Table 1. LAKAT: *summary of the results of inserting the unobserved reflexions after dividing the reciprocal lattice into six shells of increasing* $s = \sin\theta/\lambda$

$z = F^2/\langle F^2\rangle$ indicates the normalized intensity and $\sigma(F)$ is the computed standard deviation of the inserted unobserved reflexions.

Shell no.	$s_{\rm lim}$ (Å^{-1})	$F_{o_{\rm min}}$	$\sigma(F)$	$z_{\rm min}$	No. of observed reflexions	No. of generated reflexions	Total	% generated
1	0·1	20·9	3·0	0·044	8	1	9	11·1
2	0·2	10·3	1·5	0·009	51	4	55	7·3
3	0·3	12·1	1·8	0·069	115	21	136	15·4
4	0·4	12·7	1·8	0·309	125	118	243	48·6
5	0·5	12·6	1·8	0·553	116	268	384	69·8
6	0·6	13·1	1·9	1·824	16	465	481	96·7
Total					431	877	1308	67·0

$P2_12_12_1$ with $a = 11{\cdot}940$, $b = 15{\cdot}725$, $c = 7{\cdot}018$ Å (Sikirica, Vicković & Viterbo, 1978*a*).

Only 431 independent reflexions were measured out of a total of 1308 within the limiting radius $s = 0{\cdot}6$ Å^{-1}. The reflexions were divided into six shells and the unobserved ones were inserted as described above; the results are summarized in Table 1.

The data obtained in this way were then used as input to the *MULTAN* system (Declercq, Hull, Germain, Lessinger, Main & Woolfson, 1976).

The results are compared with those obtained using the measured reflexions only. In Fig. 1 the two Wilson (1942) plots show a great, but not unexpected improvement. However, the most relevant result is the easy solution of the structure, which came out entirely using the most consistent set of phases generated by *MULTAN*; no interpretable *E* map was obtained when the normalized amplitudes had been calculated using the measured reflexions only.

In a similar way we were able to solve the structure of 2-phthalimido-4-methylthio-γ-butyrolactone (Sikirica, Vicković & Viterbo, 1978*b*), crystallizing in the space group $P\bar{1}$ with four independent molecules (76 non-hydrogen atoms) in the asymmetric unit. Only 1828 reflexions were measured, constituting 37% of those within a sphere of radius $s = 0{\cdot}66$ Å^{-1}. The solution was not as straightforward as for LAKAT; only 57 out of 76 atoms were recognisable in the *E* map computed with the best set of phases. The completion and refinement of the structure showed that the observed data were not only poor in quantity but also in quality, as the crystal decomposed during the measurement.

In conclusion we wish to stress that the procedure described is a simple and rapid way to achieve the solution of reasonably complex structures by direct methods for the case where there is a large proportion of unobserved reflexions.

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The chemical and magnetic transformation of the series $Ni_xFe_2O_4$.

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Abstract

The gradual degradation of the cubic spinel phase in ferrimagnetic compounds of composition $Ni_xFe_2O_4$ ($x = 1{\cdot}0$ to $0{\cdot}1$) has been doubly confirmed by the X-ray diffraction and microwave initial magnetic-susceptibility measurements on the samples. The sharp ferrimagnetic–antiferromagnetic transition occurring at a composition corresponding to ($x = 0{\cdot}1$) indicates a change in crystal symmetry.

Introduction

The chemical and magnetic structures are well known for compounds like $NiFe_2O_4$(ferrimagnet) and α-Fe_2O_3(canted antiferromagnet). However, information regarding the chemical and magnetic transformation of the series $Ni_xFe_2O_4$ is not available in the published literature. In the present work, polycrystalline samples having compositions $Ni_xFe_2O_4$($x = 1{\cdot}0$ to $0{\cdot}1$) were prepared by sintering the

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spectroscopically-pure component oxides, mixed in the right proportions, at 1373 K in an atmosphere of air. Details of such a preparation can be found in an article by Subramanyam & Khare (1978). The X-ray and microwave magnetic measurements reported here were carried out at (293–298 K). Three X-ray diffractometric traces of each of the above samples as well as that of polycrystalline α-Fe_2O_3 were obtained using filtered Cu radiation. A dolomite base was used for packing the powdered sample in the aluminium container. Typical traces for samples of compositions x = 1·0 and 0·1 with the routine indexing of the reflections are shown in Figs. 1 and 2 respectively.

A cursory inspection of all the spectra showed that the unit-cell transformation with nickel deficiency was as follows: cubic (x = 1·0 and 0·9) → cubic + rhombohedral (x = 0·8 and 0·1) → rhombohedral (x = 0·0). Making allowance for the background intensity, the integrated intensity of the strong 311 cubic spinel reflection for each of the samples was estimated in terms of the 'peak area'. Fig. 3 shows a plot of the fractional intensity $(I_{311})_x/(I_{311})_{x=1}$ of the several reflections as a function of composition.

The real part of the initial magnetic susceptibility ($\mu' - 1$) for each sample was determined, at a randomly chosen frequency of 9·0 GHz, by employing the 'open circuit – short circuit slotted-line technique' as described by Sucher & Fox (1963). The measurements consisted of determining the input admittances of the sample as a function of two different terminations, open and short-circuit. Typical analysis of the microwave results can again be found by reference to Sucher & Fox (1963). Fig. 4. shows a plot of the real part of the initial susceptibility of the samples as a function of composition.

Discussion

The batch analyses of the component oxides, as supplied by Johnson Matthey Chemicals Ltd., were found to be spectroscopically pure to the admissible extent that they contained

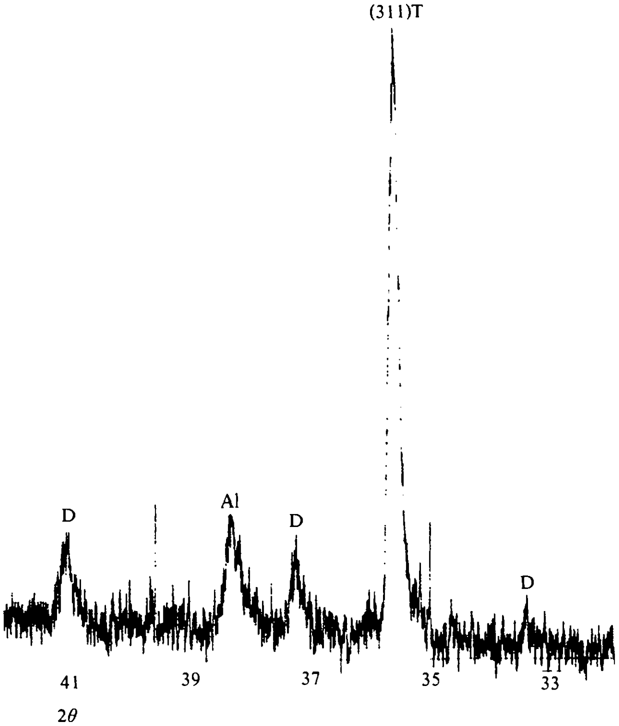

Fig. 1. Plot of the X-ray counting rate *versus* 2θ for polycrystalline $Ni_{1\cdot0}Fe_2O_4$. (T = Trevorite; D = Dolomite; Al = Aluminium.)

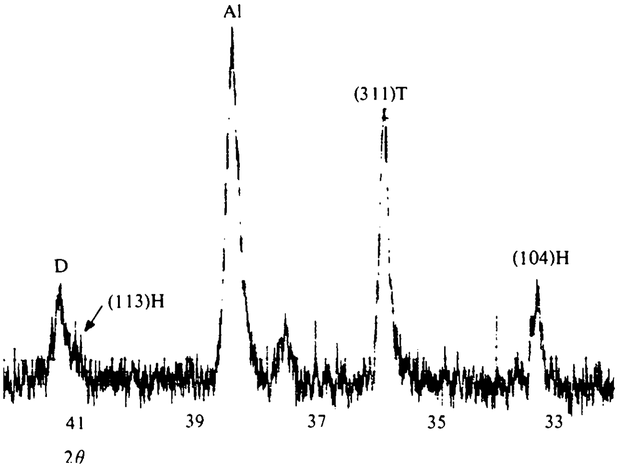

Fig. 2. Plot of the X-ray counting rate *versus* 2θ for polycrystalline $Ni_{0\cdot1}Fe_2O_4$. (T = Trevorite; H = Hematite; D = Dolomite; Al = Aluminium.)

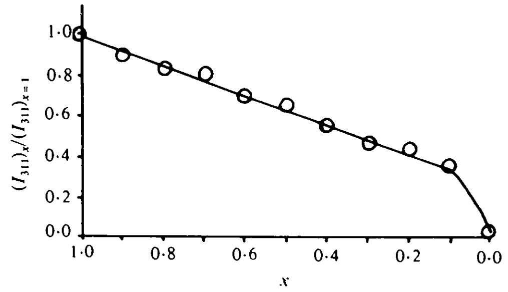

Fig. 3. Plot of the fractional X-ray intensity of the 311 cubic spinel reflection *versus* composition (x) for the polycrystalline series $Ni_xFe_2O_4$.

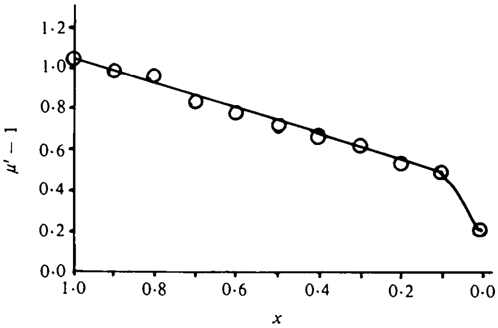

Fig. 4. Plot of the real part of the initial microwave magnetic susceptibility ($\mu' - 1$) *versus* composition (x) for the polycrystalline series $Ni_xFe_2O_4$. (μ' denotes the real part of the complex magnetic permeability.)

calcium and magnesium in quantities less than one part per million each. The chemical analyses of the formed samples showed that they were within 5% of ideal. The standard deviation in the measured X-ray intensity was about ±5%. The procedure of taking the fractional intensities (Subramanyam, 1971) obviates the necessity for absorption and temperature factor corrections. The measured value of the canted-antiferromagnetic susceptibility of α-Fe_2O_3 is in excellent agreement with the reports of Bradley (1971) and others. The maximum error in the above measurement was ±5% with each of the input admittances contributing ±2·5% to the overall error.

The present results do not necessarily show that the removal of $(NiO)_x$ from the spinel structure of $NiFe_2O_4$ causes precipitation of α-Fe_2O_3. However, it may be reasonable to claim that for specimens having compositions $x \simeq 1{\cdot}0$ and $x \simeq 0{\cdot}0$, traces of α-Fe_2O_3 and Fe_3O_4 respectively could be present (Neel, 1949).

To conclude, the gradual degradation of the cubic spinel phase in polycrystalline $Ni_xFe_2O_4$ ($x = 1{\cdot}0$ to $0{\cdot}1$) has been doubly confirmed by two independent methods of measurement and further, the sharp ferrimagnetic–antiferromagnetic transition occurring at $x = 0{\cdot}1$ in the transformation indicates a change in crystal symmetry.

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Errors in diffuse scattering measurements associated with Bragg diffraction.*

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Abstract

Multiple-scattering processes are identified as a source of error in diffuse-scattering measurements on solid solutions. Of the various methods used to account for such effects, a multiple-regression analysis using reduced weights for measurements having maximum interference appears to be the most satisfactory.

It is well known that when diffraction measurements are made on single crystals a second reciprocal-lattice point may simultaneously intersect the Ewald sphere. The first consequence of this is that the scattering from the second lattice point will attenuate the incoming beam, leading to a loss in intensity of the point under study. Secondly, the diffracted beam from this secondary point will also satisfy the Bragg condition for diffraction from a third reciprocal-lattice point, which will return intensity into the primary diffracted beam. These two effects are collectively known as the Renninger effect after their discoverer (Renninger, 1937).

Even before Renninger's work the importance of multiple scattering in studies of Compton scattering was pointed out by DuMond (1930). The methods for adequately accounting for this effect were developed more recently, and, following Halonen, Epstein, Tanner & Williams (1976), the problem appears to be reasonably well solved, although the methods are not particularly simple to apply. It has been recognized that multiple scattering is also important in the scattering from amorphous substances, where the effect is primarily limited to a 2θ dependence. Specifically, for silica the double scattering accounts for 8% of the intensity (Warren & Mozzi, 1966). The effect has also been observed (Sparks & Epperson, 1978) in the thermal diffuse scattering of graphite. In measurements of Compton scattering up to 15% of the photons have been doubly scattered (Halonen *et al.*, 1976).

To the author's knowledge, multiple-scattering processes in diffuse-scattering measurements from alloys have not been definitely identified. It was suggested (Williams, 1974) that part of the error in the intensity for a copper–aluminum alloy arose from this effect. Here I demonstrate that this suggestion is correct and give methods of eliminating or correcting for the effect.

Fig. 1 shows the geometry for measuring the diffuse scattering from point hkl, where S_0 and S are the primary and diffracted beam vectors. The circles represent the intersection of the two Ewald spheres with the S_0–S plane. If a reciprocal-lattice point, HKL, intersects the left sphere, then there will be an additional attenuation of the incoming beam due to Bragg diffraction. Similarly, the diffracted beam would be reduced in intensity if a reciprocal-lattice point intersected the right sphere. This loss of intensity is a form of extinction. As the sample is rotated around the hkl direction a whole set of reciprocal-lattice points would pass through these spheres.

A second part of the effect is that some intensity is returned to the diffracted beam by the diffuse scattering by the point $h-H$, $k-K$, $l-L$ of the intensity diffracted by point HKL. There is a second analogous contribution from the point $H-h$, $K-k$, $L-l$, where the Bragg scattering of the diffuse intensity occurs.

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