

The Refraction of the Copper *K*-Series by Quartz

In the most direct methods of measuring the index of refraction of x-rays it is necessary to measure the distance between the edges of lines on a photographic plate. Since such edges are never sharply defined the results depend to some extent on the judgment of the observer. Thus measurements by various observers and under as many different conditions as possible are necessary in order to obtain the most reliable experimental values.

The quartz prism used in the present experiments was cut from a very clear quartz crystal. Special precautions were taken to produce a very sharp 90° edge on the prism. The x-ray beam struck the first face of the prism at an angle slightly greater than the critical angle of total reflection for the copper *K* lines. This angle varied from 16' 30'' to 27' 57'' in the different exposures. The refracting edge of the prism was accurately placed on the axis of the spectrometer table by the use of the modified Michelson interferometer previously described by the writer.¹ The plate holder and the slits which were 0.01 mm wide and 400 mm apart were also adjusted as described in the above paper.¹ The plate holder was 1895.2 mm from the refracting edge of the prism.

After all adjustments and preliminary exposures had been made a series of 18 exposures was taken, using different angles of incidence and different lengths of exposures. The separations of the lines on the plates were measured with a calibrated comparator.

The index of refraction may be most easily obtained from the relation $\mu = \cos \rho / \cos \theta$, where μ is the index of refraction, ρ the angle between the x-ray beam and the first face of the prism, and θ the angle between the first face of the prism and the direction of the refracted beam. Writing $\delta = 1 - \mu$ and using the angle in place of the sin of the angle the above relation becomes

$$\delta = \theta(\rho + \theta/2).$$

The average values of δ for the copper *K α* and *K β* lines as determined from this equation were

$$\delta_{\alpha} = 8.553 \pm 0.006 \times 10^{-6}$$

$$\delta_{\beta} = 6.971 \pm 0.005 \times 10^{-6}.$$

The average variation of the different values from the mean was about 0.39 percent. This is much larger than was desired but compares

favorably with recent experiments of the same type. Larsson² obtained an average variation 0.41 percent and Stauss³ 0.70 percent.

The primary object of such measurements is to obtain an independent determination of e/m . If one assumes the usual dispersion formula

$$\mu = 1 - \delta = \frac{e^2}{2\pi m} \sum_i \frac{N_i}{\nu^2 - \nu_i^2}$$

to be valid for the x-ray region then it can be shown that

$$e/m = \frac{2\pi W \delta}{F \rho c^2 \sum_i \frac{N_i}{\nu^2 - \nu_i^2}}$$

where W is the molecular weight, $\delta = 1 - \mu$, F the Faraday constant, ρ the density of the refracting medium, c the velocity of light, N_i the number of electrons per molecule of frequency ν_i , ν the frequency of the incident radiation. The use of the simpler formula as used by the writer in a previous paper¹ cannot be used with the longer wave-lengths employed here. Using $W = 60.06$, $F = 9648.9$, $\rho = 2.649$, $c = 2.99796 \times 10^{10}$, and λ from the writer's grating measurements,¹ one obtains

$$(e/m)_{\alpha} = 1.7645 \times 10^7 \text{ emu/g}$$

$$(e/m)_{\beta} = 1.7649 \times 10^7 \text{ emu/g}.$$

Similar calculations for the results obtained by Larsson² and Stauss³ using the grating wave-lengths as above are given in the following table.

Observer	Radiation	$e/m \times 10^{-6}$
Larsson	Cu <i>Kβ</i>	1.7667
Larsson	Cu <i>Kα</i>	1.7646
Stauss	Mo <i>Kβ</i>	1.7644
Stauss	Mo <i>Kα</i>	1.7634

The close agreement of these values of e/m indicates that the experimental results are approximately correct unless some consistent error has been present in all experiments.

In the above calculations the absorption of the x-rays in the prism has been neglected. Thus the absolute value of e/m would be slightly different from these values. It has also

¹ Bearden, Phys. Rev. **37**, 1210 (1931).

² Larsson, Inaugural-Dissertation, 1929.

³ Stauss, Phys. Rev. **36**, 1101 (1930).

been shown² that the dispersion formula used is not valid near an absorption band. The theory developed by Kramers, Kallman and Mark and Kronig appears to be more satisfactory for frequencies near an absorption band. For frequencies high compared to the natural frequencies of the electrons in the refracting medium the theory leads to a formula very similar to the one used above.

At the present time measurements are in progress using the method developed by Stauss³ in which the incident x-ray beam strikes the second face of the prism at a very small angle.

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Note on the Interpretation of the BeF Bands

Inverted character of ${}^2\Pi$ in BeF.

From his analysis of the BeF bands, Jenkins showed¹ by means of the Hill and Van Vleck formula that the coupling constant A (Jenkins' $\Delta\epsilon$) between the spin and orbital electronic angular momenta in the ${}^2\Pi$ state is either $+22.10 \text{ cm}^{-1}$ or -16.46 cm^{-1} . Because of insufficient resolution of lines having low J values, it was not possible to decide between these two alternatives on the basis of the missing lines. By a consideration of the relative size of the Λ -type doubling in the F_1 and F_2 series of terms of the ${}^2\Pi$ state, however, Jenkins tentatively concluded that the ${}^2\Pi$ is normal, i.e. $A = +22.1$. A more detailed consideration of the Λ -type doubling now shows, however, that the ${}^2\Pi$ is *inverted*.

According to Jenkins' data,¹ the observed Λ -type doublet widths are in agreement with the following equations:

$$\left. \begin{aligned} F_1 \text{ levels: } \Delta\nu_{dc}(J) &= -0.00046(J + \frac{1}{2})^2 \\ F_2 \text{ levels: } \Delta\nu_{dc}(J) &= -0.00028(J + \frac{1}{2})^2 \end{aligned} \right\} (1)$$

The quantity $\Delta\nu_{dc}(J)$ is defined² as $F_d(J) - F_c(J)$. The subscripts c and d have a definite theoretical meaning.² It is only necessary to make the safe assumption that the ${}^2\Sigma$ state of the BeF bands is ${}^2\Sigma^+$ in order to show³ that Jenkins' A and B respectively correspond to the theoretical designations c and d . From Eq. (8) and p. 331 (cf. also Fig. 3) of Ref. 1, Eqs. (1) then follow. Eqs. (1) apply to data for moderate and high J values; for low J values the Λ -type doubling is too small to measure.

As can most easily be seen by referring to the series of examples in Ref. 2, Fig. 1, it is evident that the qualitative characteristics of Eqs. (1) require that the F_1 levels belong to a ${}^2\Pi_{1/2}$ state for low J values and the F_2 levels to a ${}^2\Pi_{3/2}$ state. This means,—cf. e.g. Jenkins' Fig. 3, omitting his level $F_1(\frac{1}{2})$ and adding a level $F_2(\frac{1}{2})$,—that the ${}^2\Pi$ is *inverted*. Hence $A = -16.46$ is correct. Eqs. (1), which Jenkins

does not claim hold accurately, must be only approximately correct, and for low J values the $\Delta\nu_{dc}(J)$'s must become positive in the F_2 set of levels.

Possible bearing on electron configuration.

The inverted character of the ${}^2\Pi$ state of BeF now indicates that it is analogous to the ${}^2\Pi$ states of BO, CO⁺, and CN. The negative sign of both sets of $\Delta\nu_{dc}$'s for high J values (cf. Eqs. (1)), which shows that q in Eq. (14) of Ref. 2 is *negative*, constitutes a further and independent analogy to the ${}^2\Pi$ of BO (cf. Ref. 2, p. 99). An analogy of the ${}^2\Pi$ of BeF to those of BO, C⁺O, and CN was previously suspected, but was rejected⁵ because of the much smaller *magnitude* of A in BeF than in the other molecules. In CN, $-A \sim 52$ is somewhat less than the probable value expected from the N atom while $-A \sim 126$ in BO and C⁺O is not much less than the A value of the 3P normal state of the O atom. If the electron configuration in the ${}^2\Pi$ state of BeF is $\dots 2p\pi^3 3s\sigma^2$ as in the ${}^2\Pi$ states of BO, C⁺O, and CN, one might expect $-A$ to be not much less than for the F atom, for which $-A = 271$. But the actual value $-A = 16.46$ is far smaller. It is, however, much larger than A of the lowest 3P state of Be ($A = +2.0$) or of the lowest 2P state of Be⁺ ($A = +4.7$). Before the fact of the negative sign of A , but only its small magnitude, was

¹ F. A. Jenkins, Phys. Rev. **35**, 315 (1930).

² Cf. R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87–119 (1931), Eq. (1).

³ Ref. 2, p. 103. The assignment of c and d is most easily made treating the ${}^2\Pi$ state as case b .

⁴ For the O atom, $\Delta\nu({}^3P_0 - {}^3P_2) = 226$, which gives $A = 2/3 \times -226 = -151$ (cf. R. S. Mulliken, Phys. Rev. **33**, 745, 1929). For the F atom, $\Delta\nu({}^2P_{3/2} - {}^2P_{1/2}) = 407$, giving $A = -271$. For the atoms Ca, Sr, Ba, A is $2/3$ of $\Delta\nu({}^3P_2 - {}^3P_0)$.