Phys Chem Minerals (1994) 20:541–555

PHYSICS AND CHEMISTRY OF MINERALS

Crystal Structures and Cation Distributions in Simple Spinels from Powder XRD Structural Refinements: $MgCr_2O_4$, $ZnCr_2O_4$, Fe_3O_4 and the Temperature Dependence of the Cation Distribution in $ZnAl_2O_4$

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Received May 17, 1993 / Revised, accepted November 22, 1993

Abstract. The crystal structure and cation distributions in the spinels $MgCr_2O_4$, $ZnCr_2O_4$, Fe_3O_4 and a suite of $ZnAl_2O_4$ samples annealed at 900 to 1400° C and then rapidly quenched, have been determined by powder X-ray diffraction, using several different X-ray procedures and both conventional structure-factor refinement and whole-pattern (or Rietveld) refinement methods. The chromite spinels are expected from crystal chemical considerations to have an almost completely normal cation distribution (inversion parameter, x, equal to zero). In agreement with this expectation, three samples of $MgCr_2O_4$ annealed at 900, 1100 and 1300° C, and $ZnCr_2O_4$ were all found to have $x=0$ within two estimated standard deviations (esd), suggesting that the accuracy with which cation distributions in spinels may be determined by powder XRD is close to the estimated precision. Slightly better results are obtained assuming neutral-atom scattering curves rather than half-ionized or fully ionized, but the differences are small (within the esd). The results from the Rietveld refinements are similarly in good agreement with those using the conventional structure factor refinement approach (agreement within the combined esd's), although in detail the Rietveld procedure sometimes produces small systematic differences in refined parameters.

The suite of $ZnAl_2O_4$ spinels show a smooth increase in x from 0.01 at 900° C to 0.05 at 1300° C, and this behaviour is well described by the simple thermodynamic model for disordering in spinels with $\alpha^{Zn-Al}=89$ kJ/mol, assuming $\beta=-20$ kJ/mol. The oxygen positional parameters for Fe_3O_4 are similar to those from published single crystal studies, indicating that the powder method also yields accurate interatomic distances in spinels.

Introduction

The study of cation order-disorder in the oxide spinels is a sufficiently mature field for there to be little uncertainty as regards the main features, such as whether a particular end-member spinel tends towards the normal or the inverse cation distribution. Rather, current interest centres on obtaining accurate measurements of the equilibrium cation distribution as a function of such variables as temperature and composition, with a view to building and testing thermodynamic models, and investigating the relationship between cation distribution and the physical and thermodynamic properties of multicomponent spinel solid solutions. The test of such models is that they should fit the experimental data within the data's accuracy. Unfortunately, the accuracy of much of the existing work on cation distributions in spinels is poorly known, and often where several studies of a particular spinel exist, several rather different results are available (e.g., see discussion of the previous work on the cation distribution in $NiAl_2O_4$ in O'Neill et al. 1991). Judging the merits of conflicting studies is difficult, and it would therefore be helpful if there were external criteria (rather than merely "internal consistency") for demonstrating accuracy.

In this paper we evaluate the accuracy of the powder XRD method by examining some spinels which can be relatively easily synthesized with known stoichiometry, and for which cation distributions can be predicted or at least constrained from crystal-chemical considerations. While no single method of determining cation distributions is suitable for every spinel in which one might be interested, XRD has probably the widest applicability. The advantage of the powder method over the use of single crystals is that the spinel can be synthesized under conditions which are the optimum for achieving the desired stoichiometry, without the necessity of growing large crystals. Achieving the desired composition and stoichiometry is particularly difficult for spinels containing elements with variable oxidation state, and for spinel solid solutions.

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We chose $MgCr_2O_4$ and $ZnCr_2O_4$, a suite of $ZnAl_2O_4$ samples equilibrated at different temperatures, and Fe_3O_4, for the following reasons. The large excess octahedral crystal field stabilization energy of Cr^{3+} ($\Delta CFSE_{(oct-tet)}$ is ~ -160 kJ/mol, O'Neill and Navrotsky 1984) should ensure that all chromite spinels have an almost completely normal cation distribution ($x=0$[1]), and $MgCr_2O_4$ and $ZnCr_2O_4$ were chosen since stoichiometric samples can be prepared over a forgivingly wide range of $T-fO_2$ conditions, without ambiguity of oxidation state. $ZnAl_2O_4$ is an example of a spinel which shows small departures from the completely normal cations distribution. In such cases, it may reasonably be expected that the change in x should increase smoothly with temperature, tending towards $x=0$ as $T \rightarrow 0$ K, and, since x is small, the thermodynamics of the disordering should not be sensitive to higher order terms in x. The difference in the X-ray scattering factors for Al and Zn is large enough for the resolution of the expected small changes in x. Stoichiometric $ZnAl_2O_4$ is easy to prepare, neither Al nor Zn having variable oxidation state, and the kinetics of the order/disorder process are convenient for work on quenched specimens. Good quality single crystals of $ZnAl_2O_4$ can be readily synthesized, so we have also been able to check the results of our powder XRD study against a single crystal structure refinement.

We also examined Fe_3O_4 (magnetite), since this spinel can also be easily prepared to a well-constrained stoichiometry, and there are several detailed single crystral refinement available in the literature (e.g. Fleet 1981; Della Giusta et al. 1987) for comparison. In so far as XRD hardly distinguishes between Fe^{2+} and Fe^{3+}, the cation distribution in Fe_3O_4 does not need to be refined, and therefore this spinel provides a test of how well the other crystallographic parameters (position co-ordinates and temperature factors) can be determined.

As in our earlier study of the cation distribution in $NiAl_2O_4$ spinel (O'Neill et al. 1991), we compare results from powder XRD measurements made on the same specimens in two laboratories, namely the Bayerisches Geoinstitut, Universität Bayreuth, and the Department of Earth and Space Sciences, University of California, Los Angeles (hereafter abbreviated BGI and UCLA respectively). Since the powder XRD equipment at the two laboratories is quite different (e.g., reflection versus transmission diffraction geometries), the inter-laboratory comparison provides an external criterion by which to judge the robustness of the technique, without the ambiguity which arises from comparing data from different samples. We explore the consequences of using both Cu and Mo $K\alpha$ radiations. Refinements were made using two rather different methods, a two-step peak profile fitting/conventional structure factor refinement, and a whole pattern refinement (Rietveld 1969). We also investigate the effects of assuming neutral atom, half-ionized and fully ionized atomic scattering curves.

Sample Preparation

$MgCr_2O_4$ and $ZnCr_2O_4$ were synthesized from stoichiometric oxide mixes of Cr_2O_3 (dried by firing at 1100° C) and MgO (fired at 1100° C) or ZnO (fired at 800° C). All chemicals were stated by the suppliers to be of 99.9% purity or greater. The mixes were pressed into pellets and reacted in a conventional vertical tube furnace at 1100° C under a CO/CO_2 atmosphere (75% CO_2). XRD showed the products to be single phase spinels. Attempts to synthesize chromite spinels in air ($NiCr_2O_4$ and $CoCr_2O_4$ as well as the $MgCr_2O_4$ and $ZnCr_2O_4$ of interest here) always resulted in a small amount of apparently unreacted Cr_2O_3, even when using the same batch of oxide mix which produced the single phase spinel under more reducing conditions. We believe that the excess Cr_2O_3 results from the presence of Cr^{4+} in the chromites at high fO_2, according to the reaction:

$$2\,MCr_2^{3+}O_4 + 1/4\,O_2 = M_2Cr^{4+}O_4 + 3/2\,Cr_2O_3 \qquad (1)$$

As a preliminary test of this hypothesis we tried making "$MgCr_2O_4$" and "$ZnCr_2O_4$" in air, in equilibrium with excess MgO or ZnO. The presence of excess MO should enhance the formation of the $M_2Cr^{4+}O_4$ component, as may be seen from the reaction:

$$MCr_2^{3+}O_4 + 3\,MO + 1/2\,O_2 = 2\,M_2Cr^{4+}O_4 \qquad (2)$$

If we make the simplifying approximation that the activity of $MgCr_2O_4$ is unity for the substitution of small amounts of $M_2Cr^{4+}O_4$, then comparison of Eqs. (1) and (2) show that the ratio of the mole fractions of $M_2Cr^{4+}O_4$ in equilibrium with excess MO and in equilibrium with excess Cr_2O_3 at the same temperature and fO_2 will be given by:

$$(X_{M_2Cr^{4+}O_4})_{ex\,MgO} / (X_{M_2Cr^{4+}O_4})_{ex\,Cr_2O_3} = \exp(\tfrac{3}{4}\Delta G^{o}_{f,ox}/RT) \qquad (3)$$

assuming $a_{M_2Cr^{4+}O_4} = (X_{M_2Cr^{4+}O_4})^2$ (i.e., the activity is given by ideal mixing on two sites, e.g. O'Neill and Navrotsky 1984). For $MgCr_2O_4$, $\Delta G^{o}_{f,ox} = -39.8$ kJ/mol at 1300 K (Robie et al. 1978), so if, for example, at this temperature $X_{M_2Cr^{4+}O_4} = 0.01$ in equilibrium with excess Cr_2O_3 at a particular fO_2 (e.g., air), then $X_{M_2Cr^{4+}O_4} \cong 0.15$ in equilibrium with excess MgO at the same fO_2.

Oxide mixes corresponding to Mg and Zn chromites with excess MgO or ZnO were sintered in air at 1300° C for 6 h, followed by annealing in air at 1000° C for 3 days. After quenching to room temperature, the remaining excess MgO or ZnO was removed by washing in dilute nitric acid, leaving single phase spinels which were dark olive green in colour, as opposed to the pastel green of the stoichiometric chromites. Lattice parameters were significantly higher than those of the stoichiometric chromites: for the Mg spinel, $a_0 = 8.3349$ Å versus 8.3340 Å for stoichiometric $MgCr_2O_4$ and for the Zn

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[1] A simple spinel of formula AB_2X_4 contains one tetrahedral and two octahedral cation sites per formula unit. The inversion parameter, x, is defined as the fraction of B type cations on the tetrahedral site (see O'Neill and Navrotsky 1983). For a completeley normal spinel, x is 0; for a completely inverse spinel, x is 1; and for a random distribution of A and B over the tetrahedral and octahedral sites, x would be $^2/_3$

spinel, $a_0 = 8.3277$ Å versus 8.3271 Å for stoichiometric $ZnCr_2O_4$ (all ± 0.00015 Å). This small increase in a_o is consistent with the increase in mean effective ionic radii for the $(Mg + Cr^{4+} \rightarrow 2\,Cr^{3+})$ and $(Zn + Cr^{4+} \rightarrow 2\,Cr^{3+})$ substitutions, using the ionic radii of Shannon (1976). This test therefore supports the likelihood of non-negligible Cr^{4+} in chromites synthesized in air.

Powder $ZnAl_2O_4$ was synthesized from a mixture of ZnO dried at 800° C and fine grained Al_2O_3 dried at 1100° C, with ZnO in excess. The mix was pressed into a pellet and sintered at 1200 °C for 16 h in air. The excess ZnO was then removed by dissolving in dilute nitric acid, leaving single phase spinel with a grain size of ~1 μ. Single crystals of $ZnAl_2O_4$ were grown using a lead borate flux. 25 g PbO, 2.5 g B_2O_3, 1.2 g ZnO and 0.8 g Al_2O_3 were mixed together, melted in a Pt crucible at 1240° C for 2 h, and then cooled at 6° C/h to 940° C. After annealing at this temperature for 16 h, the crucible was removed from the furnace, and allowed to cool to room temperature. The flux was dissolved in warm nitric acid, leaving subhedral to euhedral, optically clear and generally inclusion-free crystals of $ZnAl_2O_4$ with octahedral morphology, up to 2 mm in size. The lattice parameter measured on flux and powder samples quenched from the same temperature are identical within the expected uncertainty (Table 1), which is consistent with them having the same stoichiometry.

Stoichiometric Fe_3O_4 was prepared from Johnson Matthey specpure "Ferroso Ferric Oxide". Powder XRD examination of the original material showed that it was single phase Fe_3O_4 with $a_o = 8.394$ Å, indicating that it was close to stoichiometric. It was very fine grained (<1 μ), and when put into a 120° C oven it turned from black to a reddish colour, indicating surface oxidation. A sample of this material was sintered in an unsealed Ag-Pd capsule for 28 h under a CO:CO$_2$ ratio of 1:150 at 900° C (cf. Dieckmann 1982), and quenched by dropping onto dry ice. The final product had $a_o = 8.3970$ Å, a grain size of 5–10 μ, and did not develop a reddish tinge in the 120° C oven.

Table 1. Sample equilibration times and lattice parameter measurements

Sample	Temperature of anneal (°C)	Atmosphere (log fO_2)	Time	Lattice[a] parameter (Å)
$MgCr_2O_4$	900	−15.1	48 h	8.3341
	1100	−11.5	2 h	8.3342
	1300	−8.8	2 h	8.3339
$ZnCr_2O_4$	1100	−11.5	–	8.3271
Fe_3O_4	900	−11.7	28 h	8.3970
$ZnAl_2O_4$ as synthesized powder		−0.7	–	8.0869
	700	−0.7	70 h	8.0869
	700	−0.7	580 h	8.0868
	700	−0.7	867 h	8.0872
	700	−0.7	1801 h	8.0869
	900	−0.7	6 d	8.0865[b]
	1000	−0.7	14 h	8.0867[b]
	1100	−0.7	2 h 20 min	8.0871[b]
	1200	−0.7	25 min	8.0876[b]
	1300	−0.7	35 min	8.0884[b]
	1400	−0.7	9 min	8.0883[b]
single crystal	1200	−0.7	40 min	8.0875[b]

[a] estimated standard deviation is 0.0002 for the chromites, 0.0001 otherwise

[b] average of two

Samples of the other spinels were annealed for measured times either in air or under flowing CO/CO$_2$, and then quenched into water, using the following procedure. About 40 to 100 mg of sample was loaded into a Pt or Ag-Pd capsule made from 5 mm diameter tubing, arc-welded at one end. The capsule was crimped closed to prevent the sample falling out, but not sealed. The capsule plus sample was dropped through an alumina guide tube onto an alumina platform placed in the hotspot of a conventional vertical tube furnace. The furnace was pre-heated to the desired temperature. For experiments in CO/CO$_2$, the sample was first purged of air by dropping the capsule onto another platform near the top of the furnace, where it was left for approximately 30 min. Samples were quenched by rotating the alumina platform sideways, so that the capsule is brushed off by the guide tube, and falls into a beaker of water at the bottom of the furnace. Effective quench rates are estimated to be of the order of a few milliseconds (O'Neill et al. 1992). The samples were then dried in an oven at 120° C.

Lattice Parameter Measurements

Lattice parameters on the quenched samples were measured at room temperature (nominally 25° C) using Cu Kα_1 radiation ($\lambda = 1.54056$ Å) or (for Fe_3O_4) Co Kα_1 radiation ($\lambda = 1.78897$ Å) on a STOE diffractometer at the Bayerisches Geoinstitut (see O'Neill et al. 1991, 1992). All samples were run with an internal standard of NBS Si ($a_o = 5.43081$ Å, corrected from the recommended 5.43094 Å at 298.1 K for CuK$\alpha_1 = 1.5405981$ Å to the value of λ CuKα_1 used in our laboratory). The diffraction pattern was collected from 60 to 142° 2θ. For the chromites, a filter of Ti foil was used to reduce secondary fluorescence; to compensate for the loss of intensity, the scanning time was increased from approximately two hours to eight hours. Proprietary software was used to determine peak positions, by fitting entire peak profiles. The main Si peaks in the 2θ range covered were used to derive a two term (linear) correction to the observed 2θ's. The spinel lattice parameter, a_o, was then determined by a weighted non-linear least squares refinement of the positions of all but the least intense spinel peaks. The uncertainty in a_o is estimated to be ± 0.0001 Å (one standard deviation), which includes changes in room temperature (O'Neill et al. 1991, 1992), but might be slightly higher for the chromite samples, because of the reduced intensities and high backround caused by fluorescence.

The results of the lattice parameter measurements are given in Table 1. The three samples of $MgCr_2O_4$ have the same a_o, which is consistent with our expectation that this spinel should not deviate sensibly from the completely normal cation distribution over our experimental temperature range (900 to 1300° C). For $ZnAl_2O_4$, a_o increases smoothly with the temperature of anneal from 900 to 1300° C, reflecting small increases in x (see below). Below 900° C, diffusion rates apparently become too slow to achieve the equilibrium cation diffusion in reasonable laboratory times. Annealing a high temperature $ZnAl_2O_4$ sample at 700° C, for example, produced no detectable change in a_o even after 1800 h (Table 1). At 1400° C, there is no further increase in either a_o or x, which may be due to the rate of re-ordering becoming too fast to preserve during the quench (but see the thermodynamic evaluation of the change of x with temperature below).

Powder X-ray Diffraction Structural Refinements

Powder XRD intensity measurements were made at both BGI and UCLA, as in our earlier study on $NiAl_2O_4$ (O'Neill et al. 1991), in which full experimental details may be found. Briefly, at the BGI we used a STOE STADIP diffractometer in the transmission mode with $MoK\alpha_1$ radiation, and additionally for $ZnAl_2O_4$, $CuK\alpha_1$ radiation; and at UCLA, a Phillips diffractometer with reflection geometry and $CuK\alpha$ radiation. Data were collected over the range 6 to 80° 2θ ($\sin\theta/\lambda = 0.91$) for the Mo radiation measurements, and for Cu radiation from 15 to 142° 2θ ($\sin\theta/\lambda = 0.61$) at the BGI and 15 to 150° 2θ at UCLA. One advantage of using Mo radiation is that more diffraction peaks are accessible to measurement (for example, for $ZnAl_2O_4$, the Mo measurements typically result in about 50 non-zero reflections, versus 30 for Cu radiation).

Structural refinements were carried out using two different methods (see also O'Neill et al. 1992). The first method is a two step process, in which the digital X-ray powder diffraction data are first fit to a peak profile model, to obtain reflection intensities. For the Mo BGI data segments of 5 to 10° 2θ were fit using a Lorenzian-squared peak profile function. The half-widths of all peaks within each segment were constrained to be equal, so as to fit more reliably the weakers peaks. For the BGI/Cu data a Pearson VII peak profile function was used, as this gave a markedly better fit to the reflections at $2\theta > 90°$. For the UCLA/Cu data, we used a pseudo-Voigt function with the Gaussian fraction constrained to vary linearly with 2θ. The UCLA reflection-mode data were corrected, in the single case of Fe_3O_4, for the effect of surface roughness. For this sample only, due to the extreme absorption coefficient of 1157 cm^{-1} with $CuK\alpha$ radiation, even minute surface asperities preferentially intercept low angle reflections relative to higher angle reflections. Left uncorrected, this effect produces systematic errors in the refinement parameters (especially noticeable in anomalously low temperature factors). Testing of various computer simulated surfaces suggested an intensity correction of the form: $I_{corr} = I_{uncorr}\,(1/\sin\theta)^n$, where the exponent, n, is varied to produce the best fit to the data. For Fe_3O_4, this exponent refined to 0.22(3).

Reflections were indexed from their positions, and their intensities (and their estimated uncertainties) are then input into a conventional crystal structure refinement program (SIMP, Dollase, unpublished), which minimizes by least squares the deviation between observed and calculated (squared) structure factors.

Alternatively, it is possible to combine the separate steps of intensity measurement and crystal structure refinement into the procedure of whole pattern or Rietveld refinement. In this method, the quantity minimized is the difference between the whole XRD pattern (peaks and background) and a calculated model pattern. Ideally, of course, the two method should give identical answers, but in practice, for real data with its attendant experimental uncertainties, together with any inadequacies in the physical XRD model, and in the peak and background fitting functions, some differences might be anticipated. We therefore use the present experimental data for a comparative test of the two methods, as also done in O'Neill et al. (1991, 1992).

Structure Model

We assumed space group $Fd\bar{3}m$, with complete occupancy of 8(a) and 16(d) sites by the cations, with oxygen in the 32(e) sites. Such a model is in excellent agreement with extensive single crystal refinements on other spinels (e.g. Della Giusta et al. 1987), although it has occasionally been argued (e.g. Grimes 1971, 1972; Grimes et al. 1983) that some oxide spinels have a lower symmetry space group, $F\bar{4}3m$, in which the octahedral cations are displaced slightly from their $Fd\bar{3}m$ positions, and the tetrahedral and oxygen sites are each split into two sets of crystallographically distinct sites. This model was proposed by Grimes (1971) to explain the anomalously high isotropic temperature factor observed by Grimes and Hilleard (1970) in their powder XRD study of $MgCr_2O_4$ (namely, $B = 1.1$ Å^2). As the sample of Grimes and Hilleard (1970) was synthesized at 1550° C in oxygen, we suggest that this high B may be an artefact of some ($Mg + Cr^4 = 2\,Cr^{3+}$) substitution in their sample. We do not obtain an unusual value of B for $MgCr_2O_4$ (see below), nor did Infante and Fender (1973) in their neutron diffraction study.

Refined parameters were a scale factor, the inversion parameter x (except for Fe_3O_4), the oxygen positional parameter u, and the isotropic temperature factors, B. We emphasize, as in previous studies (O'Neill et al. 1991, 1992), that best results are achieved using separate temperature factors for the tetrahedral, octahedral and oxygen sites (B_{tet}, B_{oct} and B_{ox}). This will be shown empirically for the chromite spinels. Neutral atom scattering factors were used (Ibers and Hamilton 1974), corrected as appropriate for anomalous dispersion. We also refined our data using half-ionized and fully ionized scattering curves, and we will discuss the small (usually negligible) differences caused by these alternatives.

Results from Structure Factor Refinements

$MgCr_2O_4$ and $ZnCr_2O_4$

Results for $MgCr_2O_4$ and $ZnCr_2O_4$ from structure factor refinements are given in Table 2. The main external constraint on judging the accuracy of these refinements is the crystal-chemical expectation that x should be zero. How tight a constraint this is may be assessed from the following considerations. In the model of O'Neill and Navrotsky (1983, 1984) the cation distribution in a simple oxide spinel of formula AB_2O_4 (for example, A and B could be Mg and Cr^{3+} or Zn and Cr^{3+} respectively for the chromites under discussion) is described by the general equation:

$$\ln\left(\frac{x^2}{(1-x)(2-x)}\right)=-(\alpha^{A-B}+2\beta x-T\sigma^{A-B})/RT \qquad (4)$$

The term in the parentheses on the left hand side may be thought of as the equilibrium constant for the cation distribution reaction: $A^{(\text{tet site})}+B^{(\text{oct site})}=A^{(\text{oct site})}+B^{(\text{tet site})}$. The quantity α^{A-B} is the difference in the site preference energies of A and B, *i.e.*, $\alpha^{A-B}=\alpha^A-\alpha^B$. The site preference energy of a cation in a spinel is determined by a number of factors, including its ionic radius in both tetrahedral and octahedral coordination, and the difference in its *CFSE* in tetrahedral and octahedral coordination ($\Delta CFSE_{(\text{oct-tet})}$); see O'Neill and Navrotsky (1983) for a full discussion. Site preference energies may be obtained empirically from cation distribution data, where these are available (O'Neill and Navrotsky 1984). The quantity σ^{A-B} is an entropy term analogous to α^{A-B}, introduced to account for any non-configurational entropy of disordering, and which is expected to be relatively small. The term β is taken in the model to be the same for all 2–3 spinels, and has a value of -20 kJ/mol. Small values of x imply large α^{A-B}, so that for small x, $\alpha^{A-B}\gg 2\beta x$ and $\alpha^{A-B}\gg T.\sigma^{A-B}$, and hence Eq. (4) reduces to:

$$x=2\exp(-\alpha^{A-B}/2RT) \qquad (5)$$

An empirically derived value for $\alpha^{Cr^{3+}}$ is not available. O'Neill and Navrotsky (1984) suggested that since $\Delta CFSE_{(\text{oct}-\text{tet})}$ for Cr^{3+} is so large (~ -160 kJ/mol; Dunitz and Orgel 1957; McClure 1957), it would dominate the site preference energy of Cr^{3+}. Therefore $\alpha^{Cr^{3+}}$ was assumed to be also -160 kJ/mol. With $\alpha^{Mg}=20$ kJ/mol from O'Neill and Navrotsky (1984), this gives $\alpha^{Mg-Cr^{3+}}\approx 180$ kJ/mol, but it should be realised that the approximations involved make this figure only an estimate. If $\alpha^{Mg-Cr^{3+}}$ is indeed 180 kJ/mol, x is calculated to be 0.002 at 1300° C, but if $\alpha^{Mg-Cr^{3+}}$ were only 120 kJ/mol, for example, then x would be 0.004 at 900° C, increasing to 0.02 at 1300° C, which increase is large enough to be detected by the powder XRD method. It was with this possibility in mind that we annealed samples of $MgCr_2O_4$ at 900, 1100 and 1300° C. The results of the structural refinements in Table 2 show that x is effectively zero for all three samples, which is therefore consistent with $\alpha^{Mg-Cr^{3+}}\geq\sim 180$ kJ/mol. It is only fair to point out, however, that since we have not been able to produce a sample with $x\neq 0$, we cannot demonstrate equlibrium either by reversal or by following the change of x with time, so we cannot exclude other (non-Ockhamist) interpretations of these observations – e.g., if the rate of re-ordering of Mg and Cr^{3+} were unusually rapid for a spinel, then values of x greater than 0 might not be preserved during the quench.

Since α^{Zn} exceeds α^{Mg} by ~ 30 kJ/mol (O'Neill and Navrotsky 1984), the cation distribution in $ZnCr_2O_4$ should be even closer to zero than in $MgCr_2O_4$, at a given temperature. We find x is indeed indistinguishable from zero for both the BGI and UCLA data.

For $MgCr_2O_4$ and $ZnCr_2O_4$, both sets of data refine to $B_{\text{tet}}>B_{\text{oct}}$. The B parameters are likely to be determined better by the BGI Mo data, since these extend to higher $\sin\theta/\lambda$.

Many older powder XRD studies of the cation distribution in spinels used simplified models for the isotropic temperature factors, by assuming either that that the tetrahedral and octahedral cations have the same isotropic temperature factor with a different temperature factor for the oxygens ($B_{\text{tet}}=B_{\text{oct}}\neq B_{\text{ox}}$; called here the $2B$ model) or, even less realistically, that the tetrahedral and octahedral cations and the oxygens all have the same isotropic temperature factors ($B_{\text{tet}}=B_{\text{oct}}=B_{\text{ox}}$; the $1B$ model). In assessing the accuracy of such older studies, one needs to know the effect of using these simplified models on the other parameters of interest (i.e., the cation distribution and oxygen positional parameters). Accordingly, we have also refined our data adopting these constraints. The results are reported in Table 2. We find that the simplified temperature factor models produce physically unreasonable values of x (negative for $MgCr_2O_4$, too large for $ZnCr_2O_4$), which are furthermore in error by about four times the estimated standard deviation on x. We thus demonstrate that the adoption of such simplified models results not in loss of precision, as has sometimes been assumed, but in systematic error; this is an important point to remember in selecting data for the development of models for cation distributions in spinels. Similar findings are reported in O'Neill et al. (1991, 1992), and are also observed for the refinements of the UCLA data.

This effect is expected from the inverse correlation between temperature factors and mean tomic number of the scattering curves, which translates into a correlation between x and the difference $B_{\text{tet}}-B_{\text{oct}}$). The relative magnitudes of B_{tet} and B_{oct} vary from one spinel to another. Whereas here we find $B_{\text{tet}}>B_{\text{oct}}$ for the chromites, O'Neill et al. (1992) found $B_{\text{tet}}<B_{\text{oct}}$ in $MgFe_2O_4$. A study of the solid solution $MgFe_2O_4-MgCr_2O_4$ shows a smooth variation from one case to the other (H.St.C. O'Neill and D. Virgo, unpublished data). The relative magnitudes of B_{tet} and B_{oct} are not simply a matter of normal versus inverse cation distribution, as in aluminate spinels $B_{\text{tet}}>B_{\text{oct}}$ in the inverse $NiAl_2O_4$ (O'Neill et al. 1991) and in the normal $ZnAl_2O_4$ (see below) and $FeAl_2O_4$, but $B_{\text{tet}}\cong B_{\text{oct}}$ in $CoAl_2O_4$ (H.St.C. O'Neill, unpublished data)

The mean effective temperature factor for $MgCr_2O_4$ in the $1B$ model is ~ 0.3 Å^2, which is the same as that

Table 2. Powder XRD refinements, using the two step method (profile fitting/structure factor refinement). Neutral atom scattering curves

Sample/°C	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R (%)	wR (%)
	Results from data collected at UCLA (CuKα radiation)						
$MgCr_2O_4$/900	−0.017(14)	0.2607(4)	0.35(9)	0.09(3)	0.38(7)	2.6	3.6
$MgCr_2O_4$/1100	0.030(25)	0.2606(5)	0.43(13)	0.14(4)	0.26(9)	3.4	4.7
$MgCr_2O_4$/1300	0.019(20)	0.2607(4)	0.44(11)	0.26(3)	0.42(9)	2.4	3.9
$ZnCr_2O_4$	−0.005(46)	0.2611(3)	0.21(5)	0.09(5)	0.20(11)	3.6	4.4
Fe_3O_4	–	0.2551(6)	0.40(3)	0.53(3)	0.78(7)	2.3	2.8
	Results from data collected at BGI (MoKα_1) radiation)						
$MgCr_2O_4$/900	−0.004(12)	0.2610(2)	0.39(5)	0.28(1)	0.45(3)	2.5	4.2
$MgCr_2O_4$/1100	0.009(11)	0.2611(2)	0.39(5)	0.23(1)	0.44(3)	2.5	4.2
$MgCr_2O_4$/1300	0.011(13)	0.2614(2)	0.48(6)	0.30(1)	0.48(3)	3.0	4.0
$ZnCr_2O_4$	0.008(15)	0.2614(3)	0.34(2)	0.24(2)	0.56(5)	2.9	3.9
Fe_3O_4	–	0.2552(3)	0.53(2)	0.66(2)	0.81(4)	3.1	4.6

2 *B* model

Sample/°C	x	u	B_{cat} (Å^2)	B_{ox} (Å^2)	R (%)	wR (%)
$MgCr_2O_4$/900	−0.026(5)	0.2610(2)	0.29(1)	0.44(3)	2.5	4.2
$MgCr_2O_4$/1100	−0.021(6)	0.2611(2)	0.24(1)	0.42(4)	2.6	4.4
$MgCr_2O_4$/1300	−0.027(6)	0.2614(2)	0.31(1)	0.46(4)	3.3	4.5
$ZnCr_2O_4$	0.051(10)	0.2613(3)	0.29(1)	0.57(5)	3.1	4.9
Fe_3O_4	–	0.2551(4)	0.61(2)	0.83(5)	3.5	6.2

1 *B* model

Sample/°C	x	u	B(Å^2)	R (%)	wR (%)
$MgCr_2O_4$/900	−0.025(6)	0.2615(2)	0.30(1)	3.0	4.5
$MgCr_2O_4$/1100	−0.022(7)	0.2617(2)	0.26(1)	3.1	4.6
$MgCr_2O_4$/1300	−0.027(7)	0.2619(2)	0.32(1)	3.8	4.6
$ZnCr_2O_4$	0.048(12)	0.2621(3)	0.30(2)	3.8	6.6
Fe_3O_4	–	0.2559(4)	0.62(2)	3.8	7.1

estimated by Grimes (1972) from IR measurements, but significantly less than the value of $B = 1.1$ Å^2 found by Grimes and Hilleard (1970).

There is a small difference in the oxygen positional parameters (u) from the BGI and UCLA refinements. For $MgCr_2O_4$ the mean u values are 0.2612(2) and 0.2607(4) respectively, so that the disagreement is actually within the combined standard deviations. The neutron diffraction study of $MgCr_2O_4$ carried out by Infante and Fender (1973) gave $u = 0.2612(1)$, with $B_{cat} = 0.22 \pm 0.05$ Å^2 and $B_{ox} = 0.43 \pm 0.05$ Å^2 (i.e., a 2 *B* model), in agreement with the BGI data refined using the 2 *B* model.

Assuming an ionic radius of O^{2-} of 1.38 Å, the results in Table 2 imply effective ionic radii of 0.586(3) Å for Mg(IV) and 0.615(3) Å for Cr^{3+}(VI) from $MgCr_2O_4$, and 0.587(4) for Zn(IV) and 0.611(5) for Cr^{3+}(VI) from $ZnCr_2O_4$. These radii agree with the values recommended by O'Neill and Navrotsky (1983) of 0.585, 0.58 and 0.615 for Mg(IV), Zn(IV) and Cr^{3+}(VI) respectively.

The only previous structural study of $ZnCr_2O_4$ is the powder XRD investigation of Raccah et al. (1966), which produced $u = 0.2649$. This value is anomalously high, implying a ionic radius of Cr^{3+}(VI) of only ~0.58 Å.

The BGI/Mo measurements were tested for possible extinction or detector dead time effects by repeating the refinements after eliminating a) the most intense reflection (311), and b) the four lowest angle reflections (111, 220, 311 and 222). This produced negligible changes in all the refined crystallographic parameters and *R* factors.

$ZnAl_2O_4$

For the powder samples of $ZnAl_2O_4$ annealed between 900 and 1300° C, the results from three sets of measurements (i.e., using both Mo and CuKα_1 radiation at BGI and CuKα radiation at UCLA) are given in Table 3. The 1400° C sample was also examined at UCLA, but since it showed no difference from the 1300° C sample (also in a_o, Table 1) we concluded that it had failed to preserve fully its high temperature distribution during quenching, and did not pursue its investigation further. Subsequent thermodynamic analysis indicates that this conclusion may have been premature – see below. Also shown in Table 3 is a single crystal refinement on a flux-grown crystal annealed at 1200 °C. The low *R* factors indicate that this refinement is of high quality, suitable to take as a standard for comparing the powder results. The other criteria for assessing the powder data are in-

Table 3. $ZnAl_2O_4$ powder XRD refinements, using the two step method (profile fitting/structure factor refinement)

Sample/°C	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R (%)	wR (%)
UCLA (CuKα radiation)							
900	0.009(10)	0.2637(4)	0.27(4)	0.24(6)	0.32(8)	2.7	3.9
1000	0.019(9)	0.2639(3)	0.27(4)	0.25(5)	0.29(7)	2.3	3.2
1100	0.028(9)	0.2635(3)	0.25(4)	0.24(6)	0.34(7)	2.7	3.6
1200	0.041(9)	0.2636(3)	0.23(4)	0.23(5)	0.32(7)	2.6	3.4
1300	0.056(9)	0.2634(3)	0.21(4)	0.22(5)	0.36(7)	2.5	3.2
1400	0.058(8)	0.2633(3)	0.31(4)	0.32(4)	0.47(6)	2.1	3.2
BGI (MoKα_1 radiation)							
900	0.013(7)	0.2644(3)	0.373(24)	0.292(45)	0.431(71)	4.4	5.1
1000	0.018(7)	0.2642(3)	0.351(22)	0.285(43)	0.424(66)	4.1	5.2
1100	0.030(6)	0.2641(3)	0.361(23)	0.316(43)	0.395(66)	3.9	5.3
1200	0.039(6)	0.2640(3)	0.377(22)	0.286(41)	0.487(65)	4.3	4.9
1300	0.053(6)	0.2639(3)	0.351(22)	0.314(40)	0.494(64)	3.7	5.0
BGI (CuKα_1 radiation)							
900	0.008(11)	0.2642(4)	0.55(6)	0.48(8)	0.47(10)	3.1	6.6
1000	0.020(10)	0.2640(4)	0.59(6)	0.55(8)	0.56(10)	2.7	6.4
1100	0.026(8)	0.2640(3)	0.45(5)	0.40(6)	0.45(8)	2.6	4.8
1200	0.037(10)	0.2639(4)	0.54(5)	0.49(7)	0.61(9)	2.8	6.1
1300	0.056(9)	0.2639(3)	0.55(5)	0.51(7)	0.64(9)	3.1	4.9
Single crystal refinement (Mo radiation)[a]							
1200	0.0357(35)	0.26409(7)	0.321(11)	0.279(16)	0.371(16)	2.22	2.49

[a] Data collected on a Rigaku AFC-5R four circle diffractometer at Molecular Structure Corporation of Texas. Refinement carried out at MSC. No. of observations = 125

ternal consistency, and physical reasonableness (e.g., that x should not be negative).

The BGI Mo data agree well with all three criteria. The 1200° C result is effectively identical to that for the single crystal for all five structural parameters (x, u, and the three isotropic temperature factors B_{tet}, B_{oct} and B_{ox}). The five samples (900 to 1300° C) show good internal consistency with a smooth change of x and u with temperature (Fig. 1), and the same B parameters independent of temperature (Fig. 2). The slight decrease in u with increasing temperature and thus with increasing x is consistent with lattice energy considerations (O'Neill and Navrotsky 1983).

Compared to the results from the BGI Mo data, those from the BGI Cu data give the same values of x and u, but all three temperature factors (B parameters) are higher, by 0.2 to 0.3 Å^2. In addition, the measurements with Cu radiation do not constrain temperature factors as well as the Mo data, since they do not extend to as high $\sin\theta/\lambda$. The accuracy of the temperature factors in these transmission-mode measurements may also be adversely affected by the large magnitude of the absorption correction which one needs to make at high 2θ. The relative relationship $B_{tet} > B_{oct}$ is the same, however. The results from the UCLA Cu data give the same x's and B's, but systematically smaller u's. The average difference in the u parameters is 0.0005, and is similar to that found for the chromites (Table 2). The cause of this discrepancy is not known. However, as for the chromites, the u parameters furnished by the UCLA and BGI data sets agree within one combined standard deviation.

For small x, Eq. (4) reduces to:

$$RT\ln\left(\frac{x^2}{(1-x)(2-x)}\right) \cong \alpha^{Zn-Al} \tag{6}$$

and therefore $RT\ln\left(\frac{x^2}{(1-x)(2-x)}\right)$ should be nearly constant, independent of equilibration temperature. This is demonstrated for all three data sets in Fig. 3.

We fit the BGI Mo data (5 data) plus the single crystal datum to Eq. (4) by weighted non-linear least squares, assuming $\beta = -20$ kJ/mol (the mean value for 2–3 spinels recommended by O'Neill and Navrotsky 1984). We obtain $\alpha^{Zn-Al} = 89.3 \pm 1.5$ kJ/mol, with a reduced χ^2 for the regression of 0.2. This value of α^{Zn-Al} compare well with that estimated by O'Neill and Navrotsky (1984) from spinel systematics, namely 89 kJ/mol. The results for the specimen quenched from 1400° C (UCLA data) falls on the extrapolation of this model, and therefore there is in fact no reason to suppose that it failed to preserve its equilibrium value of x on the quench.

The low value of the reduced χ^2 and the level of agreement on the value of x between the three powder data sets and also with the single crystal refinement suggest that the uncertainties on x from the structure factor refinements may be overestimated by a factor of 2 to 3. The reason for this is not known.

Constraining $B_{tet} = B_{oct}$ causes x to increase by ~0.01, but the u parameter is unaffected, and the R factors hardly change. The increased x's also result in a near horizontal slope of $RT\ln\left(\frac{x^2}{(1-x)(2-x)}\right)$ vs. T, so in the case

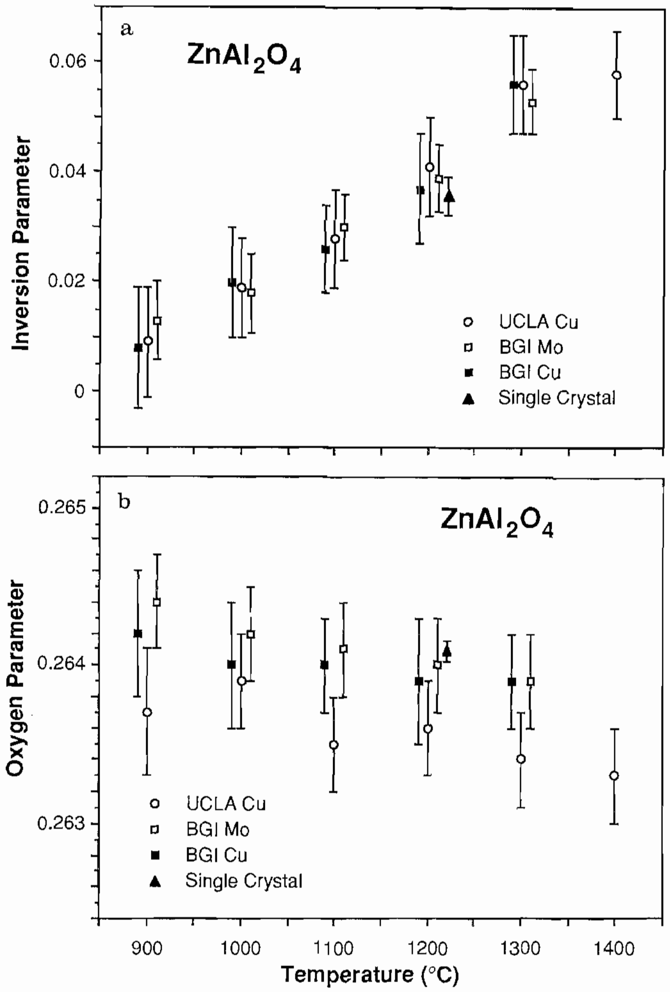

Fig. 1a, b. Results of the structure factor refinements on samples of $ZnAl_2O_4$ quenched after annealing at 900 to 1400° C. Three sets of XRD measurements were made: at UCLA with CuK radiation (plotted offset by $-10°$ C), and at the BGI with both Mo and $CuK\alpha_1$ radiation (the latter plotted offset by $+10°$ C). Also shown is the result from a single crystal structure refinement (offset by $+20°$ C). **a** Inversion parameter, x; **b** Oxygen positional parameter, u

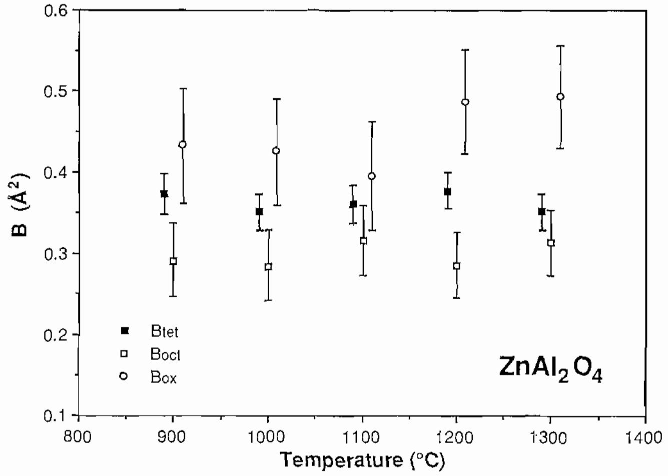

Fig. 2. $ZnAl_2O_4$: isotropic temperature factors (B) from the structure factor refinements of BGI data collected with Mo radiation. The values of B appear to be independent of the degree of inversion, and all results consistently show $B_{ox} > B_{tet} > B_{oct}$

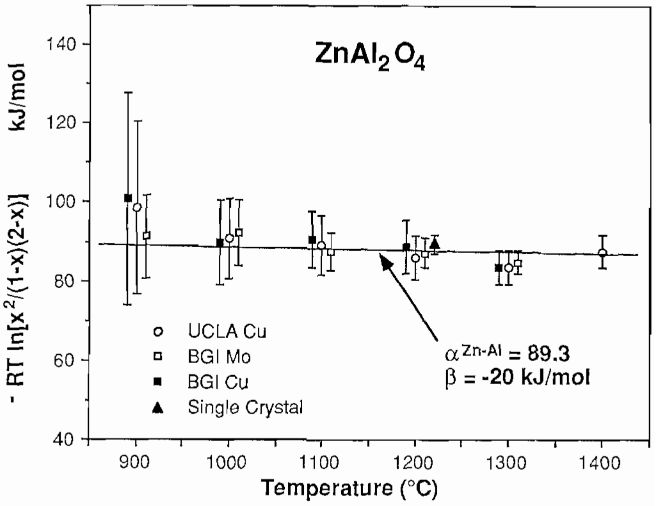

Fig. 3. $ZnAl_2O_4$: plot of vs. temperature, values of x from all three sets of powder XRD measurements, plus from the single crystal refinement. The data are fit well by a simple thermodynamic model

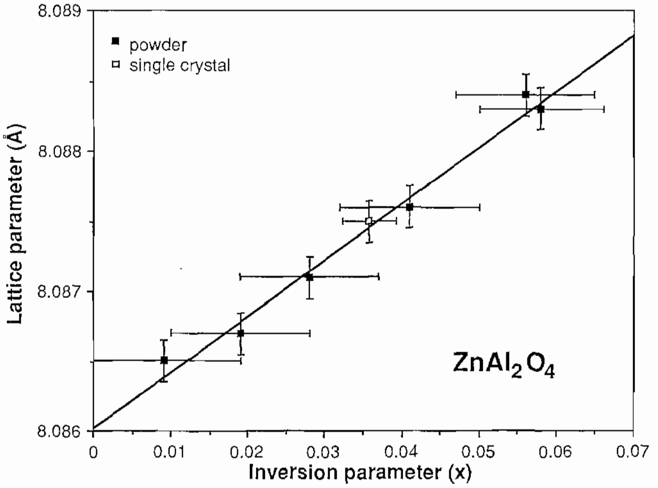

Fig. 4. $ZnAl_2O_4$: inversion parameter, x, (using the results from the UCLA structure factor refinements because of the 1400° C datum, plus the single crystal value) versus the lattice parameter, measured using an internal standard of NBS Si

of $ZnAl_2O_4$, there is actually no criterion apart from consistency for preferring the $3B$ model.

A plot of lattice parameter versus x reveals a linear relationship (Fig. 4). The quality of this fit again suggests that the uncertainties on x are overestimated – the reduced χ^2 for the regression suggest that an uncertainty in x of about ± 0.002 would be more appropriate for describing the experimental uncertainty, if our estimate of the uncertainty in a_0 (± 0.0001) is correct.

We are aware of only one previous study of the cation distribution in $ZnAl_2O_4$, that of Cooley and Reed (1972), who used powder XRD to obtain $x = 0.04$ and 0.06 at 905 and 1197° C respectively. These values may be considered in fair agreement with the present results, considering the limitations of the powder method at the time of their work – see the discussion in O'Neill et al. (1991).

Table 4. The crystal structure of Fe_3O_4 – present results and comparison with previous work

Sample	a_0 (Å)	u	B_{tet} ($Å^2$)	B_{oct} ($Å^2$)	B_{ox} ($Å^2$)
X-ray diffraction					
This study (BGI Mo)	8.3970(2)	0.2552(3)	0.53(2)	0.66(2)	0.81(4)
This study (UCLA Cu)	8.3970(2)	0.2551(6)	0.40(3)	0.53(3)	0.78(7)
Fleet (1981)	8.3941(7)	0.2549(1)	0.34(2)	0.46(2)	0.49(3)
Fleet (1982)[a]	8.3930(6)	0.2547(1)	0.34(2)	0.46(1)	0.59(3)
Finger et al. (1986)	8.395(1)[b]	0.2550(2)	0.60(2)	0.70(2)	0.73(4)
Nakagiri et al. (1986)	8.3949(3)	0.2548(2)	0.53(2)	0.82(3)	0.56(8)
Della Giusta et al. (1987)	8.3950(3)	0.2548(3)	0.57(2)	0.68(2)	0.66(3)
Neutron diffraction					
Hamilton (1958)	8.394	0.2548(2)		$B_{eq}=0.49(9)$	
Wechsler et al. (1984)	8.3958(2)	0.2547(2)	0.37(4)	0.47(4)	0.64(5)

[a] the structural model used in the refinement included an assumed defect structure and anisotropic B's

[b] as measured by Harrison and Aragón (1978); Finger et al. (1986) give = 8.3778(5) Å

Fe_3O_4

Our results for Fe_3O_4 are compared with published single crystal and neutron diffraction studies in Table 4. The lattice parameters reported by Hamilton (1958), Fleet (1981, 1982), Wechsler et al. (1984) and Nakagiri et al. (1986) are all slightly lower than that of this study, by 0.001 to 0.003 Å, which would be consistent with 1.5 to 4.5 mole percent of $Fe_{3/8}O_4$ (i.e., maghemite with the formula written to 4 oxygens; lattice parameter inferred to be 8.339 Å by Lindsley 1976). For the specimen used by Nakagiri et al. (1986), the non-stoichiometry deduced from the lattice parameter is the same as that found by direct chemical analysis. The lattice parameter reported by Della Giusta et al. (1987) is identical to ours, if allowance is made for the 1.5 mol% $FeCr_2O_4$ in their specimen. The oxygen positional parameter, u, appears to be well established from these studies, with a mean weighted value of 0.2548(1). Both our refinements are essentially in agreement with this value. Temperature factors among the previous studies show more variation. Our results agree with the majority trend $B_{tet}<B_{oct}<B_{ox}$, but tend so slightly higher values than the average.

In contrast to the results for the chromites and $ZnAl_2O_4$, using a $2B$ or $1B$ model for Fe_3O_4 results in significantly worse R factors (Table 2). This is because the cation distribution in Fe_3O_4 is effectively fixed from the point of view of X-ray scattering, so that the refinement is unable to respond to the over-simplified model by changing x. This therefore supports our contention that the $2B$ and $1B$ models give results with a systematic error (cf. O'Neill et al. 1991, 1992).

Neutral Atom versus Half-ionized or Fully Ionized Scattering Curves

Crystal structure refinements of minerals from XRD data are customarily made using neutral atom scattering curves. However, in other mineralogical contexts, spinels are often treated as ionic substances – for example, interatomic distances are described in terms of ionic radii (e.g., O'Neill and Navrotsky 1983). Accordingly, it might be thought that the use of ionized scattering curves would be more appropriate.

We have tested this using several data sets; refinements with fully-ionized scattering curves are reported in Table 5. The differences between these results and the neutral-atom results given in Tables 2 and 5 are small, the refined parameters generally being within one combined standard deviation. Overall, there is a slight tendency for the indices of refinement (R factors) to improve with the fully-ionized model. However, there are systematic differences in the values of x which suggest that the neutral-atom model should be preferred. For $MgCr_2O_4$, the fully-ionized model gives negative values for x (physically impossible); the mean of the three data is -0.008 with a standard error of the mean of 0.005, versus a physically realistic mean of $+0.005$ for the neutral-atom model, standard error of the mean also 0.005. For $ZnCr_2O_4$, the fully-ionized model increases x to 0.029 ± 0.013 (from 0.008 ± 0.015), and therefore gives a result contrary to the expectation that x in $ZnCr_2O_4$ should be even closer to zero than in $MgCr_2O_4$. For $ZnAl_2O_4$, the fully-ionized model causes the values of x from both the Mo and the Cu data to decrease by ~ 0.01, giving a trend which extrapolates towards negative values of x below 900° C. As a result, we obtain significantly poorer fits to thermodynamic models (Eq. (4)). The R factors increase slightly for the Mo data, but decrease for the Cu data.

The scattering curves for neutral, half-ionized or fully ionized atoms only really differ from each other below approximately $\sin\theta/\lambda = 0.3$. Our Mo data is collected to $\sin\theta/\lambda = 0.9$ whereas the Cu data extend only to $\sin\theta/\lambda = 0.6$. Since a higher proportion of the Cu data is within the range where the scattering factors are sensitive to the degree of ionization, it might be thought that the Cu data would be more affected by the choice of scattering curves. Comparison of the results for $ZnAl_2O_4$ (Tables 2 and 5) shows empirically that this is not so.

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Table 5. Powder XRD structure factor refinements with fully-ionized scattering curves. All data collected at the Bayerisches Geoinstitut

Sample/°C	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R (%)	wR (%)
MoKα_1 radiation							
$MgCr_2O_4$/900	−0.017(11)	0.2610(2)	0.347(47)	0.287(10)	0.407(27)	2.3	3.8
$MgCr_2O_4$/1100	−0.008(10)	0.2611(2)	0.342(44)	0.239(10)	0.397(28)	2.2	3.7
$MgCr_2O_4$/1300	−0.001(12)	0.2613(2)	0.444(52)	0.302(11)	0.441(30)	2.9	3.9
$ZnCr_2O_4$	0.029(13)	0.2615(2)	0.324(18)	0.247(17)	0.481(43)	2.7	4.2
$ZnAl_2O_4$: MoKα_1 radiation							
900	−0.001(6)	0.2645(3)	0.349(23)	0.201(44)	0.369(71)	4.5	5.9
1000	0.003(6)	0.2643(3)	0.329(21)	0.196(40)	0.356(63)	4.2	5.2
1100	0.016(6)	0.2642(3)	0.339(22)	0.227(42)	0.326(66)	3.9	5.8
1200	0.025(6)	0.2640(3)	0.357(21)	0.201(40)	0.419(63)	4.3	5.2
1300	0.040(6)	0.2639(3)	0.330(21)	0.236(39)	0.425(63)	3.7	5.9
$ZnAl_2O_4$: CuKα_1 radiation							
900	0.002(9)	0.2643(3)	0.51(5)	0.39(7)	0.39(9)	2.8	5.3
1000	0.013(8)	0.2641(3)	0.54(5)	0.47(6)	0.48(8)	2.4	6.2
1100	0.020(6)	0.2641(2)	0.41(4)	0.32(5)	0.39(6)	2.1	4.5
1200	0.027(8)	0.2639(3)	0.51(4)	0.40(6)	0.52(8)	2.5	4.6
1300	0.048(8)	0.2639(3)	0.51(4)	0.43(6)	0.54(8)	2.8	5.8

Table 6. Powder XRD structure factor refinements with half-ionized scattering curves

Sample/°C	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R (%)	wR (%)
BGI (Mo radiation)							
$MgCr_2O_4$/900	−0.008(11)	0.2610(2)	0.371(41)	0.285(10)	0.440(27)	2.2	3.8
$MgCr_2O_4$/1100	0.002(10)	0.2611(2)	0.367(44)	0.236(10)	0.424(29)	2.2	3.9
$MgCr_2O_4$/1300	0.007(12)	0.2614(2)	0.466(50)	0.300(11)	0.473(30)	2.7	3.9
$ZnCr_2O_4$	0.022(14)	0.2615(2)	0.334(18)	0.249(17)	0.516(43)	2.7	4.2
UCLA (Cu radiation)							
$MgCr_2O_4$/900	−0.029(12)	0.2607(3)	0.32(7)	0.12(3)	0.41(7)	2.0	2.9
$MgCr_2O_4$/1100	0.002(10)	0.2607(4)	0.43(9)	0.18(3)	0.31(7)	2.6	3.2
$MgCr_2O_4$/1300	0.007(12)	0.2607(3)	0.43(7)	0.26(3)	0.46(6)	1.8	2.7

occurring Cr-bearing spinels, Della Giusta et al. (1986) pointed out that that half-ionized scattering curves give a better fit to the (222)reflection. Of the low $\sin\theta/\lambda$ reflections, it is the rather weak (222)reflection whose structure factor is most sensitive to the contribution from oxygen, and which therefore gives the clearest indication of the ionization level. Our data confirm this finding. However, as regards the refined parameters, the results using the half-ionized model differ either slightly (for the chromites – Table 6) or negligibly (in Fe_3O_4 and $ZnAl_2O_4$ only the temperature factors change) from those from the neutral-atom model (and, as might be expected, fall in between the neutral-atom and fully-ionized models). For $MgCr_2O_4$, the mean x of the BGI data decreases to 0.000; this is not necessarily a better results than the mean of 0.005 from the neutral-atom model, as some disordering in $MgCr_2O_4$ is possible (e.g., from the parameters in O'Neill and Navrotsky (1984, Table A1) x is calculated to vary from 0.001 at 900° C to 0.003 at 1300° C). The UCLA 900° C datum becomes more than two standard deviations negative. For $ZnCr_2O_4$, x becomes larger, and thus less preferable.

In summary: the use of half-ionized scattering curves is justified only by the improved fit it gives to just one reflection (which anyway might be due to some other kind of imperfection in the powder XRD model such as non-spherical electron density); and, empirically, the refined crystallographic parameters do not appear more accurate than those from the more customary neutral atom model.

Results from Refinements Using the Rietveld Method

Simultaneous refinement of diffraction pattern parameters and structure parameters, as done in the Rietveld refinement method (Rietveld 1969), has both advantages and disadvantages. A major advantage is the simplified treatment of the generally severe peak overlap occurring with structures of lower symmetry and larger unit cell dimensions than spinels. A potential disadvantage is that with real (and therefore imperfect) data, the minimum disagreement between the observed and calculated patterns may not coincide with the minimum disagreement between the observed and calculated structure factors. The present data provide a good opportunity to test whether this possibility has any significant effects on results.

Table 7. Powder XRD refinements, from data collected at BGI (MoKα_1 radiation), using the Rietveld method. Neutral atom scattering curves

Sample/°C	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R_{Bragg} (%)	R_F (%)
Original background							
$MgCr_2O_4$/900	−0.001(4)	0.2617(1)	0.39(4)	0.26(1)	0.25(3)	4.29	4.87
$MgCr_2O_4$/1100	0.005(4)	0.2616(1)	0.35(3)	0.21(1)	0.25(3)	3.94	4.24
$MgCr_2O_4$/1300	0.003(4)	0.2620(1)	0.42(4)	0.26(1)	0.24(3)	4.38	4.69
$ZnCr_2O_4$	−0.010(8)	0.2622(2)	0.31(2)	0.18(2)	0.29(4)	3.61	4.75
Fe_3O_4	–	0.2550(2)	0.38(2)	0.55(2)	0.54(4)	2.90	4.85
Original background less 7 to 18° 2θ (i.e., less the (111), (220), (311) and (222) reflections)							
$MgCr_2O_4$/900	−0.002(5)	0.2615(1)	0.39(4)	0.27(1)	0.38(3)	2.97	2.91
$MgCr_2O_4$/1100	0.012(6)	0.2616(1)	0.41(4)	0.23(1)	0.39(3)	3.05	3.40
$MgCr_2O_4$/1300	0.010(6)	0.2618(1)	0.48(4)	0.28(1)	0.42(3)	2.79	2.62
$ZnCr_2O_4$	0.018(9)	0.2616(2)	0.31(2)	0.22(2)	0.48(4)	3.41	4.68
Fe_3O_4	–	0.2553(2)	0.38(2)	0.54(2)	0.58(4)	3.44	4.11
Background subtracted							
$MgCr_2O_4$/900	0.010(5)	0.2612(2)	0.43(4)	0.23(1)	0.31(4)	3.07	2.75
$MgCr_2O_4$/1100	0.003(5)	0.2615(2)	0.35(5)	0.20(1)	0.26(3)	3.51	3.40
$MgCr_2O_4$/1300	0.008(5)	0.2616(2)	0.41(4)	0.25(1)	0.30(4)	3.60	3.25
$ZnCr_2O_4$	−0.008(9)	0.2619(2)	0.27(2)	0.15(2)	0.33(5)	3.09	3.75
Fe_3O_4	–	0.2549(2)	0.40(2)	0.55(2)	0.60(4)	2.43	3.51

Table 8. $ZnAl_2O_4$ powder XRD refinements, using the Rietveld method. Results from data collected at BGI (MoKα_1 radiation)

Sample (°C)	x	u	B_{tet} (Å^2)	B_{oct} (Å^2)	B_{ox} (Å^2)	R_{Bragg} (%)	R_F (%)
Original background							
900	0.013(2)	0.2646(1)	0.339(13)	0.242(24)	0.183(35)	3.13	4.82
1000	0.013(2)	0.2642(1)	0.321(14)	0.255(26)	0.291(36)	2.93	5.79
1100	0.024(2)	0.2642(1)	0.349(13)	0.283(24)	0.266(36)	2.55	4.60
1200	0.034(3)	0.2641(1)	0.329(15)	0.239(26)	0.331(39)	2.48	5.67
1300	0.047(2)	0.2640(1)	0.335(14)	0.274(24)	0.359(37)	2.35	3.97
Background subtracted							
900	0.010(3)	0.2646(2)	0.318(16)	0.234(27)	0.269(43)	3.04	4.30
1000	0.016(3)	0.2644(2)	0.305(16)	0.230(28)	0.334(45)	2.86	4.31
1100	0.024(3)	0.2643(2)	0.331(16)	0.253(29)	0.315(47)	2.70	4.65
1200	0.036(4)	0.2641(2)	0.319(18)	0.220(30)	0.451(52)	2.89	5.53
1300	0.050(3)	0.2641(2)	0.301(17)	0.246(28)	0.382(47)	2.62	4.56

Accordingly, we have also refined the data of the present study using the Rietveld method. We use the program DBW version 3.2 (Wiles and Young 1981). Previous comparisons between Rietveld and structure factor refinements are given in O'Neill et al. (1991) for a series of $NiAl_2O4$ spinels equilibrated at different temperatures, and in O'Neill et al. (1992) for a series of $MgFe_2O_4$ spinels, in which papers may be found full details of the models and refinement procedures. For the Mo data a Pearson VII peak profile functions was used, whereas for the Cu data a pseudo-Voigt function was found to give a better fit. Note that in addition to the different minimization strategies, small differences between the two methods of data treatment may ensure from use of different peak profile functions, and also from the capability of the Rietveld program to vary the peak profile parameters smoothly as a function of 2θ, and to incorporate an asymmetry correction.

The results from the Rietveld refinements of the BGI/Mo data are reported in Table 7 (chromites and Fe_3O_4) and Table 8 ($ZnAl_2O_4$). In general, the refined parameters are very similar to those from the structure factor refinements. The reported estimated standard deviations (esd's) are, however, consistently lower, particularly the esd's of the x-values, which are typically only half those from the structure factor refinements. There is theoretical reason to believe that this may be due to the effects on the Rietveld refinement of serial correlation in the data (e.g., Hill and Flack 1987; Post and Bish 1989), as judged from our consistently low Durban-Watson d statistic (see Ross et al. 1990); on the other hand, the lower esd's from the Rietveld refinements are invariably in good agreement with estimates from the internal consistency and reproducibility of the data (here and also in the studies of O'Neill et al. 1991, 1992). The cause of this paradox is not known.

Of all the spinels for which we have comparisons between structure-factor refinement and Rietveld refinement of the same Mo data collected at BGI, the greatest difference occurs for the chromites (cf. results in Table 7 with those in Table 2). Although the x-values are effectively indistinguishable, the u-values from the Rietveld refinements are on average 0.0006 (2 to $3\,\sigma$) greater, and the B_{ox} values 0.23 Å^2 ($\sim 6\,\sigma$) lower. The disagreement is due to a combination of factors, mainly the inability to fit the low-angle peak shapes satisfactorily, and the greater weighting given these relatively intense low-angle reflections in the Rietveld procedure compared to the structure factor refinement. Thus eliminating the first four reflections (111), (220), (311) and (222), from the Rietveld refinement (Table 7) gives results which are much closer to those from the structure factor refinements, and with much lower R factors. That this is primarily a matter of weighting is shown by the fact that removing the same four reflections from the structure factor refinements changes neither the values of the refined parameters nor the R factors significantly. The low angle peaks are highly asymmetric, and there is also a consistent hump in the background in this region which cannot be fit entirely satisfactorily (see also Ross et al. 1990). These problems are greater for the data collected with Mo radiation, because of the shift of the pattern to low angles.

The low B_{ox} values from the Rietveld refinement are partly due to the greater weight given to the (222)reflection. This is the reflection which is sensitive the degree of ionization of the oxygen, and is best fit by the half-ionized scattering curve (Della Giusta et al. 1986). Using fully-ionized scattering curves in the Rietveld refinements results in values of B_{ox} which are similar to those from the structure factor refinements, while using half-ionized scattering curves gives intermediate values.

The reason that the chromites are more affected than other spinels by the different weighting given to the low $\sin\theta/\lambda$ reflections, is that the (111) and (222)reflections are much more intense. In $ZnAl_2O_4$ these reflections are very weak, so that their relative uncertainty from counting statistics is large, and they have fairly minimal weight in both refinement methods. Thus there are no significant differences between the structure factor and Rietveld refinements (Tables 3 and 8).

For the chromites and Fe_3O_4 we find empirically that subtracting most of the background from the BGI/Mo raw data before inputting into the Rietveld program results in slightly but consistently lower R_{Bragg} and R_{F}, and slightly better agreement with both the external constraints and with the structure factor refinements (Table 7). Similar slight improvements following this procedure have also been observed in Rietveld refinements of $NiAl_2O_4$ (O'Neill et al. 1991) and $MgFe_2O_4$ (O'Neill et al. 1992), but there is negligible difference in the results for $ZnAl_2O_4$. Background subtraction was originally tried with the aim of improving the fit to the background in the 6 of 12° 2θ region, but it is also a simple if ad hoc way of giving less weight to the intense but poorly fit lower angle reflections. Eliminating the lowest angle reflections from the refinement, and altering the weighting by using the background subtraction procedure, are easily carried-out tests of the Rietveld method in other situations.

The low-angle peak asymmetry is less of a problem with the Cu measurements, and therefore it is not surprising to find that Rietveld refinement of both sets of Cu data produce trivial differences from the structure factor refinements, provided the same peak profile function is employed. Estimated standard deviations from the Rietveld refinements are approximately a factor of three lower, presumably due to serial correlation, but, as noted above, these lower esd's seem to agree better with estimates from the external constraints. Trials of the BGI/Cu data with the background subtraction procedure showed that this tended to increase the R factors, and also resulted in somewhat anomalous values for the B parameters. The likely reason for this is that, for the BGI/Cu data, the intensities of the high 2θ reflections, which are given a greater relative weight by this procedure, are subject to additional experimental errors from the absorption effect.

Statistical Analysis of the Refinement Results

From the 94 different structure determinations reported above (plus consideration of literature data in the case of magnetite) a "preferred" set of structure parameters may be defined. These preferred values, given in Table 9 are the best estimates of the correct value for each refined parameter for the 8 different spinel samples reported here. These are basically averages excluding those values that are anomalous or unreliable due to some

Table 9. Preferred values of spinel structure parameters

Spinel (°C)	a(Å)	x	u	B_{tet}[a]	B_{oct}[a]	$B_{(\mathrm{ox})}$[a]
$MgCr_2O_4$	8.3341(2)	0.01(1)	0.2612(2)	0.41(5)	0.26(2)	0.42(3)
$ZnCr_2O_4$	8.3271(2)	0.00(2)	0.2614(2)	0.32(2)	0.23(2)	0.52(4)
Fe_3O_4	8.3970(1)	–	0.2550(2)	0.46(3)	0.59(3)	0.64(6)
$ZnAl_2O_4$						
900	8.0865(1)	0.011(7)	0.2642(2)	0.31(4)	0.26(4)	0.36(6)
1000	8.0867(1)	0.018(7)	0.2640(2)	0.31(4)	0.26(4)	0.36(6)
1100	8.0871(1)	0.027(6)	0.2640(2)	0.31(4)	0.26(4)	0.36(6)
1200	8.0976(1)	0.037(6)	0.2639(2)	0.31(4)	0.26(4)	0.36(6)
1300	8.0884(1)	0.053(6)	0.2638(2)	0.31(4)	0.26(4)	0.36(6)

[a] Isotropic temperature factors in units of Å^2

identified or unidentified systematic error in the data or model. Due to the large number of refined data sets, changing the weights or exclusion criteria of the individual contributing values has little effect on the resulting preferred values. The estimated uncertainties included in Table 9 are a combination of the least-squares estimated uncertainties from a single experiment, and the scatter in the values from the different refinements on the same sample. They are a guide to the expected accuracy of such powder-data refinements but do not affect the statistical analysis carried out below.

In addition to establishing the best set of structural parameters for these spinels, Table 9 allows comparison of each refinement with what is presumed to be the most nearly correct answer, in order to draw conclusions about the individual techniques themselves. This comparison is conveniently performed with a χ^2 test:

$$\chi_k^2 = \sum_{ij} ([x_{ijk} - p_i]/\sigma_{ijk})^2 \qquad (7)$$

where x_{ijk} is the i-th structural parameter of the j-th spinel analyzed using the k-th refinement method, σ_{ijk} is the estimated standard least-squares error in this parameter and p_i is the preferred value of the i-th parameter. Each spinel has up to 5 structure parameters (degree of inversion, oxygen location and temperature factors). There are 14 different refinement methods presented in this paper applied to as many as 10 samples for some cases and as few as one sample in others (such as the one single crystal experiment). The results of the χ^2 tests, conveniently compared as rms(χ), are reported in Table 10.

The rms χ values ought to tend towards 1.00. That some obviously do not indicates one (or both) of two possibilities: either there are clearly anomalous refinement values resulting from recognized or cryptic systematic errors, or the esd's furnished by the refinement programs are in error. The following conclusions may be drawn from this table:

a) Mo data with its greater 2θ range and smaller absorption coefficients produce superior results compared to Cu data, irrespective of the refinement method.

b) Artificially constraining the temperature factors (2*B* and 1*B* models) results in systematic errors in the remaining variables and should be avoided.

c) Analyses of the individual contributions to the χ^2 sums demonstrate that even with the recommended separate temperature factors, it is largely the scatter in the temperature factors that cause the high χ^2 sums, at least in the structure-factor refinements. This is due to the fact that temperature factors tend to "absorb" systematic errors in the data, as is easily demonstrated for systematic errors related to absorption (surface roughness, too thin a sample, or absorption correction for transmission geometry) and is one of the reasons why Mo radiation gives better results. The error in determination of temperature factors using the techniques of this paper may be as large as 0.2 Å using Cu-radiation and as much as 0.1 Å^2 using Mo-radiation (as was encountered with Fe_3O_4). Even when accurate measurement of temperature factors is not the primary goal, the covariance between the refined parameters makes temperature factor determination important.

d) Use of half- or fully-ionized scattering curves raises χ^2 sums in most cases but only marginally, and overall has little to recommend it.

e) Except as noted, the rms χ values given in Table 10 for the Rietveld refinements are uncorrected for serial correlation. As has been well documented elsewhere, these esd's are too small leading to rms χ of mostly over 2. Correction for serial correlation (Bérar and Lelann 1991) reduces rms χ to values similar to those found for structure factor refinements. Interestingly, the precision, as indicated by the reproducibility of Rietveld refinement parameters from the same or a closely related series of samples, approaches the (uncorrected) Rietveld esd's.

Table 10. Chi-square test of the different refinement methods

Method[a]	Samples	var	rms(χ)	Comments
Mo *B SF* 3*B*	10	49	1.66	
Mo *B SF* 3*B*	10	46	1.29	excluding Fe_3O_4 B's
Mo *B SF* 2*B*	5	19	3.22	syst. error in *x*
Mo *B SF* 1*B*	5	14	3.65	syst. error in *x, u*
Mo sing. xtal	1	5	1.44	
Mo *B SF* ion	9	45	1.47	full-ion scat. curves
Mo *B SF* ion	4	20	1.45	half-ion scat. curves
Mo *B Rt*	10	49	2.87	
Mo *B Rt*>18	5	24	2.44	beginning at 18° 2θ
Mo *B Rt*−BG	10	49	1.95	background subtracted
Cu *C* SF	10	49	1.52	
Cu *C SF* ion	3	15	1.86	half-ionized scat. curves
Cu *C Rt*	1	5	5.34	uncorr. σ's
Cu *C Rt*	1	5	1.66	corrected σ's
Cu *B SF*	5	25	2.56	
Cu *B SF* ion	5	25	2.37	full-ion scat. curves

[a] Method: Mo or Cu = radiation used, *B* or *C* = BGI or UCLA, *SF* or *Rt* = structure factor or Rietveld, 3*B*, 2*B*, 1*B* refer to temperature factor model (= 3*B* when not otherwise indicated), other method variables indicated under comments

f) The rms χ value of 1.44 for the Mo/single-crystal refinement does not indicate problems with this technique; the higher-than-unity value is largely due to the esd's being so very small that tiny variations in the preferred values greatly effect χ^2.

Conclusions

The results of this study indicate that powder XRD may be used to determine all crystal structural parameters of spinels to quite high accuracy. Specifically, cell dimensions may be routinely determined within an error of ≈ 0.0002, and atomic fractional coordinates (oxygen u-parameter) within an error of ≈ 0.0002, leading to interatomic distance esd's of 0.002 to 0.003 Å. One immediate application of these more accurate interatomic distances will be an improved accuracy of spinel "ionic radii" (e.g., O'Neill and Navrotsky 1983).

The values of the isotropic temperature factors in a spinel XRD refinement may not be of immediate interest, but are nevertheless important because of the correlation of the inversion parameter, x, with the difference $(B_{tet} - B_{oct})$. Unless it fortuitously happens that $B_{tet} = B_{oct}$ in a spinel, constraining B_{tet} and B_{oct} to be equal (1B or 2B models) will result in systematic errors, not just loss of precision, in the determination of x (Table 2). The systematic error may be many times the quoted esd in x. The effects of the correlation between x and $(B_{tet} - B_{oct})$ may be minimized if the values of B are determined as accurately as possible, i.e., by collecting data over a wide a range of θ/λ as possible. This emphasizes the advantage in using the shorter wavelength Mo radiation.

The effectiveness of normal X-ray diffraction methods in determing cation distributions depends primarily on the difference between the atomic numbers of the cations concerned. In Fig. 5 we show a plot of the inverse of the atomic number difference versus the mean esd's obtained by Rietveld refinements of several series of spinels carried out under nearly identical conditions at the BGI with Mo radiation. We find that:

$$\mathrm{esd}(x) = 0.058/|N_A - N_B| \qquad (8)$$

This suggests that the powder XRD method should be useful for distinguishing the major features of the cation distribution in spinel solid solutions even when near-neighbour atoms from the periodic table are involved.

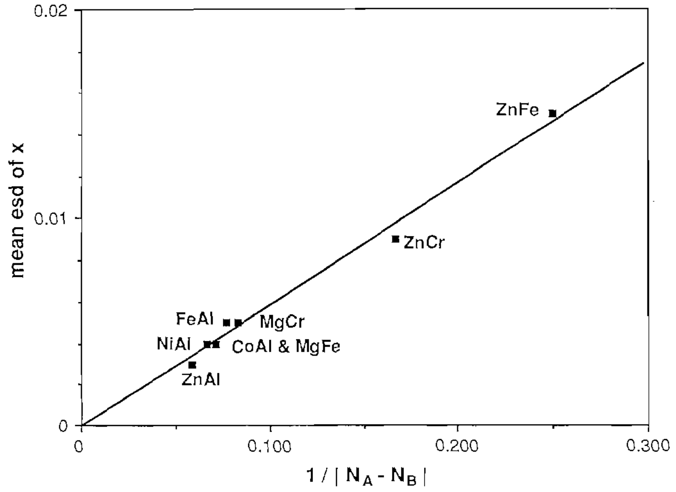

Fig. 5. The mean of the estimated standard deviations (esd's) of the inversion parameter (x) in some simple oxide spinels, from Rietveld refinements of data collected at the BGI with Mo radiation, versus the inverse of the absolute difference in the atomic number of the two cations. Data from: $MgCr_2O_4$, $ZnCr_2O_4$, $ZnAl_2O_4$ (all this study), $MgFe_2O_4$ (O'Neill et al. 1992), $ZnFe_2O_4$ (O'Neill 1992) and $FeAl_2O_4$ and $CoAl_2O_4$ (O'Neill, unpublished)

Acknowledgements. We thank Charles Ross for much help with the XRD work at Bayreuth.

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