THE X-RAY SCATTERING POWERS OF NICKEL AND OXYGEN IN NICKEL OXIDE

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Abstract

Atomic F-curves for the nickel and oxygen atoms in NiO have been obtained from measurements of the intensities of the principal powder reflections of molybdenum, copper and nickel $K\alpha$ radiations. Though the scattering power of oxygen remains nearly constant with respect to NaCl for these wave-lengths, that of nickel shows important variations.

THIS paper forms part of a series of studies of the dependence of the diffracting power of an atom upon the wave-length of the x-rays being scattered. Accurate measurement[1] has shown that with wave-lengths as near together as the $K\alpha$ lines of molybdenum and rhodium the F-values of NaCl are equal for the same $\sin\ \theta/\lambda$. There is likewise some indication[2] that the atoms in this crystal do not have very different scattering powers for copper radiation. Recent comparisons of NaCl and metallic silicon[3] prove that the ratio of their diffracting powers is nearly the same for molybdenum and for copper $K\alpha$ x-rays. All of these observations are with radiations far removed in frequency from any critical values for the diffracting atoms.

Such a parallelism as that prevailing between NaCl and silicon no longer seems to hold if the comparisons involve metallic copper and iron reflecting molybdenum and copper rays. The experiments already made[4] with these metals indicate that their scattering powers decrease more rapidly with increasing wave-length than do those of the atoms of NaCl. This conclusion is dependent upon the essential correctness of measured absorption coefficients.

Observations upon NiO avoid such an uncertainty by containing within themselves a comparison of the scattering powers of two atoms—nickel and oxygen. These data consist of determinations of the F-curves of nickel and oxygen using molybdenum, copper and nickel $K\alpha$ radiation. The measurements upon which they are based are spectrometer studies of the intensities of the principal x-ray reflections of powdered NiO. The methods used in obtaining these intensities[5] and reducing them to atomic scattering powers have been described.

[1] R. W. James and E. M. Firth, Proc. Roy. Soc. **117A,** 62 (1927).

[2] E. Wagner and H. Kulenkampff, Ann. d. Physik **68,** 369 (1922).

[3] R. W. G. Wyckoff, Zeit. f. Krist. in press (1930).

[4] A. H. Armstrong, Phys. Rev. **34,** 931 (1929).

[5] A. H. Compton, X-rays and Electrons (New York, 1926) Chap. V; R. W. G. Wyckoff and A. H. Armstrong, Zeit. f. Krist. **72,** 319 (1929).

Two different samples of chemically pure green NiO gave results which were identical within the limit of experimental error. In order to suppress the effects of extinction both crystal powders were ground thoroughly in an agate mortar and passed through a 325 mesh per linear inch sieve before being formed into a cake.

Molybdenum radiation was obtained from a water-cooled General Electric tube operated from a synchronous motor-generator-kenetron-condenser

TABLE I. *The relative intensities of powder reflections of nickel oxide.*

Indices	Intensities for $K\alpha$ wave-length of Molybdenum	Copper	Nickel
111	111.8	112.4	129.7
200	159.4	196.1	207.3
220	[100]	[100]	[100]
113	48.9	36.4	42.2
222	29.1	26.4	28.3
400	13.4	10.7	—
133	19.1	—	—
240	28.8	—	—
224	20.5	—	—
333,115	12.5	—	—

set at 30 kv with a current consumption of 5 or 10 ma. The copper and nickel radiations were supplied by Siemens-Phoenix tubes passing 6 ma at 25 kv. The molybdenum rays were rendered essentially monochromatic with a ZrO_2 screen. No attempt was made to filter the x-rays emitted by the copper and nickel target tubes but calculation showed that with the resolution used none of the measured $K\alpha$ spectra was contaminated by other reflections.

TABLE II. *The F-values of powder reflections of nickel oxide.*

Indices	$\sin\theta/\lambda$	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
111	0.2076	14.13	11.41	13.01
200	.2398	22.60	20.56	22.52
220	.3391	18.28	15.83	16.88
113	.3976	10.76	8.13	9.16
222	.4153	15.12	12.52	13.43
400	.4796	13.65	10.12	—
133	.5223	9.22	—	—
240	.5359	11.65	—	—
224	.5871	10.96	—	—
333,115	.6229	7.96	—	—

The crystal structure of NiO is identical with that of NaCl. Reflections with odd indices therefore represent differences between the contributions of nickel and oxygen atoms, those with even indices (all even order spectra) are due to the cooperation of these two atoms. The relative intensities of the observed reflections for Ni $K\alpha$, Cu $K\alpha$ and Mo $K\alpha$ rays are shown in Table I.

The absolute F-values for molybdenum radiation have been found by comparing the (200) reflection of NiO with (220) of NaCl. A mean of several determinations using both samples of NiO gave (200)NiO:(220)NaCl = 49.6:100. The apparent accuracy of this ratio is better than 5 percent. The mass obsorption coefficient of NiO according to the experiments of Windgardh[6] is $\mu/\rho = 37.93$. If Allen's[7] value for nickel is used, μ/ρ becomes 37.21. The absorption coefficient of NaCl as provided by Windgardh's data is $\mu = 18.21$ ($\rho = 2.16$). Of the other quantities[8] needed to calculate absolute F's, ρ has been taken as 6.75, $a_0(\text{NiO}) = 4.17A$, $a_0(\text{NaCl}) = 5.628A$, $F(220, \text{NaCl}) = 15.62$. Introduction of these values into the customary expressions leads to the reflection F's recorded in Table II and Fig. 1. Points on the smooth F-curves drawn through them, when separated by addition and subtraction into

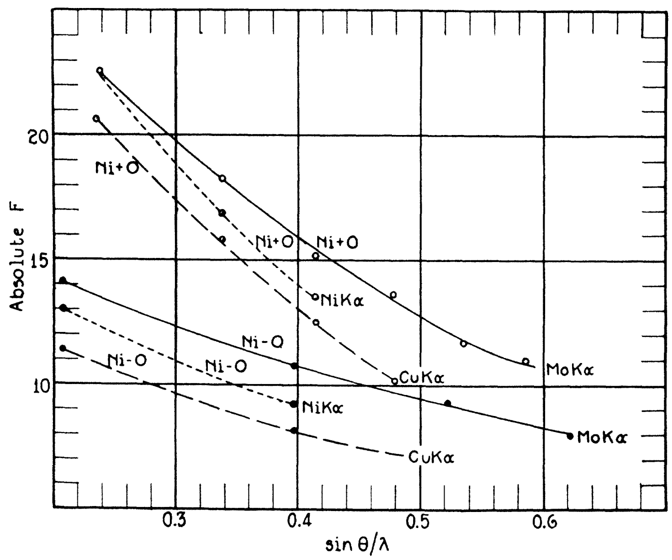

Fig. 1. The reflection F-values observed from NiO using molybdenum, copper and nickel $K\alpha$ radiations.

atomic F-values for nickel and oxygen, give the numbers listed in Tables III and IV and plotted in Fig. 2.

In order to place the F-curves for copper and nickel radiation upon an "absolute" scale for comparison with those for molybdenum x-rays, it has been assumed that $F(220, \text{NaCl}) = 15.62$ for all three radiations. The absorption coefficients for NiO as calculated by Jönsson's formula[9] are $\mu = 276.8$ for Cu $K\alpha$ and $\mu = 345.1$ for Ni $K\alpha$. They are in good agreement with existing experimental values. Absorption coefficients for NaCl obtained in the same way are $\mu = 161.2$ for Cu $K\alpha$ and $\mu = 196.2$ for Ni $K\alpha$. Measurements of the

[6] K. A. Windgardh, Zeits. f. Physik **8**, 363 (1922).
[7] S. J. M. Allen, Phys. Rev. **28**, 907 (1926).
[8] Internat. Critical Tables (New York, 1926) Vol. I p. 343; R. W. James and E. M. Firth, op. cit.
[9] E. Jönsson, Uppsala Univers. Årsskrift (1928).

relative intensities of (220) NaCl and (220) NiO have led to the ratios (220)NiO:(220)NaCl = 100:57.5 for Cu $K\alpha$ and (220)NiO:(220)NaCl = 100:51.8 for Ni $K\alpha$. The reflection F's calculated from these data are recorded

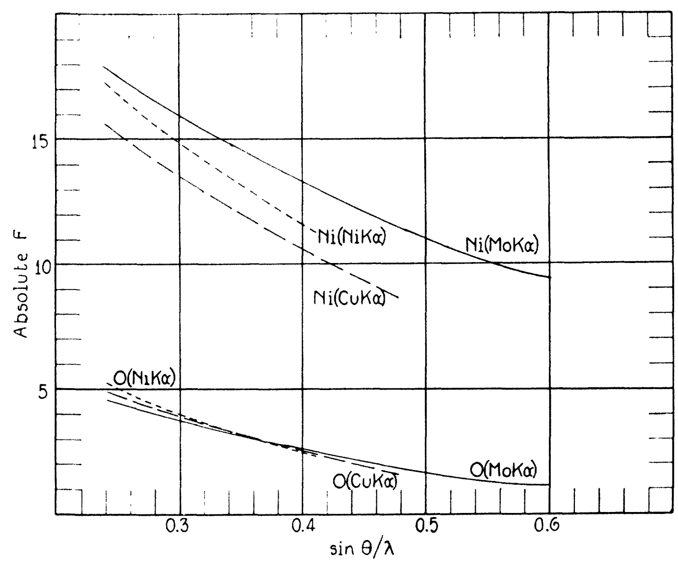

Fig. 2. The F-curves of nickel and oxygen atoms in NiO.

in Table II and plotted in Fig. 1. The atomic F's derived from them are listed in Tables III and IV and shown graphically in Fig. 2.

TABLE III. *Atomic F-values of oxygen in nickel oxide.*

sin θ/λ	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
0.240	4.55	4.87	5.23
.270	4.14	4.42	4.62
.300	3.77	3.96	4.06
.330	3.42	3.52	3.52
.360	3.05	3.10	3.05
.390	2.72	2.67	2.58
.420	2.39	2.27	2.30
.450	2.09	(1.87)	—
.480	1.81	(1.53)	—
.510	1.57	—	—
.540	1.35	—	—
.570	1.22	—	—
.600	1.15	—	—

Note: Values in parentheses in this and the following table are obtained by extrapolating the Ni-O curve of Fig. 1.

A check upon the accuracy of the measurements of this paper can be had by comparing the oxygen F-curves for Mo $K\alpha$ from NiO and[10] MgO. Though

[10] R. W. G. Wyckoff and A. H. Armstrong, Zeits. f. Krist. **72**, 433 (1930).

it is scarcely to be expected that they should be identical, these two curves ought to lie close to one another (Fig. 3).

The most significant feature of these results is the fact that though the oxygen *F*-curves are nearly identical for the three radiations—or, more accurately, vary in the same manner as does NaCl—relatively large differences exist in the curves for the nickel atoms. Since critical wave-lengths of oxygen are farther from the wave-lengths used than are those of NaCl, the observed slight increase in the oxygen *F*-curves at low angles with increasing wave-lengths is not contrary to expectation. The *F*-curves of nickel, lower for copper than for molybdenum radiation, agree with existing data upon copper[4] and iron in indicating that for atoms having critical frequencies within the experimental range, coherent scattering decreases with increasing wave-length as this critical range is approached. The greater diffraction of nickel for the nickel than for the copper $K\alpha$ line indicates that this downward trend is broken either some time before or when a wave-length characteristic of the scatterer is reached.

TABLE IV. *Atomic F-values of nickel in nickel oxide.*

$\sin \theta/\lambda$	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
0.240	17.95	15.62	17.37
.270	16.94	14.55	16.07
.300	16.03	13.57	14.87
.330	15.16	12.62	13.78
.360	14.33	11.72	12.81
.390	13.54	10.88	11.90
.420	12.79	10.04	11.37
.450	12.09	(9.25)	—
.480	11.41	(8.55)	—
.510	10.81	—	—
.540	10.25	—	—
.570	9.76	—	—
.600	9.39	—	—

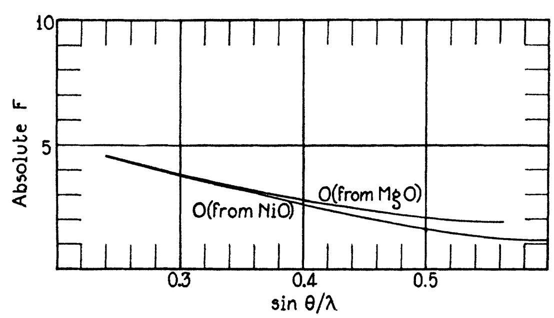

Fig. 3. A comparison of the oxygen *F*-curves for Mo $K\alpha$ rays as measured in MgO and NiO.

Further experiments are being made with various metals and with several wave-lengths which will bear upon these phenomena.