.8	10.2	7.7	6.0
13.9	...	...	9.4
17.2	...	15.7	⎰12.5
20.1	21.0		⎱17.6
23.3	...	27.2	23.0
27.9	...	45.7	47.0
33.4	31.2		
Pt[e]	Pt[b]	Se[k]	Se[l]
3.3	...	4.5	⎰2.5
...	6.1		⎱6.9
20.3	23.2	13.0	12.1
33.3	34.8	20.5	20.0
53.3	⎰46.0	...	40.0
	⎱61.4		
Zn[d, e]	Zn[b]		
3.8	...		
6.0	5.7		
10.1	9.9		
17.1	17.0		
23.0	23.1		
35.6	...		

[a] Munier, Bearden, and Shaw, Phys. Rev. **58**, 537 (1940).
[b] See reference b of Table I.
[c] See reference 28.
[d] J. Veldkamp, Z. Physik **77**, 250 (1932); **82**, 776 (1933).
[e] W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).
[f] S. T. Stephenson, Phys. Rev. **58**, 877 (1940).
[g] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **161**, 420 (1939).
[h] See reference 7.
[i] A. E. Sandstrom, Arkiv. Mat. Astron. Fysik **28A**, 1 (1942).
[j] See reference 23.
[k] W. H. Zinn, Phys. Rev. **46**, 659 (1934).
[l] H. Friedman, Naturwiss. **24**, 569 (1954).

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[31] J. B. Platt, Phys. Rev. **69**, 337 (1946).
[32] K. C. Rule, Phys. Rev. **66**, 199 (1944).

Several such metals for which data are available can be compared in this way. In Table IX we compare the spectra of copper and zinc. Both have a completed $3d$ shell, and copper has one, while zinc has two, $4s$ electrons. However, zinc is close-packed hexagonal ($a=2.665$ A, $c=4.947$ A)[33] while copper is face-centered cubic ($a=3.615$ A). In order to determine a possible lattice dependence, we must approximate an ideal close-packed hexagonal lattice for zinc. For such a lattice, the axial ratio c/a should be 1.633. In zinc $c/a=1.86$, indicating a departure from the ideal lattice. The axial constants for the ideal lattice are found to be $a_1=2.88$ A and $c_1=4.70$ A.[34] We then determine the distance of closest neighbors in this ideal lattice by multiplying the a_1 by $\sqrt{2}$. We can now calculate the loss values for zinc expected on the basis of the measured copper values by multiplying the zinc values by $(3.615/4.07)^2=0.79$. These calculated values are given in column three of Table IX. Considering that we had to approximate the zinc lattice we get surprisingly good results which indicate that the two spectra are indeed similar and do show a lattice dependence.

Another pair of metals which should have the same spectra are gold and platinum which are both face-centered cubic ($a=4.079$ A and $a=3.923$ A, respectively). Both have one electron in the $6s$ shell, but Au has a completed $5d$ shell while Pt lacks one electron to complete its $5d$ shell. Since gold has been more thoroughly measured, we will use it as the standard. From the lattice constants, we would expect Pt to have slightly larger characteristic losses. The expected differences here are actually smaller than the probable errors involved in the measurements, but we might expect a trend to be apparent. In Table X we show the measured values in the first two columns and the calculated values for Pt in the third column. We find that Pt does have slightly larger losses in agreement with the calculated values. The 46-ev loss for Pt is possibly an average of two losses as indicated in the table.

TABLE VI. Comparison of the values for sodium chloride.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
0.9	...
3.8	4.8
...	8.3
11.2	12.4
...	15.4
20.5	21.0
27.2	33.3
39.4	36.8

[a] See reference 32.
[b] See reference 7.

TABLE VII. Comparison of the values for potassium chloride.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
1.4	...
5.0	...
7.7	7.9
10.3	9.6
12.1 14.9	13.5
17.5	...
20.9	20.0
22.9	22.4
...	26.1
28.7	28.6

[a] See reference 27 and S. Kiyono, Sci. Repts. Tohoku Univ. **36**, 1 (1952).
[b] See reference 7.

TABLE VIII. Comparison of the values for potassium bromide.

Fine structure[a] (ev)	Characteristic losses[b] (ev)
1.1	...
4.2	...
7.2	6.9
9.6	8.9
12.6	12.8
16.3	18.0
19.8	19.9
22.4	21.9
25.4	25.6
27.1	28.0

[a] See reference a of Table VII.
[b] See reference 7.

TABLE IX. Comparison between the characteristic losses for Cu and Zn. In the last column are given the values calculated for Zn, using the ratio of the square of the lattice constants.

Cu	Zn	Zn (calc)
3.5	...	2.8
6.8	5.7	5.4
12.0	9.9	9.5
20.3	17.0	16.0
(25.5)	23.1	20.1
34.5	...	27.3

In Table XI we show the energy loss values for silver and cadmium. The Ag values are averages of the measurements of several investigators while the cadmium values are our own. These metals both have a completed $4d$ shell. Silver has one electron in the $5s$ shell and Cd has two. As in the case of Cu and Zn we compare a cubic lattice (Ag, $a=4.086$ A) with a close-packed hexagonal lattice (Cd, $a=2.98$ A, $c=5.62$ A). If we approximate an ideal lattice for Cd as we did for Zn, we obtain a nearest neighbor distance of 4.60 A. This would indicate that the Cd losses should be less than those of copper. Actually, we find that the first two Cd losses are greater than those of Cu.

We can also compare the spectra of the compounds KCl and KBr, both of which are face-centered cubic crystals. Their lattice constants are 6.293 and 6.600 A respectively, so that the KCl losses should be 1.1 times the KBr losses if there is a lattice constant dependence. In Table XII the measured characteristic losses are given in columns 1 and 2 and the calculated values for

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[33] All the lattice constant values used are taken from H. E. Swanson, National Bureau of Standards Circular 539 (U. S. Government Printing Office, 1953–1955).

[34] The axial constants for the ideal close-packed hexagonal lattice are found from the two relationships, $c_1/a_1=1.633$ and $2a_1^2+c_1^2=2a^2+c^2$.

TABLE X. Comparison of the characteristic losses for Au and Pt. In the last column are given the values calculated for Pt using the ratio of the square of the lattice constants.

Gold	Platinum	Platinum (calc)
6.3	6.6	6.5
12.0	11.7	12.5
18.0	...	18.7
24.0	24.8	25.0
33.0	34.0	34.3
41.0 50.0	46.0	42.6 52.0 } 47.3
58.0	61.4	60.3

KCl in column 3. Again we see that the spectra are similar and that there is some reason to believe a lattice constant dependence exists. For comparison purposes we have included the characteristic losses for K in column 4.

DISCUSSION

We have shown that in many cases a numerical correlation exists between the fine structure of the K-absorption edge of x-rays and the characteristic energy losses of electrons in solids.

The x-ray fine structure has been related to the periodic properties of the lattice by Kronig and Hayasi. We would expect that the Kronig theory is probably valid only for large distances from the K-edge because he treats the electron in the solid as being essentially free. On the other hand, we would not expect the Hayasi theory to hold for large distances from the K-edge. This is because his theory is based on "imperfections" in the periodic lattice which perturb the ideal periodic potential. The perturbing potentials tend to localize the electron within a small region in the lattice—a quasi-stationary level. Unless the perturbing potential is very large compared to the unperturbed lattice potential, only the energy levels close to the K-edge would be affected. Therefore, if the photoelectron has an energy which brings it to a level much above the K-edge, this level will probably exhibit the properties of a similar level in an unperturbed solid. Although the Hayasi approach may be successful for the levels close to the K-edge, we cannot discard the possibility that some of the fine structure maxima close in may arise from double excitation by the photon, e.g., K-excitation plus, possibly, an L- or M-excitation.

If we assume that there is a lattice dependence in the characteristic loss spectra, then we would expect it to be exhibited as an inverse function of the lattice constant squared. This has been noted in some cases. As in the case of the x-ray fine structure, we can get a trapping potential extending over a region of a few lattice spacings from impurities (and finite size of crystallites). Therefore, we can expect to find localized levels around these "impurity" sites, and the energies of these levels will be a function of the inverse square of the extension of the perturbing potential. For metals this extension is usually of the order of magnitude of the lattice constant.

TABLE XI. Comparison of the characteristic losses for Ag and Cd. In the last column are given the values calculated for Cd using the ratio of the square of the lattice constants.

Ag	Cd	Cd (calc)
4.1	4.4	3.2
7.4	8.1	5.8
16.7	...	13.2
23.3	18.7	18.4
45.3	...	35.8

The characteristic loss values used for the comparison are taken either from our own measurements or are the combined measurements of several investigators. These values may be in error as much as 1 or 2 ev because of several factors which have not been taken into account, such as; line shape, influence of prominent lines on less prominent neighbors, purity of specimens, and temperature. Also, the x-ray K-edge position from which the fine structure is measured cannot be determined with great accuracy. One must bear in mind that these errors will cause some deviations.

TABLE XII. Comparison of the characteristic loss spectra for KBr and KCl. The calculated values for KCl are obtained by multiplying the KBr values by the ratio of the square of the lattice constants. The loss values for potassium are given in the last column.

KBr	KCl	KCl (calc)	K
6.9	7.8	7.6	8.3
8.9	9.6	9.8	11.4
12.8	13.5	14.1	15.4
18.0	...	19.8	19.5
19.9	20.0	21.9	22.6
21.9	22.4	24.1	25.5
25.6	26.1	28.2	29.6
28.0	28.6	30.8	32.0

Since we have considered here only the K-edge fine structure the initial state in the x-ray process is an s-state as compared to the various possible angular momentum states for the initial states in the electron scattering experiments. However, since the various angular momentum states in the bands are very close to each other energy-wise, it is not expected that any significant differences in the energy levels would be observed due to the angular momentum selection rules. It should, however, be noted that the initial state in the x-ray absorption is sharp while the initial state in the electron absorption may be considerably broader. Therefore, without an accurate knowledge of the densities of states in the bands, it would be extremely difficult to make meaningful comparisons of the line shapes or intensities for the two cases.

As in the case of the x-ray absorption spectra near the K-edge, where some of the lines may arise from an additional photoejection from the outer shells to the bands, so also in the case of the electron absorption we may expect excitations of the outer shell electrons. This could possibly explain some of the cases where there is a correlation between the fine structure and the characteristic spectra but no apparent energy dependence on the lattice.

In order to have a complete theory of the characteristic energy losses in terms of the band picture, more information concerning the densities of states is necessary.

ACKNOWLEDGMENTS

We are very much indebted to Professor K. Lark-Horovitz, Professor L. G. Parratt, Professor D. Pines, and Professor R. A. Ferrell for reading an early draft of this paper and for the constructive suggestions they made concerning it.

PHYSICAL REVIEW VOLUME 101, NUMBER 5 MARCH 1, 1956

Cohesive Energy of Potassium*

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(Received October 27, 1955)

The cellular method has been applied to a calculation of the cohesive energy of metallic potassium. The crystal potential is taken from a self-consistent field with exchange for the potassium ion. An approximate exchange interaction between the valence and the core electrons was included. The cohesive energy was found to be 18.5 or 19.3 cal/mole according as Pines' or Wigner's expression for the correlation energy is used, and the effective mass to be 86% of the free-electron mass. The experimental value is 22.6 cal/mole.

INTRODUCTION

THE cohesive energy of potassium was first calculated by Gorin[1] who used the cellular method. Unlike previous calculations for lithium and sodium by Wigner and Seitz[2] and by Seitz,[3] Gorin did not obtain reasonable agreement with experiment, but found a value considerably too small. Gorin attributed the failure to the supposed greater importance of the electron interaction, i.e., correlation between valence and core electrons. The subject has since been taken up again by Kuhn and Van Vleck[4] and by Brooks[5] who use the "quantum defect method" which avoids explicit use of a potential, but rather makes use of knowledge of the energy levels of the free potassium atom, determined by atomic spectroscopy. These authors find much better agreement; in particular Brooks finds a cohesive energy which differs from the experimental value by only 0.4 cal/mole neglecting the Coulomb interactions of the valence electrons—a discrepancy probably well within both the experimental and theoretical uncertainties.

The basic assumption of the Wigner-Seitz method is that the atomic polyhedron can be replaced by a sphere of equal volume. Each atomic cell is regarded as electrically neutral, so that the valence electron moves in the field of the corresponding positive ion. In this approximation, the cohesive energy is essentially the difference of two quantities: first, the boundary correction due to the fact that the wave function of the ground state of the valence electron is flat at the surface of the atomic sphere. Hence there is a decrease in the kinetic energy of the ground-state wave function, and at the same time, the valence electron is forced back into the ion core to a certain extent, i.e., into a region of more negative potential energy. The second quantity is the kinetic energy of the electron distribution, occasioned by the fact that only one electron of each spin can be in a given state. This kinetic or Fermi energy can be calculated by the method of Bardeen[6] (which has been extended by Silverman[7]) where it is determined by the effective mass of the electrons. The contribution from the Coulomb interaction of the valence electrons is considered to be that for a free-electron gas, diminished by the exchange and correlation holes. The net effect of the Coulomb interaction turns out to be small. This surprising result has been explained by Bohm and Pines[8] as a consequence of the screening effect of the rest of the electron distribution on the field of any single electron.

We have repeated Gorin's calculation with some improvements. The potential of the K ion is taken from a self-consistent field with exchange calculated by Hartree and Hartree.[9] (The K^+ ion field used by Gorin

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* This research was supported by the Office of Naval Research.

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