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Experimental Aspects of Relativistic Effect in Electron Diffraction

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(1) On the basis of relativistic formula, the mean inner potential V_0 of MgO crystal was determined from the observations of refraction multiplets on (220) Debye rings, with electrons of energies ranging from 100 kV to 300 kV. The result is $V_0=13.4\pm0.3$ volt. The magnitude of the additional term to the apparent mean inner potential due to inelastic scattering was also estimated. (2) Change of the profile of symmetrical Kikuchi band with the electron energy by the relativistic effect was experimentally demonstrated. (3) The necessity of relativistic correction, which is to be applied to Honjo-Kitamura's method of eliminating the primary extinction effect in observed intensities of reflexions, was pointed out. (4) Some remarks on the relativistic effect on the contrast in electronmicroscopic images were given.

1. Introduction

The relativistic factor due to the mass correction of electron in scattering formulae of electron waves was introduced first by Mott[1], and discussed also by Laue[2] in relation with the kinematical theory of electron diffraction by crystals and other scattering systems. Recently, one of us (K. F.)[3] has formulated a relativistic dynamical theory of electron diffraction by crystals, and emphasized the practical importance of this factor not only for electrons of high energies, say higher than 100 keV but for electrons of moderate energies, say 40~100 keV as utilized most ordinarily in electron diffraction experiments.

The relativistic mass correction for electrons is expressed as

$$m=m_0\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}, \qquad (1)$$

where m_0 is the rest mass of electron, h is Planck constant, c is the light velocity and λ the wavelength of electron.

The electron mass appears in scattering formulae of electrons always combined with the potential field $V(\boldsymbol{r})$. Therefore, in problems of electron diffraction by crystals, a convenient relativistic-revision of the results of current kinematical and dynamical theories may be derieved alternatively by the replacements

$$V_h\rightarrow V_h\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}, \qquad (2)$$

and by assuming the electron mass appearing in the relevant formula to be the rest mass, where V_h is the Fourier potential of the field in the crystal.

In this paper, some observations revealing distinctly the relativistic effects, and some due remarks on results of non-relativistic diffraction theory are presented.

2. Refractive indices of electrons in crystals

The relativistic formula for the mean refractive index $\mu=1+\delta_0$ of electron in a crystal is given by

$$\delta_0=\frac{m_0e\lambda^2}{h^2}V_0{}^R\equiv\frac{m_0e\lambda^2}{h^2}V_0\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}, \qquad (3)$$

where V_0 is the mean inner potential. This relation had been derived by Yamaguti[4] as early as in 1930, but the simpler formula $\delta_0=V_0/2E$ has been applied more often, where E is the accelerating potential. Similarly, in observation of the double refraction phenomena accompanying the reflexion $\boldsymbol{h}$, the relation $\delta_h=(V_0\pm V_h)/2E$ has been usually adopted for the unit increment of refraction indices at exact Bragg condition, while its relativistic expression should be

$$\delta_h=\frac{m_0e\lambda^2}{h^2}(V_0\pm V_h)\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}. \qquad (4)$$

In measurements of the inner potential of crystal performed with electrons of energies lower than, say, 50 keV, errors arising from the use of non-relativistic relations can be comparatively small, although they cannot be disregarded as is understood by the following formula[3] which is convenient to estimate the order of magnitudes of the mass-correction factor,

$$\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}=1+1.96(eE)_{\mathrm{MeV}}, \qquad (5)$$

where the unit for eE in the right-hand side is assumed to be one million electron volt. For electrons of higher energies, however, reasonable results may hardly be attained without adopting the correct relativistic relation. In this respect, the present authors have studied the dependence of refractive indices for electron on the electron energy, by observing refraction multiplets on (220)-rings in Debye patterns from magnesium oxide smoke-particles, with a diffraction apparatus having a van de Graaf generator as the high tension source.

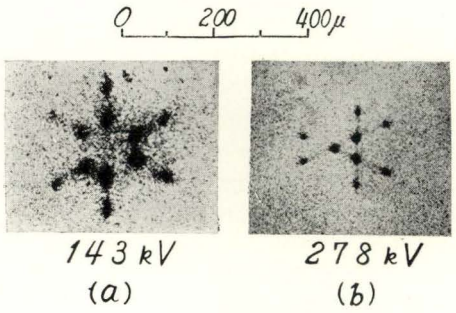

Fig. 1. Examples of refraction multiplets on MgO (220)-rings. Camera length: 68 cm.

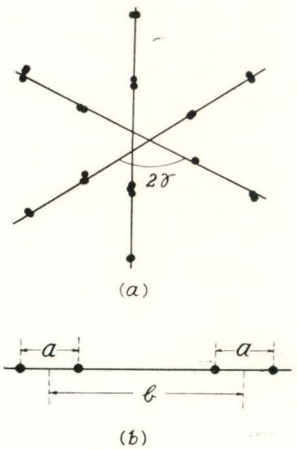

Fig. 2. (a): Sketch of the refraction multiplet shown in Fig. 1(a). (b): Schematic diagram of a refraction quartet.

Fig. 1 shows magnified examples of the mutiplets, and Fig. 2 is a sketch of the multiplet corresponding to Fig. 1a, which was obtained by an accurate measurement of the position of each spot with a comparator.

The mean and double refractive indices can be obtained by measuring the wavelength of electron, the distances a and b in quartets of spots as illustrated in Fig. 2b, the angle γ in Fig. 2a, etc.[5),6)] The wavelength was determined from the radius of (200)-rings in MgO patterns, or that of (220)-rings in reference patterns from a gold film.

Fig. 3 shows the result for the measurement of the mean refractive index, where the absscissa corresponds to electron energy and the ordinate to the quantity $V_0{}^R$ in the relation (3). The data for $E=25\sim50$ keV were taken from the data of Honjo and Mihama[5)] after due relativistic corrections. The increase of the value $V_0{}^R$ from 15 volt to 22 volt with the increase of E shows the relativistic effect distinctly.

According to (3) the value V_0 is given by

$$V_0=V_0{}^R\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{-\frac{1}{2}}. \qquad (6)$$

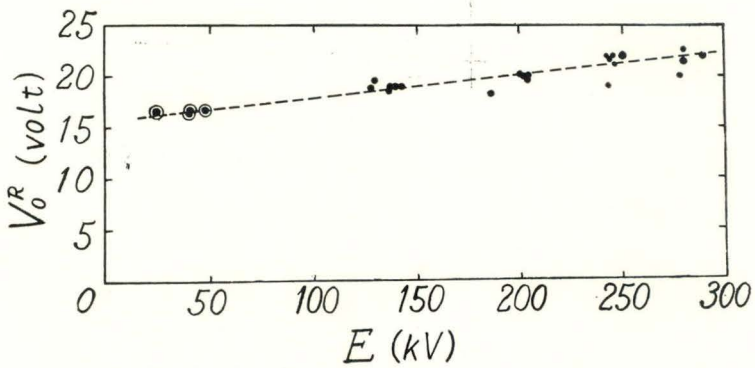

Fig. 3. Variation of $V_0{}^R$ defined by the relation (3). Data taken from Honjo and Mihama's observation are shown by ⊙.

The calculated values of V_0 by (6), which are shown in Fig. 4, are fairly constant as it should be, but its slight decrease with increasing electron energy cannot be overlooked.

The decrease of the calculated values of V_0^R shown by Fig. 4 seems to be interpreted as the effect of inelastic scattering which was formulated by Yoshioka[7]. According to his theory, the apparent mean inner potential is given by a sum of V_0 and an additional term, and is expressed, after a relativistic correction, as

$$V_0^{\text{appt.}} = V_0\left[1+\frac{\lambda}{2a_0}\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}\right], \quad (7)$$

where a_0 is Bohr radius 0.55Å. Fig. 5 is a re-plot of the value V_0 shown in Fig. 4 against $\lambda(1+h^2/m_0^2c^2\lambda^2)^{\frac{1}{2}}$. We can see that the plotted points are fairly linear, and by this plot the value of mean inner potential V_0 is obtained at the virtual limit of the extrapolation of the experimental line to the zero-value of abscissa. The value thus obtained is

$$V_0 = 13.4 \pm 0.3 \text{ volt.}$$

This value may be compared with the theoretical value 12.8 volt calculated by Tull[8], and 18.0 volt which is calculated on basis of the tabulation of scattering factor for electron given by Ibers[9]. The discrepancy between the experimental result and the latter of the theoretical values is rather large, but it should be noticed that the table of Ibers is to be applied only to neutral atoms.

From the inclination of the linear curve in Fig. 5, we can obtain the experimental value of a_0. The result

$$(a_0)_{\text{exp}} = 0.22\text{Å}$$

is smaller than a half of Bohr radius. This discrepancy, however, seems to be not unreasonable, since, as was pointed out by Yoshioka and Kainuma[10),11)], there may be contri-

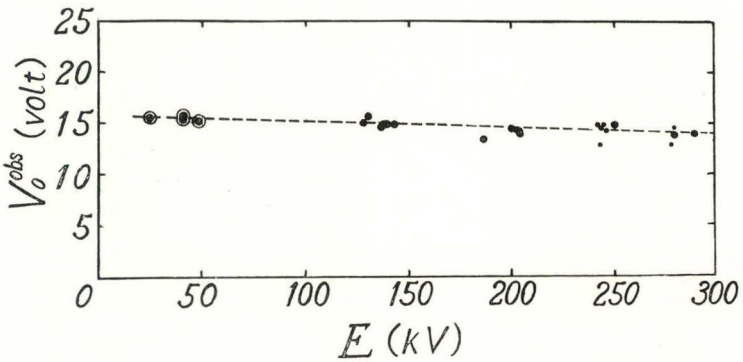

Fig. 4. Variation of V_0 defined by the relation (6). Honjo and Mihama's data are shown by ⊙.

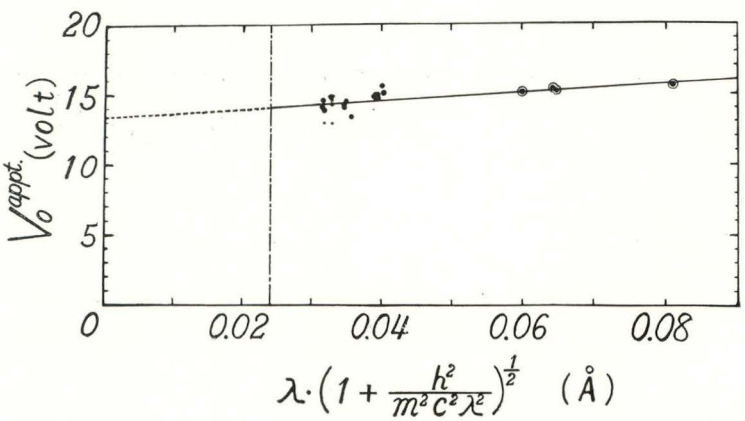

Fig. 5. Re-plot of V_0 in Fig. 4 against $\lambda\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}$. Honjo and Mihama's data are shown by ⊙.

butions of inelastic scattering of electrons, especially those coming from the thermal scattering, to the apparent value of the inner potential besides that due to transitions of atomic levels, and only the latter has been taken into account in Yoshioka's original theory.

The study of the relativistic effect in the double refraction in the refraction multiplets in MgO Debye patterns is now in progress.

3. Profile of Kikuchi band

Similar relativistic effects may appear variously in electron diffraction phenomena relating to Fourier potential V_h ($h \neq 0$), not only in refraction multiplets. However, the change of the intensity profile of Kikuchi bands with the electron energy is here discsssed as an example.

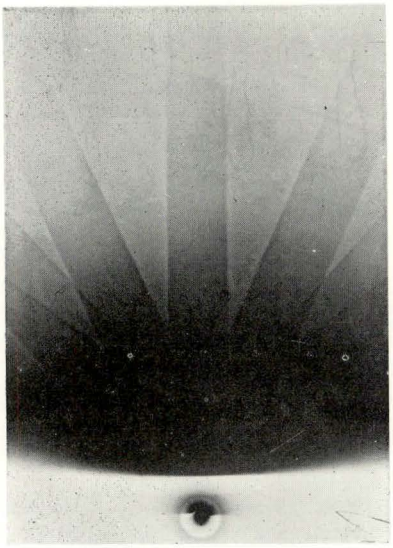

Fig. 6. Kikuchi bands from a rock-salt surface. Vertical one the (220)-band.

As was theoretically derived by Laue[12] and Kainuma[13], the intensity profile of the symmetrical Kikuchi band (Fig. 6) at its edges is given by

$$I \sim \frac{W}{1+W^2},$$

where W is a parameter indicating the deviation from Bragg condition of diffracted wave, and is given, after the relativistic correction, by

$$W=\theta\cdot\Delta\theta\cdot\left(V_h\cdot\frac{m_0e\lambda^2}{h^2}\right)^{-1}\cdot\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{-\frac{1}{2}}, \quad (9)$$

with sufficient accuracy, where θ is the Bragg angle. The valley and peak of the profile correspond $W=1$ and -1, respectively (Fig. 7a and b). The breadth of the band b, and the distance $2a$ between valley and peak change almost proportionally to each other with the change of electron energy, but the breadth $2a$ depends on the scattering factor, and accordingly, is subject to the relativistic effect.

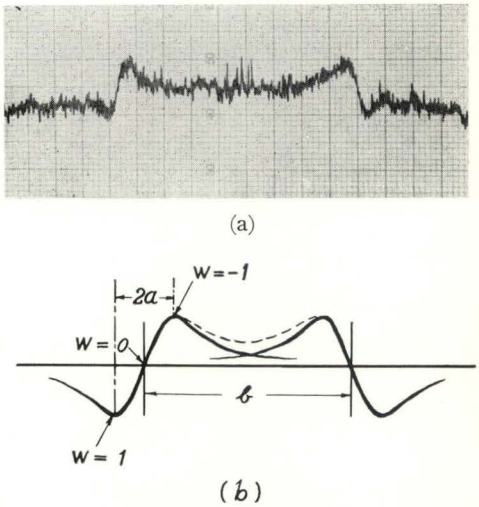

Fig. 7. (a) Photometry curve accross a part of the (220)-band (117 kV), (b) Schematic diagram of the profile of Kikuchi band.

The ratio $P \equiv a/b$ for a certain value of electron energy is thus given by

$$P(E)=\left(\frac{a}{b}\right)_E=d^2\left(\frac{2m_0e}{h^2}\right)V_h\left(1+\frac{h^2}{m_0^2c^2\lambda^2}\right)^{\frac{1}{2}}, \quad (10)$$

where d is the spacing of the net plane concerned.

Our observation on the (220) Kikuchi band in patterns from a cleavage face (001) of rock salt with the incident electrons parallel to [$\bar{1}$10] gave the result

$$P(265\text{kV})/P(117\text{kV})=1.18$$

This value may be compared with the theoretical value 1.23.

4. Remark on Honjo & Kitamura's method of eliminating the primary extinction effect

G. Honjo and N. Kitamura[14] proposed previously a method of obtaining the kinematical values of reflexions by extrapolation of the intensities observed at various wavelengths λ to the limit $\lambda=0$. Their method was based on the theory of primary extinc-

tion, according to which the observed value of the intensity I_h can be approximately given by

$$I_h = K \cdot \exp\left(-\frac{1}{3}A^2\right) \cdot |V_h|^2,$$
$$A = \lambda |V_h| \cdot D \cdot \left(\frac{2\pi m_0 e}{h^2}\right), \qquad (11)$$

where D is the effective crystal thickness and K a conventional factor. Thus, the logarithm of the relative intensity, after the relativistic correction, is expressed as

$$\log\frac{I_h}{I_{h'}} = 2\log\frac{|V_h|}{|V_{h'}|} - \frac{1}{3}\left(\lambda^2 + \frac{h^2}{m_0^2c^2}\right) \cdot (|V_h|^2 - |V_{h'}|^2) \cdot D^2 \cdot \left(\frac{2\pi m_0 e}{h^2}\right) + C. \qquad (12)$$

Since the term C is indepencent of λ, the relative value $|V_h|/|V_{h'}|$ is given at the virtual limit $\lambda^2+(h^2/m_0^2c^2)=0$, but not at the limit $\lambda^2=0$ as was previously proposed. Applications of the revised method are being published in another paper by S. M., K. F., G. H. and N. K.[15], and in a paper by N.K.[16]

5. Relativistic effect on contrasts in electronmicroscopic images

The relativistic factor due to the correction of electron mass should be taken into account not only for elastic but for inelastic scatterings. Since the contrasts in electronmicrographs may result both from elastic and inelastic scatterings of electrons, the relativistic effect should never be disregarded in consideration of the image contrasts, especially in view of the recent trend of electronmicroscopy applying very high accelerating potential of electrons, sometimes as high as 1000 kV.

The influence of the relativistic effect on the image contrasts will appear variously according to kinds of substances, thicknesses of samples, and electron energy. Qualitatively speaking, however, it may be pointed out that the decrease of the contrast in a sample image with the increasing energy of electrons will be less appreciable than expected from non-relativistic consideration. Further, relativistic consideration of the imaginary part of Yoshioka's term should be very important in interpreting the phenomena of anomalous transmission and absorption, or the Borrmann effect for electron waves, at high electron energies.

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DISCUSSION

Y. KAINUMA: In connection with Miyake, Fujiwara and Suzuki's experiment, I should like to point out a possibility of applying their result to evaluate imaginary part of the apparent mean inner potential.

We can prove that there exists a general relation between C^r_{gh} and C^i_{hg} which, respectively, are real and imaginary parts of Yoshioka's additional terms to Fourier coefficient of potential V_{g-h}. The relation is a dispersion relation of Kronig-Kramers type as follows:

$$C^r_{gh}(k_z) = -\frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{k_z' C^i_{gh}(k_z')}{(k_z')^2-(k_z)^2}\,dk_z' \qquad (1)$$

$$C^i_{gh}(k_z) = -\frac{2}{\pi}k_z\mathrm{P}\int_0^\infty \frac{C^r_{gh}(k_z')}{(k_z')^2-(k_z)^2}\,dk_z' \qquad (2)$$

where k_z is the normal component of $\boldsymbol{k}_0$ and P before integrals denotes Cauchy's principal value of the integrals. The equations (1) and (2) show that if C_{gh}^r is known as a function of k_z, C_{gh}^i can be calculated for any value of k_z, and *vice versa*. This relation holds irrespective of the kinds of damping processes of electron waves in crystals, including those due to inelastic scatterings exciting thermal vibrations or electronic transitions as well as elastic scattering exciting weak reflections.

This relation holds for C_{gh} even when the integrand of $A(\boldsymbol{r}, \boldsymbol{r}')$ in the equation

$$C_{gh}=\frac{1}{V}\int_V\int_V A(\boldsymbol{r}, \boldsymbol{r}')\exp\{-i(\boldsymbol{k}_g\cdot\boldsymbol{r})+i(\boldsymbol{k}_h\cdot\boldsymbol{r}')\}d\boldsymbol{r}d\boldsymbol{r}' \qquad (3)$$

includes terms due to multiple virtual transitions or multiple weak reflections so that it takes the following form

$$A(\boldsymbol{r}, \boldsymbol{r}')=A_1(\boldsymbol{r}, \boldsymbol{r}')+A_2(\boldsymbol{r}, \boldsymbol{r}')+A_3(\boldsymbol{r}, \boldsymbol{r}')+\cdots \qquad (4)$$

where A_1 is a term due to single virtual transitions or single weak reflections, and so on. Detail of my theory and its application using the experimental data, many of which are reported in this Symposium, will be published elsewhere.

K. Molière: I should like to mention that in the measurements of structure potential we always observed an influence of the current density and the decharger current on the apparent value of the mean inner potential, in agreement with an unpublished observation of some years ago in the Laboratory of Prof. Blackman.

S. Miyake: It is to be mentioned that our study was performed by using powder samples and by applying very high potential, and, at least, there took place no experimental trouble by the charging. The fluctuation of the obtained value might be due to the effect of charging. But I don't know at present whether this effect is actually present or not in our experiment.

R. Uyeda: I'd like to point out two facts related to Yoshioka's real terms. The first point which was told me by Yoshioka, Fujimoto and Kainuma is as follows: In the original paper of Yoshioka, the thickness of crystal was assumed to be infinitely thick. Exactly speaking, however, Yoshioka's terms are functions of thickness.

Second point is related to an experiment of Lenz and Scheffels. They observed that the mean inner potential changes when a specimen is irradiated by a strong electron beam. This is caused by the ionization in the specimen. This effect cannot be explained by Yoshioka's theory, probably because his theory treats with one electron falling on the crystal. The effect might be explained if we assume many electrons falling on the specimen at the same time. Then the generalized Yoshioka's terms might become a function of the current density of incident beam as well as of the wave vector of incident beam and of the thickness of the specimen.

S. Miyake: As to the first point, I admit that Yoshioka's term, or the dispersion term, may depend on the crystal size. But I suppose that each refraction multiplet observed in our study comes from a particle of rather large crystal-size, say larger than 1000Å, therefore the effect of crystal size would not be appreciable.

As to the second point, I must mention at first the difference in experimental condition that the study of Lenz and Scheffels' experiment was made on amorphous carbon, while each of the refraction multiplets observed in our study comes from a single crystal particle. Furthermore, it is conceived that the electron current density in our experiment is much less than that appropriate for electron microscopy. Incidentally, in view of the sharpness of each spot in a multiplet, it is plausible that the damage of the crystal lattice did not take place appreciably so far as our observation is concerned.