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Reconsideration of the wavelength dependence of extinction: a γ-ray case

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The wavelength dependence of extinction has been re-examined by means of new γ-ray diffraction data collected from NiF_2 at 0.0205, 0.0265 and 0.0392 Å. The standard model of extinction has been confirmed and substantiated by experimentally accessible parameters such as the intrinsic mosaic width. The predicted kinematic limit values are in accordance with the results from charge-density analyses. The model proposed by Mathieson & Stevenson [*Acta Cryst.* (2002), A**58**, 185–189] leads to a purely phenomenological polynomial fit function. The extrapolated values are shown to be inconsistent with structure analyses based on extended γ-ray data sets and cannot be recommended for use.

1. Introduction

Recently, Mathieson & Stevenson (2002), hereafter MS02, have examined the question of extrapolation to zero extinction in the γ-ray region. Seven low-order NiF_2 structure-factor squares, measured at room temperature with four different wavelengths between 0.0205 and 0.0603 Å, were taken from Palmer & Jauch (1995), hereafter PJ95. The data were fitted by a polynomial up to second order in λ, $F_o^2 = F_{\rm kin}^2 - \alpha\lambda + \beta\lambda^2$. Here, F_o^2 and $F_{\rm kin}^2$ denote the observed and kinematic values, respectively. The quadratic term was significant only for two reflections. For the remaining five reflections, only the linear term was used. This extrapolation procedure leads to higher limit values than those of PJ95. According to Mathieson & Stevenson, 'it is difficult to avoid the conclusion that MS02 corresponds to a more straightforward procedure with clearly defined end points'. Structural parameters, estimated from photometry of an *hk*0 Weissenberg photograph (Baur, 1958; Baur & Khan, 1971), lead to higher independent spherical-atom model structure factors than the limit values of PJ95, which has been considered by MS02 as a further support of the plotting procedure. According to MS02, their extrapolated values 'more reliably establish the true kinematical limit values for NiF_2'.

The purpose of this note is to present an assessment and critical discussion of MS02 by means of an examination of additional γ-ray diffraction data. The predicted limit values will be compared with results from modern high-precision work.

2. Standard model of extinction

According to the standard model of secondary extinction (Zachariasen, 1967; Becker & Coppens, 1974), for small Bragg angles and moderate deviation from kinematic conditions the wavelength dependence may be approximated by $F_o^2 = F_{\rm kin}^2(1 - k\lambda^2)$. It is important to note that this relationship does not represent just another fitting scheme but that the model parameters can be tested independently by measuring the physical parameters that describe the degree of crystal perfection. The slope parameter is given as $k = gTd(F_{\rm kin}/V)^2$ for high-energy diffraction from a mosaic crystal with a Gaussian tilt-angle distribution (g = 0.6643/FWHM [rad], T: absorption-weighted mean path length of diffracted beam, d: interplanar spacing, V: unit-cell volume, $F_{\rm kin}$: structure factor in units of scattering length). The mosaic spread derived from the slope can thus be compared with the intrinsic reflection profiles recorded by high-resolution γ-ray diffraction, for example. Mosaicities close to the observed ones have been obtained in PJ95. It is also important to note in this connection that the linear relationship between F_o^2 and λ^2 applies only for the case of sufficiently weak extinction. Considerable deviations from linearity have been observed in PJ95 despite the use of high-energy photons between 200 and 600 keV.

The standard model has a simple but important mathematical consequence. The rate of change of F_o^2 with respect to λ, $dF_o^2/d\lambda$, must vanish for λ = 0. No matter how severe the extinction conditions are at finite wavelength, the zero-interaction limit is approached with negative curvature in a universal manner independent of the individual reflection and the sample properties. This implied prediction should be contrasted with MS02 where even positive curvatures may occur, which correspond to an accelerated change in the level of extinction close to the extrapolated value.

3. Examination of additional data

Wavelength-dependent measurements of 14 structure factors from NiF_2 at room temperature and 15 K have been performed during the course of a charge-density investigation (Palmer & Jauch, 1993, hereafter PJ93). Since the data have remained unpublished so far, it seems to be of interest to

Table 1
Scaled values of F_o^2 and their associated standard deviations at the three different wavelengths.

The first entry refers to room temperature, the second one to 15 K.

λ (Å)	101	211	121	$\bar{2}20$	220	002	301
0.0205	1167 (39)	1815 (48)	1805 (48)	2129 (57)	2105 (57)	2558 (69)	2026 (57)
	1171 (46)	1830 (43)	1837 (43)	2198 (49)	2174 (47)	2625 (55)	2152 (48)
0.0265	1134 (11)	1763 (17)	1758 (17)	2028 (20)	1954 (19)	2407 (24)	1971 (19)
	1183 (14)	1803 (18)	1803 (18)	2159 (21)	2102 (21)	2406 (24)	2079 (21)
0.0392	1054 (11)	1661 (17)	1662 (17)	1821 (18)	1786 (18)	2081 (21)	1862 (19)
	1067 (11)	1706 (17)	1694 (17)	1898 (19)	1815 (18)	2013 (20)	1974 (20)

Table 2
Comparison of the limit values of F^2 obtained by extrapolation from the data given in Table 1.

Except for the entries under MS02, linearity of F_o^2 with respect to λ^2 is assumed. The calculated values are derived from multipole model refinements of extended data sets (PJ93). The limit values for the PJ95 data are deduced from the three shortest wavelengths (for 002, an error in the scale factor has been corrected). The first entry refers to room temperature, the second one to 15 K.

hkl	F^2 (λ = 0)	PJ93 F_c^2	MS02 F^2 (λ = 0)	PJ95 F^2 (λ = 0)
101	1202 (21)	1211	1299 (38)	
	1267 (26)	1254	1399 (45)	
211	1854 (32)	1789	1978 (58)	
	1883 (31)	1859	1994 (56)	
121	1843 (32)	1789	1959 (58)	1766 (26)
	1894 (31)	1859	2019 (56)	
$\bar{2}20$	2211 (36)	2206	2462 (64)	2217 (26)
	2361 (36)	2362	2646 (64)	
220	2121 (36)	2206	2341 (64)	2116 (24)
	2334 (36)	2362	2655 (63)	
002	2690 (39)	2724	3086 (71)	2728 (30)
	2767 (40)	2826	3248 (70)	
301	2068 (36)	2003	2200 (65)	1957 (23)
	2182 (36)	2162	2315 (65)	

reconsider them in the present context. Three wavelengths were used: 0.0205, 0.0265 and 0.0392 Å. The crystal was the same as in PJ95 ($330/\bar{3}30$ have not been measured since they are barely extinction affected for the shortest γ-ray wavelengths). For the scaling of energy-dependent factors, such as detector efficiency and absorption, the integrated intensities of three higher-order reflections have been used. Their absolute structure factors are known from the highly accurate standard structural parameters. The final absolute scale was obtained by combining the extrapolated data with the extended data sets at λ = 0.0392 Å (284 and 253 additional independent reflections at room temperature and 15 K, respectively, with the smallest extinction factor on F^2 being y = 0.9). The final scale differed by 10.6% from the preliminary one. The scaled values of F_o^2 for a representative selection at the three different wavelengths are listed in Table 1.

The experimental data have been extrapolated assuming either (i) linearity with respect to λ^2 (standard model) or (ii) linearity with respect to λ (MS02). The corresponding limit values are presented in Table 2. Also shown in Table 2 are the calculated (extinction-free) values, F_c^2, as obtained from multipole model refinements with the program system *VALRAY* (Stewart & Spackman, 1983) where only reflections with $y \geq 0.9$ had to be corrected for extinction. Fixing the extinction parameter g to the observed average mosaicity had no statistically significant effect on the other parameters. Finally, limit values of the standard model for the available PJ95 data, based on the three shortest wavelengths, are also shown in Table 2 (for 002, an error in the scale factor has been corrected). For simple extrapolation to be justified, the wavelength range has to meet two conditions: (i) it has to be large enough to define the curve sufficiently near the point λ = 0; and (ii) it has to be close enough to that point, *i.e.* the case of weak extinction should be realized. It is the longer wavelength of 0.0603 Å in PJ95 that gives rise to the non-linear dependence $F^2(\lambda^2)$ observed for the strongest reflections.

4. Discussion

Some of the results are illustrated in Fig. 1. As can be seen, both straight-line models match the data equally well. The limit values, however, which are the basic reason for the extrapolation differ considerably. As noted above, the values derived from the MS02 scheme are always the higher ones. Which model is the appropriate one can be judged by the compatibility of the best-fit parameters with other available evidence such as the electron-density distribution and the mosaic width of the sample.

The results from Table 2 may be conveniently summarized by R factors. For the standard model, $R(F^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2 = 0.015$ and $R(\sigma) = \sum\sigma(F_o^2)/\sum F_o^2 =$ 0.016. The residuals are thus compatible with the experimental standard deviations. The slopes have been converted into mosaicities. The values are in the range from 14 to 19″ (FWHM), which is in satisfactory agreement with the experimental rocking-curve widths. R factors of similar quality are obtained for the PJ95 data: $R(F^2)$ = 0.016 and $R(\sigma)$ = 0.012.

Extrapolation according to MS02 leads to limit values that are not reconcilable with the F_c^2 values derived from the extended data sets: $R(F^2)$ = 0.095 and $R(\sigma)$ = 0.026. It is obvious that the fitting procedure is inappropriate to extract reliable structure factors.

NiF_2 has also been investigated by pulsed neutron diffraction employing the time-resolved Laue technique with a wavelength band of 0.4 to 2.4 Å (Jauch *et al.*, 1993). The use of such a broad bandpass implies large wavelength variations of extinction effects. Since the same crystal as in the γ-ray studies was used, the level of extinction was rather severe. Yet close agreement was obtained between the observed and refined mosaicities as well as in the structural parameters derived from the two complementary diffraction methods. The refinements were of course based on the general expressions of the standard model and not on the approximation suitable in the γ-ray regime. The range of applicability of the standard model is therefore much broader than often assumed.

Finally, the discussion of the $220/\bar{2}20$ pair as given in MS02 deserves two comments. Firstly, MS02 attribute the different wavelength dependencies to differences in crystallite distortions and recommend further investigations to clarify the question of internal morphology. However, the mosaic widths have been measured, and are reported in PJ95 to amount to 23 and 22″ (FWHM), *i.e.* they are virtually identical. The different behaviour of the symmetry-equivalent pair is due to rather different mean path lengths through the crystal. Secondly, according to MS02, the $hh0$ and $\bar{h}h0$ structure factors should have slightly different magnitudes owing to a term in the temperature factor. The temperature-factor components of F, $T_j(hkl) = \exp[-2\pi^2\langle(U_j/d_{hkl})^2\rangle]$, depend on the mean-square atomic displacement in the direction perpendicular to the reflecting plane, given as a fraction of the interplanar distance. Hence, $T_j(hh0) = T_j(\bar{h}h0)$ for the rutile structure (see also Table 2).

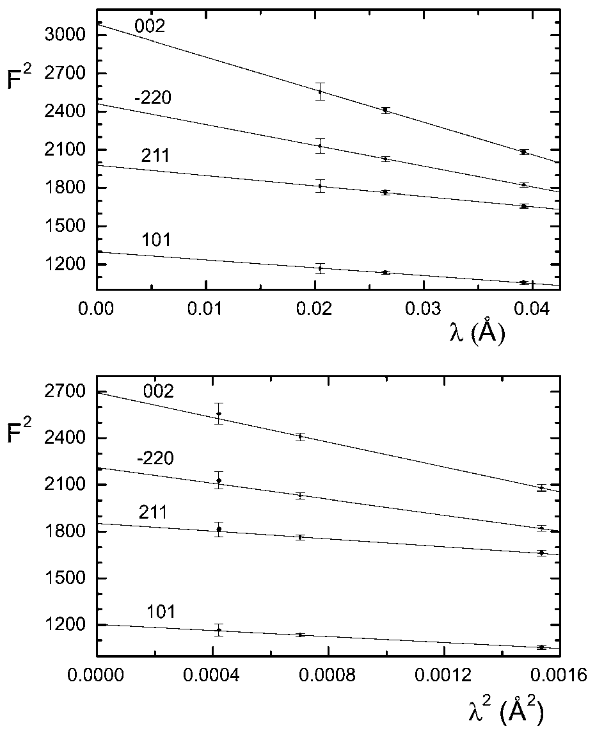

Figure 1
(*a*) Plots of structure-factor squares (room temperature) against λ with $F_o^2 = F_{\rm kin}^2 - \alpha\lambda$ fitted to the data points. (*b*) The same experimental values with $F_o^2 = F_{\rm kin}^2(1 - k\lambda^2)$ fitted to the data points.

5. Conclusions

The wavelength dependence of secondary extinction has been re-examined on the basis of γ-ray diffraction data. The predictions from the standard model have been firmly established by experimentally accessible parameters such as the intrinsic mosaic width as well as by comparison with accurate structure factors from multipole refinements. Reliable limit values, $F^2(\lambda = 0)$, cannot be obtained by simple trend curves against λ as advocated by MS02.

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