to all the rare earths, has been derived by de Gennes[9] and by Brout and Suhl[10]:

$$\theta = 4\beta^2 J(J+1)(g-1)^2 n/3k;$$

this reduces to Néel's formula when $J=L+S$, appropriate to the elements Gd to Lu, and to the formula

$$\theta = 4\beta^2 S^2 J(J+1)^{-1} n/3k,$$

when $J=L-S$, appropriate to the rare earths La to Gd.

---

[9] P. G. de Gennes, Compt. rend. **247**, 1836 (1958).

[10] R. Brout and H. Suhl, Phys. Rev. Letters **2**, 387 (1959).

PHYSICAL REVIEW VOLUME 118, NUMBER 6 JUNE 15, 1960

Elastic Constants of Palladium from 4.2–300°K

J. A. RAYNE
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received January 20, 1960)

Elastic constant measurements have been made on a single crystal of palladium in the temperature range 4.2–300°K. Extrapolation of the data to absolute zero gives

$$c_{11}=2.341\pm0.027\times10^{12}\text{ dyne cm}^{-2},$$
$$c_{12}=1.761\pm0.027\times10^{12}\text{ dyne cm}^{-2},$$
$$c_{44}=0.712\pm0.003\times10^{12}\text{ dyne cm}^{-2}.$$

The corresponding value of Debye temperature is $\theta_0=275\pm8$°K, which compares well with the calorimetric figure of $\theta_0=274\pm3$°K. Both shear constants show an anomalous temperature dependence. This dependence can be correlated with the temperature variation of the contribution to $C=c_{44}$ and $C'=\frac{1}{2}(c_{11}-c_{12})$, resulting from the presence of holes in the d band of palladium.

I. INTRODUCTION

THE elastic properties of the transition metals are of considerable interest. If there is a contribution to the bulk modulus of a metal arising from the conduction electrons, as has been suggested by DeLaunay,[1] the effect should be most pronounced in the transition elements, which have narrow unfilled d bands containing a considerable number of electrons. Again from the work of Leigh,[2] it might be anticipated that the holes in the d bands should contribute to the shear constants. For those metals having almost filled d bands, and hence a low degeneracy temperature, this hole contribution would vary significantly with temperature, thereby causing an anomalous temperature dependence of the shear constants.

Thus far, the only transition metal to be studied in detail has been nickel,[3] which has the added complication of being ferromagnetic. Of the nonferromagnetic cubic transition metals, palladium is especially well suited to an investigation of the above effects, since it has an almost filled d band and the grosser features of its band structure are reasonably well understood from susceptibility and specific heat measurements[4,5] on silver-palladium alloys. In addition, elastic data would be of use in providing a reliable value for the Debye temperature of palladium, since the accuracy of that obtained from calorimetric data[5,6] is quite low owing to the high electronic heat capacity of the metal. In this paper the results of elastic constant measurements on palladium from 4.2–300°K will be presented.

II. EXPERIMENTAL

The specimen of palladium used in these experiments was prepared from a single crystal ingot having a purity of 99.8%, the principal contaminants being iron and platinum. This ingot was prepared, using the Czochralski technique, by Dr. James Kirn of the Virginia Institute for Scientific Research. When etched electrolytically in solution of sulfuric acid and glycerin, it revealed no appreciable mosaic structure. The ingot was oriented by the usual Laue back reflection technique and a cylinder, approximately $\frac{5}{8}$ in. in length and $\frac{5}{8}$ in. in diameter with its axis along the [110] direction, was then cut from it. The cylinder ends were lapped for parallelism to within 0.0001 in., after which they were lightly etched using the same solution as used previously.

The ultrasonic measurements were made using an Arenberg[7] ultrasonic pulse generator and wide band amplifier together with a Tektronix type 545 oscillograph. Details of the measuring techniques have been

---

[1] J. DeLaunay, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 277.

[2] R. S. Leigh, Phil. Mag. **42**, 139 (1951).

[3] G. A. Alers, J. R. Neighbours, and H. Sato, J. Phys. Chem. Solids **9**, 21 (1959).

[4] F. E. Hoare, J. C. Matthews, and J. C. Walling, Proc. Roy. Soc. (London) **A216**, 502 (1953).

[5] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42 (1957).

[6] J. A. Rayne, Phys. Rev. **107**, 669 (1957).

[7] Arenberg Ultrasonic Laboratory, Boston, Massachusetts.

described previously[8,9] and need no further elaboration, except as regards the bonding used between the crystal and transducer. Thus, in these experiments it was found that glycerin gave satisfactory echoes from slightly below room temperature down to 4.2°K. Salol was used to obtain room-temperature values of the elastic constants.

To obtain the temperature variation of the elastic constants for palladium, it is necessary to know the corresponding variation of its lattice parameter. Measurements of the latter were made at 300°K, 77°K, and 4.2°K, in a cryostat to be described in a later paper, using a counter spectrometer and crystal monochromated molybdenum radiation. For the measurements a slice of the crystal, cut adjacent to the ultrasonic specimen as to expose a (110) face, was employed. This slice was electropolished and oriented in the cryostat so that the [001] axis was vertical. Room-temperature data were obtained for the unsymmetrical reflections (10,4,0) and (10,2,0), using the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines. Extrapolation against $\cos^2\theta$ gave a mean lattice parameter at 300°K of $a=3.8896\pm 0.0002$ A, corresponding to a density of 12.038 gram cm^{-3}. Values in the literature for the lattice parameter of palladium differ considerably. According to Pearson,[10] the most reliable figure is that due to Coles,[11] who gives $a=3.8907\pm 0.0001$ A at 295°K for a specimen having a purity of 99.95%. After correcting for the difference in temperature between the measurements, there is still a residual discrepancy outside the combined limits of error. This could, however, be due to the differences in purity between the samples, and hence our value of lattice parameter has been used in obtaining the elastic constants.

For the low-temperature measurements, the (10,4,0) reflections alone were used to obtain the *changes* in lattice parameter. On combining this data with the mean value of the lattice parameter at 300°K, we obtain the results in Table I. It is of interest that the present work gives a total expansion coefficient between 300°K and 77°K of $\alpha=23.5\times 10^{-4}$, which figure agrees well with the value $\alpha=23.4\times 10^{-4}$ given by Nix and McNair.[12] The changes in density at intermediate temperatures were obtained graphically, assuming that the variation was linear above 77°K and that the curve of density vs temperature had zero slope near absolute zero.

TABLE I. Values of the lattice parameter of palladium.

Temperature (°K)	Lattice parameter (A)
300	3.8818
77	3.8727
4.2	3.8718

III. RESULTS

The results of the present experiments are given graphically in Figs. 1, 2, and 3. Table II gives smoothed values of the elastic constants, obtained from the graphs, from 0 to 300°K. As may be seen from the figures, the *internal* consistency of the data is considerably better than one percent. However, the over-all accuracy of the data, as a result of transit time errors, is somewhat poorer. In computing the error estimates given in the table, it has been assumed that there is a 0.01 μsec transit time error, although it is believed that this may *overestimate* the effect.

IV. DISCUSSION

(a) Magnitude of Bulk Modulus

The bulk modulus of palladium at 0°K is $(c_{11}+2c_{12})/3=1.954\times 10^{12}$ dyne cm^{-2}, which figure is much higher than that for silver,[13] viz., $(c_{11}+2c_{12})/3=1.087\times 10^{12}$ dyne cm^{-2}, even though these elements occupy adjacent positions in the periodic table and have similar lattice parameters. It is believed that this increase is due to the bulk modulus of the electrons in the *d* band of palladium.

TABLE II. Smoothed values of elastic constants of palladium.[a]

Temperature	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	c_{44}	$\frac{1}{2}(c_{11}-c_{12})$
0	2.763±0.023	0.7117±0.0030	0.2899±0.0005
20	2.763	0.7112	0.2891
40	2.761	0.7084	0.2860
60	2.757	0.7050	0.2825
80	2.751	0.7023	0.2792
100	2.744	0.7008	0.2760
120	2.735	0.7005	0.2730
140	2.727	0.7011	0.2701
160	2.720	0.7022	0.2677
180	2.716	0.7038	0.2655
200	2.712	0.7056	0.2635
220	2.711	0.7077	0.2618
240	2.712	0.7100	0.2601
260	2.716	0.7125	0.2585
280	2.724	0.7148	0.2569
300	2.733	0.7173	0.2553

[a] All data expressed in units of 10^{12} dyne cm^{-2}.

DeLaunay[1] has shown that the bulk modulus of the electron gas in a metal contributes to c_{11} and c_{12} by an amount

$$K_e=Vd^2U/dV^2, \tag{1}$$

where V is the volume and U is the internal energy of the electron gas. At absolute zero, the latter is given by

$$U=U_0+V\int_0^{\zeta} N(E)EdE, \tag{2}$$

---

[8] J. A. Rayne, Phys. Rev. **112**, 1125 (1958).

[9] J. A. Rayne, Phys. Rev. **115**, 63 (1959).

[10] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, London, 1958).

[11] B. R. Coles, J. Inst. Metals **84**, 346 (1956).

[12] F. C. Nix and D. McNair, Phys. Rev. **61**, 74 (1942).

[13] J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).

when U_0 takes into account all the contributions from filled bands, etc. For the case of overlapping s and d bands, (2) may be written as

$$U=U_0+V\int_{E_s}^{\zeta} N_s(E)EdE+V\int_{Ed}^{\zeta} N_d(E)EdE, \quad (3)$$

where E_s and E_d are the energies of the origin of the s and d bands, respectively. Equation (3) may further be written as

$$U=U_0+V\left(n_sE_s+n_dE_d+\int_0^{\zeta-E_s} N_s(\epsilon)\epsilon d\epsilon +\int_0^{\zeta-E_d} N_d(\epsilon)\epsilon d\epsilon\right), \quad (4)$$

where n_s and n_d are the number of electrons per unit volume in the s and d bands and N_s and N_d are the respective densities of states. We thus have, assuming[14] that the number of electrons in each band remains unchanged on deformation,

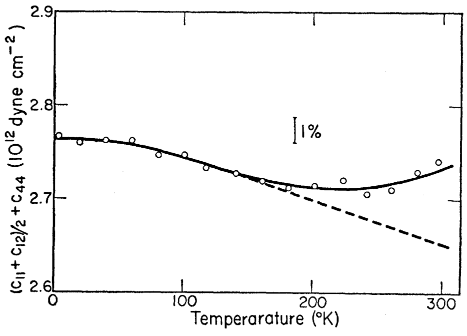

FIG. 1. Variation with temperature of $(c_{11}+c_{12})/2+c_{44}$ for palladium. The dashed curve represents the expected behavior for a temperature independent d-band contribution to the elastic constants.

$$V\frac{d^2U}{dV^2}=V\left(\frac{d^2U_0}{dV^2}+n_sV\frac{d^2E_s}{dV^2}+n_dV\frac{d^2E_d}{dV^2}+\frac{d^2U_s}{dV^2}+\frac{d^2U_d}{dV^2}\right), \quad (5)$$

where

$$U_s=V\int_0^{\zeta-E_s} N_s(\epsilon)\epsilon d\epsilon \text{ and } U_d=V\int_0^{\zeta-E_d} N_d(\epsilon)\epsilon d\epsilon. \quad (6)$$

If we neglect the explicit dependence of N_s on V, we have

$$\frac{dU_s}{dV}=\int_0^{\zeta-E_s} N_s(\epsilon)\epsilon d\epsilon-(\zeta-E_s)\cdot n_s(\zeta-E_s), \quad (7)$$

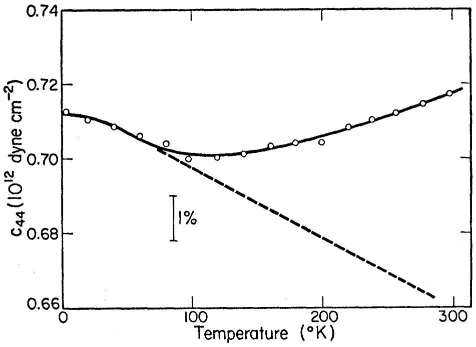

FIG. 2. Variation with temperature of c_{44} for palladium. The dashed curve represents the expected behavior for a temperature independent overlap contribution to the shear constant.

where we have used the fact that

$$\partial(\zeta-E_s)/\partial V=-n_s/VN_s.$$

Differentiation of (7) then gives

$$Vd^2U_s/dV^2=-Vn_s\partial(\zeta-E_s)/\partial V,$$

that is,

$$Vd^2U_s/dV^2=n_s^2/N_s. \quad (8)$$

A similar expression holds for the contribution from the d band. In the case of a parabolic band, where $N_s=3n_s/2(\zeta-E_s)$, Eq. (8) reduces to

$$Vd^2U_s/dV^2=\tfrac{2}{3}n_s(\zeta-E_s), \quad (9)$$

which is identical with Eq. (11.18) of DeLaunay.[1] Thus, if we assume that the s band in palladium is parabolic with a density of 0.6 electrons/atom,[4,5] we have $\zeta-E_s=4.3$ ev, $n_s=6.5\times10^{22}$ cm^{-3}, so that

$$Vd^2U_s/dV^2=0.3\times10^{12} \text{ dyne cm}^{-2}. \quad (10)$$

For the d band, $n_d=6.1\times10^{23}$ cm^{-3}, $N_d=1.6\times10^{35}$ cm^{-3} erg^{-1}, hence from Eq. (5)

$$Vd^2U_d/dV^2=2.3\times10^{12} \text{ dyne cm}^{-2}. \quad (11)$$

If we suppose that the first three terms in (5) do not alter appreciably in going from palladium to silver, they

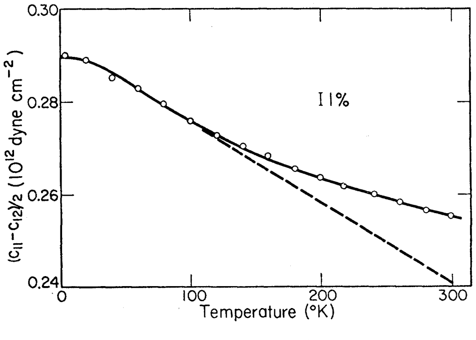

FIG. 3. Variation with temperature of $(c_{11}-c_{12})/2$ for palladium. The dashed curve represents the expected behavior for a temperature independent overlap contribution to the shear constant.

---

[14] Strictly speaking this assumption is not correct, since we should also take into account electron transfer between bands. For the present purposes, however, the latter effect can be neglected.

may be disregarded and hence for palladium[15]

$$K_e=V\left(\frac{d^2U_s}{dV^2}+\frac{d^2U_d}{dV^2}\right)=2.6\times10^{12}\text{ dyne cm}^{-2}. \tag{12}$$

Since silver has a filled d band, there will be no term in K_e analogous to (11). Hence again assuming a parabolic s band with $\zeta-E_s=5.5$ ev, $n_s=5.9\times10^{22}$ cm^{-3},

$$K_e=Vd^2U_s/dV^2=0.3\times10^{12}\text{ dyne cm}^{-2}. \tag{13}$$

The difference $(K_e)_{\text{palladium}}-(K_e)_{\text{silver}}=2.3\times10^{12}$ dyne cm^{-2} is considerably larger than the difference between their bulk moduli, viz., $B_{\text{palladium}}-B_{\text{silver}}=0.97\times10^{12}$ dyne cm^{-2}. It seems reasonable to suppose, however, that our neglect of the first three terms in (5), together with the neglect of the explicit dependence of N on the volume, is responsible for this overestimate.

(b) Temperature Dependence of Elastic Constants

Reference to Figs. 2 and 3 shows that both c_{44} and $(c_{11}-c_{12})/2$ have an anomalous temperature variation. For most metals, both shear constants increase almost linearly with decreasing temperature down to about 100°K. For palladium, c_{44} initially *decreases* with decreasing temperature, while $(c_{11}-c_{12})/2$ has a pronounced concavity toward the abscissa. It is believed that this behavior is due to the change with temperature of the contribution to the shear constants, resulting from the holes in the 4d band of palladium. This change is quite marked owing to the low degeneracy temperature of the holes. The dashed lines in Figs. 2 and 3 are the estimated behavior of the shear constants, if the hole contribution did not alter with temperature. As may be seen, the difference is much more pronounced in c_{44} than in $(c_{11}-c_{12})/2$.

A more quantitative understanding of the above effects may be obtained if we apply the theory of Leigh,[2] which was originally developed to explain the magnitude of the shear constants of aluminum. Accordingly, let us consider the five Brillouin zones associated with the d electrons of palladium. If we denote by $N_i(E_i-\zeta)$ the contribution to the density of states per atom arising from one particular set of holes at an energy E_i relative to the zone center and n_i the corresponding number density of holes, then it may be shown that the contributions to the shear constants are given by expressions of the type

$$d^2U/dx^2=\textstyle\sum_i\left[-\lambda_i n_i E_i-\mu_i N_i(E_i-\zeta)E_i^2\right], \tag{14}$$

where λ_i, μ_i are numerical coefficients and x is the appropriate strain parameter. In deriving this expression, it has been assumed that the energy at a point on the zone is proportional to its distance from the zone center.

Now, assuming that the holes have a parabolic dependence on $E_i-\zeta$, it is easily shown that[16]

$$E_i-\zeta=(E_i-\zeta_0)[1-(\pi^2/12)(T/T_0)^2], \tag{15}$$

where $kT_0=E_i-\zeta_0$. For metals with a low degeneracy temperature and a steep density-of-states curve, the second term will thus vary quite appreciably with temperature. Thus from (14) we have

$$\begin{aligned}\Delta(d^2U_i/dx^2)&=-\mu_iE_i^2[N_i(E_i-\zeta)-N_i(E_i-\zeta_0)]\\&=-\mu_iE_i^2N_i'(E_i-\zeta_0)\cdot\Delta(E_i-\zeta)\\&=(\pi^2/12)(T/T_0)^2\mu_iE_i^2N_i'(E_i-\zeta_0)\cdot(E_i-\zeta_0)\\&=(\pi^2/24)(T/T_0)^2\mu_iN_iE_i^2\end{aligned}$$

i.e.,

$$\frac{\Delta(d^2U_i/dx^2)}{\mu_iN_iE_i^2}=\frac{\pi^2}{24}\left(\frac{T}{T_0}\right)^2. \tag{16}$$

To estimate the increase, let us assume the existence of only one type of hole and take $\mu=1$, $N=1$ level/ev/atom. We then have

$$\mu_iN_iE_i^2\sim0.9\times10^{12}\text{ dyne cm}^{-2}. \tag{17}$$

Since $T_0\sim1500$°K for palladium, Eq. (16) then gives for $T=300$°K

$$\Delta(d^2U_i/dx^2)\sim2\times10^{10}\text{ dyne cm}^{-2}, \tag{18}$$

which is at least in order-of-magnitude agreement with experiment. Actually, Leigh's calculations give $\mu=0$ for holes at the zone corners and holes over the square faces, and $\mu=16/9$ for holes over the hexagonal faces. Thus, on the basis of these values, the large temperature change in c_{44} would seem to require the existence of the latter type of hole. Such a situation is, however, not consistent with the original assumption that the energies at the zone faces are proportional to the squares of the respective distances from the zone center, since the hexagonal faces are much closer to the center than the square faces or the zone corners. In view of the simplifying assumptions made in the theory, this inconsistency should not be taken too seriously and we should rather take μ_i, λ_i to be adjustable parameters. On this view, the values obtained from experiment are not unreasonable and lend strength to the conviction as to the essential correctness of the theory.

In the same way the anomalous temperature dependence of the bulk modulus of palladium, implicit in Fig. 1, may be explained. Thus considering only the d band contribution, we have from (8)

$$\frac{\Delta K_e}{K_e}=-\frac{N_d'(E_i-\zeta_0)}{N_d(E_i-\zeta_0)}\Delta(E_i-\zeta). \tag{19}$$

For a parabolic band this becomes

$$\begin{aligned}\frac{\Delta K_e}{K_e}&=-\frac{1}{2}\frac{\Delta(E_i-\zeta)}{(E_i-\zeta_0)}\\&=\frac{\pi^2}{24}\left(\frac{T}{T_0}\right)^2.\end{aligned} \tag{20}$$

---

[15] This value has been derived from the electronic heat capacity of palladium[5,6] after subtracting off the contribution to the density-of-states arising from the s band.

[16] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 178.

At $T=300°\text{K}$, Eq. (20) gives

$$\Delta K_e \sim 5\times 10^{10} \text{ dyne cm}^{-2}, \tag{21}$$

which is again of the required order of magnitude.

(c) Debye Temperature of Palladium

Using the method of DeLaunay[17] to compute θ_0 and taking $\rho_0=12.132$ gram cc^{-3}, $V_0=8.7949$ cm^3, we obtain from the elastic data extrapolated to absolute zero

$$\theta = 275 - 0.06T^2 \text{ °K}. \tag{22}$$

The value $\theta_0=275\pm8°\text{K}$ is in excellent agreement with that obtained by Hoare and Yates,[5] who found from their calorimetric data a value $\theta_0=274\pm3°\text{K}$. Owing to the large electronic heat capacity of palladium, it is difficult to determine the Debye temperature with much accuracy from calorimetry. Their error estimate is a measure only of the internal consistency of the data and hence the above agreement is somewhat misleading, since a small systematic error could easily cause a fairly large change in the calorimetric value of θ. It is believed that an error of this sort is responsible for the higher Debye temperature $\theta_0=299°\text{K}$ reported by Rayne.[6] Owing to the small specimen mass used in the latter work, an error in the specific heat of the addenda could easily be responsible for the discrepancy.

It is of interest that measurements in the liquid hydrogen range[18,19] give $\theta=275°\text{K}$. This circumstance is difficult to understand since, according to Eq. (22), θ should be considerably lower than the liquid helium value and should be varying quite rapidly with temperature. One possible explanation is that the electronic heat capacity is not constant up to these temperatures, but this hardly seems likely since the degeneracy temperature of the holes in the d band is in excess of 1000°K. It would thus seem desirable to have more accurate heat capacity data in the liquid hydrogen region to check the validity of Eq. (22).

V. CONCLUSION

Elastic data have been obtained on a single crystal of palladium from 4.2–300°K. The data extrapolated to absolute zero give a value of Debye temperature in good agreement with that obtained from calorimetry. The anomalous behavior of C and C' is satisfactorily correlated with the temperature dependence of the contribution to the shear constants, arising from the holes in the d band of palladium.

ACKNOWLEDGMENT

The author gratefully acknowledges the help of Dr. James Kirn of the Virginia Institute for Scientific Research in providing the single crystal of palladium used in this work.

---

[17] J. DeLaunay, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 285.

[18] G. L. Pickard and F. Simon, Proc. Phys. Soc. (London) **61**, 1 (1948).

[19] K. Clusius and L. Schachinger, Z. Naturforsch. **2a**, 90 (1947)

PHYSICAL REVIEW VOLUME 118, NUMBER 6 JUNE 15, 1960

Retardation and K X-Ray Relative Intensities*

G. R. Taylor and W. B. Payne
Virginia Polytechnic Institute, Blacksburg, Virginia

(Received December 7, 1959)

The matrix elements for electric dipole transitions with retardation have been numerically evaluated for transitions between the $1s$ and higher discrete states of a single Dirac electron in a Coulomb field. The results are used to calculate the relative intensities of the principal K x-ray lines in elements of high atomic number. Comparison of the retarded and nonretarded matrix elements confirms the earlier result for lead that the effect of retardation is significant in heavy elements only when the total angular momentum of the electron changes. Comparison with the experiments of Beckman indicate that this conclusion is correct, and that in the $K\alpha_2$ to $K\alpha_1$ intensity ratio the effect of retardation is more significant than screening effects.

INTRODUCTION

THE matrix elements for K x-ray transitions in the Dirac hydrogenic atom have been numerically evaluated for atomic numbers ranging from 1 to 100. These matrix elements are presented in algebraic form in an earlier paper[1] and will not be repeated here. The matrix elements have been used to compute the relative intensity (intensity in energy/unit time) of K x-ray lines in heavy elements. These relative intensities are compared first with earlier calculations[2] of these relative intensities in which retardation effects were neglected and with recent experiments.[3]

The intensity of an x-ray transition from an initial state a to a final state b is given in ergs/sec by

$$I_{ab} = (2e^2\hbar/mc^3)\omega_{ab}{}^3 f_{ab}, \tag{1}$$

---

* Supported by the Research Corporation.

[1] W. B. Payne and J. S. Levinger, Phys. Rev. **101**, 1020 (1956). This paper is referred to throughout this article as (PL).

[2] W. B. Payne, dissertation, Louisiana State University, 1955 (unpublished).

[3] O. Beckman, Arkiv Fysik **9**, 495 (1955).