

trons still in atoms but capable of going over to adjacent ions—becomes small. If we imagine a condition, at some low temperature, in which λ' becomes zero, the distinction between free electrons and associated electrons will be extinguished. In such a case the electrons, if once started in a given direction by an applied e.m.f., might go on indefinitely in that direction, there being nothing to stop them. That is, we should have supra-conductivity. I first made a suggestion to this effect,¹ though without the conception of free path that I have used in this paper, in 1926.

Thermal Conductivity at Low Temperature.—Since, according to my theory of the matter, thermal conductivity in metals depends mainly upon the dual character of electric conductivity and upon the heat of ionization, it should be especially small when, as in my conception of supra-conductivity, “free” electrons and “associated” electrons become indistinguishable, the heat of ionization becoming zero. It should not, however, be entirely lacking, as the elastic vibrations of the metal would have some heat-carrying power.

¹ See page 417 of *Phys. Rev.*, 28.

DISPERSION OF LONG WAVE-LENGTH X-RAYS IN PLATINUM AND CALCITE

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The problem of indices of refraction and dispersion in the x-ray region was first brought to the attention of physicists by the observation that the apparent wave-length of x-ray lines measured in different orders did not agree and that the discrepancies were such as to be explained by the theory that the crystal used had an index of refraction slightly less than unity.¹ From these measurements the order of magnitude of the index could be calculated but the method was indirect and not capable of much accuracy. The results, however, showed the importance of finding the x-ray refractive indices of crystals in order to correct existing wave-length measurements for this effect.

A. H. Compton² attacked the problem in a more direct way by showing that polished surfaces would reflect x-rays if the glancing angle of incidence were sufficiently small and that a critical angle of total reflection could be measured and the index of refraction computed as in ordinary optics. He also showed that the indices measured in this way were in good agreement with an extension to these high frequencies of theories

of dispersion developed by Drude³ and Lorentz⁴ for the region of optical frequencies. This may be expressed in the following formulas:

$$1 - \mu = \delta$$

$$\delta = \frac{e^2 N}{2\pi m} \sum_1^Z \frac{n_c}{\nu^2 - \nu_c^2}$$

in which μ is the index of refraction, e and m the charge and mass of an electron, N the number of atoms per cc., ν the frequency of the incident x-ray, ν_c a critical frequency of the atom, n_c the number of electrons in the atom having this critical frequency, and Z the total number of electrons in the atom or its atomic number.

If this formula applies then δ should have large positive values when the frequency of the incident x-ray is just slightly larger than one of the critical frequencies of the atom and large negative values for frequencies slightly smaller than a critical frequency. In other words, the phenomenon of anomalous dispersion should appear.

Hjalmar and Siegbahn⁵ thought to have found evidence of anomalous dispersion from a consideration of the apparent differences of the same wave-length reflected from calcite and gypsum. von Nardroff,⁶ Hatley⁷ and Edwards⁸ have sought to identify the x-ray absorption limit frequencies with the critical frequencies of the above formula.

Kronig⁹ and Kallman and Mark¹⁰ have shown that from a consideration of the type of absorption curve found near an x-ray absorption limit frequency, a dispersion formula may be developed which Doan¹¹ has put into the following form:

$$\delta = \frac{NZe^2}{2\pi m\nu^2} + \frac{Nc^4CZ^4}{8\pi^2\nu^4} \ln \left(\frac{\nu_c^2 - \nu^2}{\nu_c^2} \right)^2$$

in which C is the constant of the fluorescent absorption coefficient and the other symbols have the meaning used above. The effect of the logarithmic term is to give lower values of δ on both sides of the absorption limit wave-length instead of lower values on the long wave-length side only and higher values on the short wave-length side as is the case with the Drude-Lorentz formula. For frequencies not near an absorption limit both formulas lead to the same values.

The experimental data on which these theories might be tested have previously been very meager and confined to a small number of isolated measurements of δ for a few favorable wave-lengths in the region of high frequency x-rays such as may be easily obtained from an ordinary x-ray tube in air. The formulas, however, indicated that larger values of δ should be obtained at longer wave-lengths, such as could be obtained only in a vacuum.

A large vacuum spectrograph was constructed to carry out this work. The evacuated bowl in which the apparatus was enclosed was two feet in inside diameter, being much larger than the usual vacuum x-ray spectrograph and thus permitting greater wave-length resolution. An especially designed water-cooled x-ray tube was connected to the bowl and the arrangement was such that a beam of x-rays entering the bowl from the tube was collimated by passing through two narrow slits 25 cm. apart. This beam then impinged upon a gypsum crystal at the center of the spectrograph and was partly reflected by it to a photographic plate tangent to a circle of 29 cm. radius having the gypsum crystal at the center. This reflected beam was nearly monochromatic and its wave-length could be determined from Bragg's law after the instrument had been calibrated by photographing the L spectrum of tungsten. A mirror surface of the substance to be investigated could then be introduced into this beam at a distance of 5 cm. from the crystal and 24 cm. from the plate, its angle of inclination varied and the maximum angle at which reflection occurred determined. The experimental values of δ were then calculated from the equation

$$1 - \mu = \delta = 2 \sin^2 \frac{\phi}{2}$$

ϕ being the maximum glancing angle at which reflection occurred. With this apparatus it was found possible to secure sufficient intensity even when

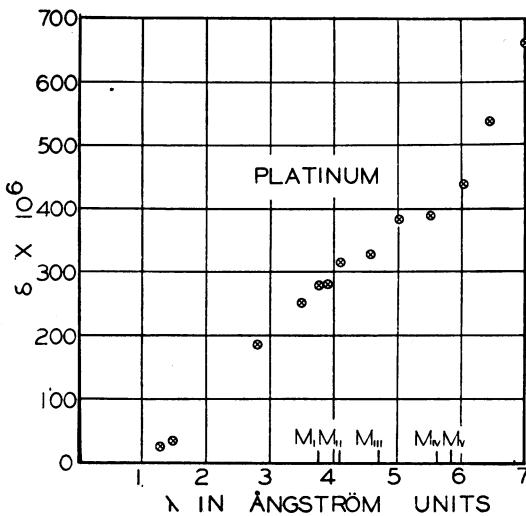


FIGURE 1

the beam of general radiation was so narrow that variations from the mean wave-lengths were less than $1/5\%$. This ability to make use of general radiation removed one of the most serious limitations that had hampered all previous investigations in which only characteristic line radiation was used and permitted the measurement of δ using any wave-length within the range of crystal reflection. It is expected that a more complete description of this apparatus and the methods

employed together with other data obtained will be published elsewhere, the purpose of this paper being to state briefly the results so far secured

with platinum and calcite and the bearing of these results on the previously mentioned theories.

Platinum was first chosen as a reflector since smooth mirror surfaces which do not readily tarnish may be easily obtained of this metal by thermal sputtering upon plate glass. Platinum is also very dense and δ should, through a certain range at least, be approximately proportional to density. Also its M series absorption limit wave-lengths were within easy range of the instrument and it was thought that perhaps δ would undergo large changes as one passed to frequencies lower than those of these limits. The values of δ and the corresponding values of λ are shown in figure 1. It may be seen that while sufficient points have not been obtained to determine the fine structure of a dispersion curve the values of δ continue to increase with λ and to do this at an accelerated rate even after passing to frequencies lower than the characteristic frequencies of 28 of the 78 electrons of platinum. In other words, δ continues to increase and the index of refraction to become smaller although more than one-third of the electrons have characteristic frequencies greater than that of the incident x-ray. Carbon paper was used to protect the photographic plates from the light of the x-ray tube filament and as this appears to become nearly

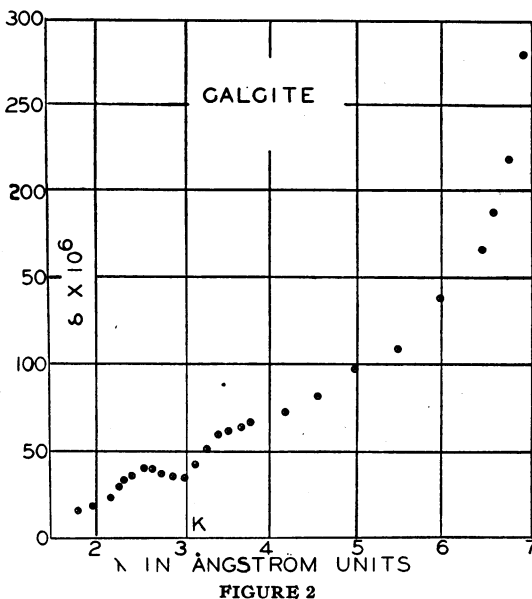


FIGURE 2

opaque for x-radiation at a wave-length of about 7 Ångstrom units the work was not carried, for the time being, to greater wave-lengths. However, from these results it would appear very probable that δ in the case of platinum continues to increase with increase in λ over a much greater range, at least as far as the beginning of the N series of absorption limits at about 17 Ångstrom units.

Calcite was next chosen because its use as a crystal grating made it desirable to study its dispersion curve in order that wave-lengths determined by its use might be corrected for refractive index effects. The K limit of calcium was also in a favorable region for study. Certain improvements in the technique of handling the spectrograph made it possible

to use narrower slits and thus a more nearly monochromatic source and at the same time work more rapidly. Figure 2 shows values of δ plotted against λ .

These results show very clearly the type of anomalous dispersion occurring near a K absorption limit. It is of the form predicted by the theories of Kronig and of Kallmann and Mark. It is doubtful that a quantitative agreement exists. For one thing the fluorescent absorption coefficient of calcium is not accurately known in this region. If the dispersion theory were quantitatively reliable perhaps the absorption coefficient could be derived from the dispersion curve. However, it must be noted that in the range of from six to seven Ångstrom units δ more than doubles in value. This is much more than can be explained by either theory.

¹ Stenstrom, also Hjalmar; see Siegbahn, *Spectroscopy of X-Rays*, p. 21, 1925.

² Compton, *X-Rays and Electrons*, p. 205, 1926.

³ Drude, *Theory of Optics*, p. 382.

⁴ Lorentz, *Theory of Electrons*, 2d ed., p. 150.

⁵ Hjalmar and Siegbahn, *Nature*, **115**, 85 (1925).

⁶ von Nardroff, *Phys. Rev.*, **24**, 143 (1924).

⁷ Hatley, *Phys. Rev.*, **24**, 486 (1924).

⁸ Edwards, *Phys. Rev.*, **30**, 91 (1927).

⁹ Kronig, *J. Optical Soc.*, **12**, 547 (1926).

¹⁰ Kallmann and Mark, *Ann. Physik*, **82**, 585 (1927).

¹¹ Doan, *Phil. Mag.*, **4**, 100 (1927).

MOBILITIES OF GASEOUS IONS IN SO₂ AND SO₂-H₂ MIXTURES

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Introduction.—In order to throw possible light on the nature of gaseous ions one of the writers began the study of mobilities of ions in mixtures of various gases of diverse chemical nature.^{1,2,3} This study constitutes a continuation of the work extending it to SO₂-H₂ mixtures. Despite the fact that mobilities have already been measured in pure SO₂ the results obtained in the pure gas alone merit some discussion.^{4,5} While theoretically an easy gas to work with and assumedly easy to prepare in pure form, it was found to be the most difficult gas yet encountered. The results are therefore not entirely satisfactory, but inasmuch as the work must be temporarily discontinued, it seemed best to report the results obtained to date.

Effect of Fine Gauzes in Mobility Measurement.—Before undertaking measurements the writers briefly investigated the question of the nature