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STRUCTURE REFINEMENT OF GICS USING 00L REFLECTIONS AND APPLYING THE NEW LORENTZ FACTOR

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Abstract The large mosaic spread of GICs has to be taken into account if structural information is extracted from structure refinements or Fourier syntheses. The application of the new Lorentz factor, an additional geometrical correction, leads to significantly improved structural parameters compared to results obtained from common evaluation procedures.

INTRODUCTION

In order to obtain entire information about the structure of the intercalate layer in GICs it is necessary to work with graphite flakes rather than with HOPG. A disadvantage one has to deal with is the great mosaic spread of the GICs received from flakes. The resulting wide rocking curve of 00L reflections leads to a loss of intensity depending on the detector aperture. Using the integrated intensities to calculate structural parameters large errors must be expected. This defective intensity measurement can be taken into account by a further geometrical correction, the new Lorentz factor.[1,2] This factor, depending on the spectral distribution, the crystal and focus divergence functions, the mosaic spread, and the detector aperture, is calculated by a multi-dimensional numerical convolution procedure.

For this work 00L intensities of $FeCl_3$ GIC stage 1 and $InCl_3$ GIC stage 1 and 2 were measured with a four circle X-ray diffractometer. Structural informations were obtained as well from structure refinement with a least-squares algorithm as from one dimensional Fourier synthesis. From the comparison of computed parameters with earlier results obtained by EXAFS measurements[3] the occured error of the refinement resulting from neglection of the mentioned intensity loss could be estimated. Also the significant improvement by application of the new Lorentz factor could be shown.

EXPERIMENTAL

The $InCl_3$ GICs, stage 2, were prepared in sealed glas ampoules at a temperature of 480 °C containing 1 bar chlorine during a reaction time of 21 d. For the stage 1 compound 10 bar chlorine and 6 d were taken. The $FeCl_3$ GIC was prepared at 300 °C over 6 days without added chlorine.
The XRD measurements were carried out with a four circle diffractometer using filtered Cu-K_α radiation for the $InCl_3$ GICs and Mo-K_α for the $FeCl_3$ GIC.

RESULTS

Structure Refinement

Due to the preparation conditions, which ensure saturation with intercalate, stage disorder can be excluded for the $FeCl_3$ GIC. The 00L intensities of $InCl_3$ GICs were measured with a slight degree of stage disorder (stage number less than 2.0). The deviations of the extracted structural parameters are in good accordance with the theoretical results from stage disorder simulation.[4]

The measured and the calculated 00L intensities are contained in the Tables 1, 2 and 3. The calculated intensities were obtained from a structural model, which was refined with the measured integrated intensities. In all cases the model consists of two chloride layers with the distance ±z(Cl) from the central metal atom layer, a graphene layer at the distance of $c_1/2$ from the metal (c_1 : repeat distance of the stage 1 compound), and a further graphene layer with a distance of 335 pm from the first one for the stage 2 compounds. The refined structural parameters were the distance z(Cl), two additional stoichiometric factors for the metal and the graphene layers Δv(Me) and Δv(C), and an over all Debye-Waller factor. The formulas of the GICs to be refined were

$FeCl_3$ GIC stage 1 : $C_{4.05 + \Delta v(C)}\ Fe_{0.67 + \Delta v(Fe)}\ Cl_2$
$InCl_3$ GIC stage 1 : $C_{4.66 + \Delta v(C)}\ In_{0.67 + \Delta v(In)}\ Cl_2$
$InCl_3$ GIC stage 2 : $C_{9.32 + \Delta v(C)}\ In_{0.67 + \Delta v(In)}\ Cl_2$

The calculated intensities I(calc) in the Tables were corrected with the common single crystal Lorentz factor, the Polarisation factor, and an absorption factor especially for GICs. The inten-

sities I_T(calc) were obtained by applying the new Lorentz factor, expressed by the T value.[1] Table 4 contains the refined structural parameters for the different GICs in each case with and without applying the new Lorentz factor.

TABLE 1 Measured and calculated integrated intensities of the $FeCl_3$ GIC stage 1. I is the calculated intensity obtained in the common way. I_T results from applying the new Lorentz factor (FWHM of the rocking curve was 9°).

00L	001	002	003	004	005	006	007	008
I(obs) [a.u.]	73.64	155.83	38.87	13.69	0.90	23.05	3.48	3.42
I(calc) [a.u.]	73.62	156.03	38.76	13.32	1.60	23.50	3.06	1.57
I_T(calc) [a.u.]	72.85	156.46	38.29	12.34	1.23	23.67	3.18	2.44
T	0.829	0.521	0.365	0.279	0.225	0.189	0.162	0.142

TABLE 2 Measured and calculated integrated intensities of the $InCl_3$ GICs with stage number S=1.98 and S=1.97. I is the calculated intensity obtained in the common way. I_T results from applying the new Lorentz factor (FWHM of the rocking curve was 6°).

00L	stage-number	001	002	003	004	005	006
I(obs) [a.u.]	1.98	112.25	188.89	221.57	183.05	34.41	16.78
I(calc) [a.u.]		124.04	165.17	234.47	181.47	22.56	16.12
I_T(calc) [a.u.]		116.76	157.41	234.61	181.56	25.58	17.62
T		0.851	0.534	0.380	0.291	0.236	0.198
00L	stage-number	007	008	009	00.10	00.11	00.12
I(obs) [a.u.]	1.98	--	120.49	9.60	10.17	23.15	--
I(calc) [a.u.]		2.27	118.27	23.82	12.93	13.00	0.11
I_T(calc) [a.u.]		1.71	119.30	20.90	11.98	18.81	0.37
T		0.170	0.150	0.133	0.120	0.109	0.908
00L	stage-number	001	002	003	004	005	006
I(obs) [a.u.]	1.97	63.09	80.03	190.33	190.35	11.41	5.89
I(calc) [a.u.]		50.63	96.91	182.15	192.67	20.61	14.57
I_T(calc) [a.u.]		21.07	79.14	183.60	195.27	24.54	16.17
T		0.793	0.483	0.340	0.260	0.210	0.176
00L	stage-number	007	008	009	00.10	00.11	00.12
I(obs) [a.u.]	1.97	--	125.43	2.93	2.46	6.28	--
I(calc) [a.u.]		0.98	119.52	19.97	10.60	13.56	1.13
I_T(calc) [a.u.]		0.42	120.88	15.29	8.05	19.39	6.50
T		0.151	0.133	0.118	0.106	0.097	0.089

TABLE 3 Measured and calculated integrated intensities of the $InCl_3$ GIC stage 1. I is the calculated intensity obtained in the common way. I_T results from applying the new Lorentz factor (FWHM of the rocking curve was 5°).

00L	001	002	003	004	005	006	007
I(obs) [a.u.]	373.40	792.70	447.65	16.50	3.18	171.70	22.25
I(calc) [a.u.]	372.71	793.11	447.29	11.08	3.62	171.28	36.08
I_T(calc) [a.u.]	363.88	793.97	447.65	15.96	2.41	170.21	33.15
T	0.921	0.524	0.377	0.291	0.236	0.198	0.171
00L	008	009	00.10	00.11	00.12	00.13	00.14
I(obs) [a.u.]	41.65	--	--	1.83	2.94	--	3.12
I(calc) [a.u.]	31.09	0.0074	0.022	0.25	0.030	0.0066	0.017
I_T(calc) [a.u.]	38.68	0.270	0.024	1.13	0.49	0.14	0.49
T	0.150	0.134	0.121	0.110	0.101	0.093	0.086

TABLE 4 Structural parameter of the $FeCl_3$ GIC stage 1, $InCl_3$ GIC stage 1, and $InCl_3$ GICs with stage number S=1.97 and S=1.98. R_B denotes the residual of the least-squares refinement.

compound	z(Cl) [pm]	Δu(C)	Δu(Me)	Debye-Waller factor [pm²]	R_B [%]
$FeCl_3$ GIC stage 1 without correction T	132.25 ± 0.18	-0.213 ± 0.003	0.046 ± 0.002	91339 ± 573	2.11
$FeCl_3$ GIC stage 1 with correction T	135.08 ± 0.03	0.010 ± 0.001	0.022 ± 0.0005	44061 ± 82	3.83
$InCl_3$ GIC stage 1 without correction T	142.82 ± 0.75	-0.248 ± 0.012	-0.139 ± 0.006	116455 ± 334	1.40
$InCl_3$ GIC stage 1 with correction T	144.91 ± 0.27	-0.068 ± 0.006	-0.148 ± 0.002	59746 ± 168	3.28
$InCl_3$ GIC S=1.98 without correction T	142.80 ± 0.32	-0.476 ± 0.004	-0.143 ± 0.002	67558 ± 621	10.23
$InCl_3$ GIC S=1.98 with correction T	147.09 ± 0.05	-0.202 ± 0.002	-0.140 ± 0.0005	11422 ± 100	9.77
$InCl_3$ GIC S=1.97 without correction T	145.37 ± 0.41	-0.284 ± 0.007	-0.182 ± 0.003	54176 ± 567	9.36
$InCl_3$ GIC S=1.97 with correction T	150.35 ± 0.11	0.085 ± 0.006	-0.186 ± 0.001	-2615 ± 61	11.74

From EXAFS measurements[3] a z(Cl) value of 135 pm for the $FeCl_3$ GIC stage 1 was found. This distance corresponds to the value determined for pristine $FeCl_3$.[5] Furthermore, the in-plane lattice of the intercalate layer could be determined by the monochromatic Laue technique with good precision. In comparison to these results the structural parameters obtained from the refinement without considering the large mosaic spread show a significant deviation. For the distance z(Cl) an error of about 2.5% occured, the additional stoichiometric factor for the graphene layer even shows an error of about 5%. When the large mosaic spread was taken into account by the new Lorentz factor the structure refinement led to the expected structural parameters (z(Cl)=135.1pm, only slight deviation in the Δu values). Due to the strong correlation between z(Cl) and the Debye-Waller factor, the latter turned out to be almost two times higher if the new Lorentz factor was not applied.

In case of the $InCl_3$ GICs the exact structure parameters are not yet available. Again we assume the results obtained for the first stage to be quite exact because of the obviously missing presence of stage disorder. In contrast to the stage 1 compound both the deviation caused by the mosaic spread and the influence of stage disorder has to be considered for the $InCl_3$ GICs (S=1.97 and S=1.98). The occured errors (increasing z(Cl), decreasing Debye-Waller factors) are in good accordance with the results obtained from stage disorder simulation.[4] Although stage disorder and the large mosaic spread lead to contrasting effects, especially in case of the distance z(Cl) and the Debye-Waller factor, the increased residual (R_B) indicates a defective structure refinement.

One dimensional Fourier synthesis

Another common way to obtain structural information aside from structure refinement is the Fourier synthesis. In order to calculate a one dimensional Fourier synthesis with measured 00L intensities a model structure has to be assumed. In this case the missing phase information of the observed structure amplitudes can be taken from the theoretical structure factors. Figure 1 and 2 show the one dimensional Fourier syntheses of $FeCl_3$ GIC stage 1 and $InCl_3$ GIC stage 2. The Fourier coefficients were extracted from the measured intensities (Table 1 and 3), the signs (phases) of the coefficients were computed with the centrosymmetrical model mentioned above.

Corresponding to the structure refinement, the distance z(Cl)

extracted from the Fourier synthesis turned out to be improved when the new Lorentz factor had been applied to the structure factor computation. For the $FeCl_3$ GIC stage 1, for example, a distance of z(CL)=133 pm was found with the common single crystal correction factors, whereas 135.7 pm were extracted from a fourier synthesis calculated with T corrected structure factors.

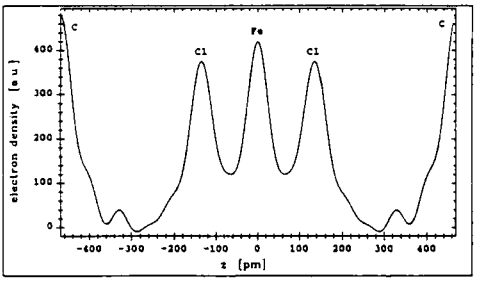

FIGURE 1 One dimensional Fourier synthesis for $FeCl_3$ GIC stage 1.

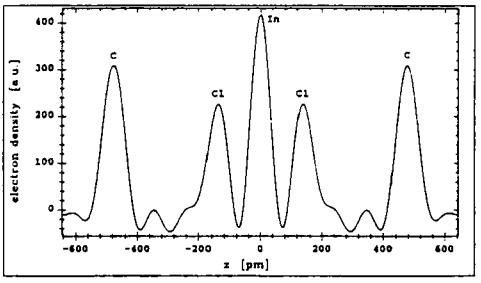

FIGURE 2 One dimensional Fourier synthesis for $InCl_3$ GIC stage 2.

CONCLUSION

In order to obtain information from structure refinements or Fourier syntheses, the large mosaic spread of the GICs,especially those received from flakes, has to be taken into account. If the refinement or the Fourier synthesis are carried out only with the common single crystal corrections, an error of at least 3% for the distance z(Cl) and the stoichiometric factors, and an extremely increased Debye-Waller factor must be expected. On the other hand the application of the new Lorentz factor leads to significantly improved results. In accordance with stage disorder simulations[4] an increased error of the parameters occurs for compounds with slight deviations from the pure stage.

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