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Comment on 'Order–disorder phase transition induced by swift ions in $MgAl_2O_4$ and $ZnAl_2O_4$ spinels' by D. Simeone et al., J. Nucl. Mater. 300 (2002) 151–160

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Abstract

In this letter, structure factor calculations and computer simulated powder X-ray diffraction patterns are used to challenge conclusions reached in a recent study by D. Simeone et al. regarding radiation-induced phase transformations in $MgAl_2O_4$ spinel. Based on experimental results presented by D. Simeone et al. and previously by other researchers, and based on the structure factor results presented here, spinel most likely succumbs to a phase transformation under irradiation that involves a profound change in the arrangement of cations in the lattice. The space group is modified by the transformation and the new, metastable structure is most likely a defective rocksalt structure. These conclusions are at odds with the description of the spinel metastable phase offered by Simeone et al.

In a recent study published by Simeone et al. [1], the authors observed an order–disorder transition in $MgAl_2O_4$ under swift ion irradiation. Their report cited two previous studies wherein an irradiation-induced structural change of $MgAl_2O_4$ had been observed [2,3]. The original observation of an irradiation-induced structural change in spinel was reported by Yu et al. [4] and it was discussed further by Sickafus et al. [5], Bordes et al. [6], and several other authors. All studies previous to Simeone et al. attributed the irradiation-induced transition in spinel to a phase transformation, complete with changes in cation arrangement, lattice parameter, and space group symmetry. In each of these studies, it was concluded that the phase transformation involves not only disordering of cations, but a rearrangement of cations onto interstices that are normally unoccupied in spinel. Cation disordering without substantial interstice rearrangement was observed in high-dose neutron irradiated $MgAl_2O_4$ single crystals by Sickafus et al. [7]. It is believed that the neutron irradiation did not induce the phase transformation often observed in ion irradiation experiments, because high temperatures (658–1023 K) were used during neutron irradiation, which facilitated significant lattice recovery and prevented the transformation from initiating. Simeone et al. proposed that the observed ion-irradiation-induced transition can be explained in terms of cation disordering, without necessity for a change in structure, lattice parameter, or space group symmetry. The purpose of this comment is to point out that in the ion irradiation study by Simeone et al., an erroneous interpretation of the irradiation-induced spinel structure was made, as will be elucidated in this comment.

Ordered spinel is a cubic structure with $F\frac{4_1}{d}\bar{3}\frac{2}{m}$ ($Fd\bar{3}m$) space group (SG) symmetry. The unit cell of $MgAl_2O_4$ consists of 56 atoms: 8 Mg atoms on Wycoff equipoint 8a; 16 Al atoms on equipoint 16d; and 32 O atoms in a pseudo-cubic-closed-packed arrangement on equipoint 32e (assuming a setting for the SG with origin at $\bar{4}3m$). The repeat unit of the cubic cell is approximately $a = 0.808$ nm.

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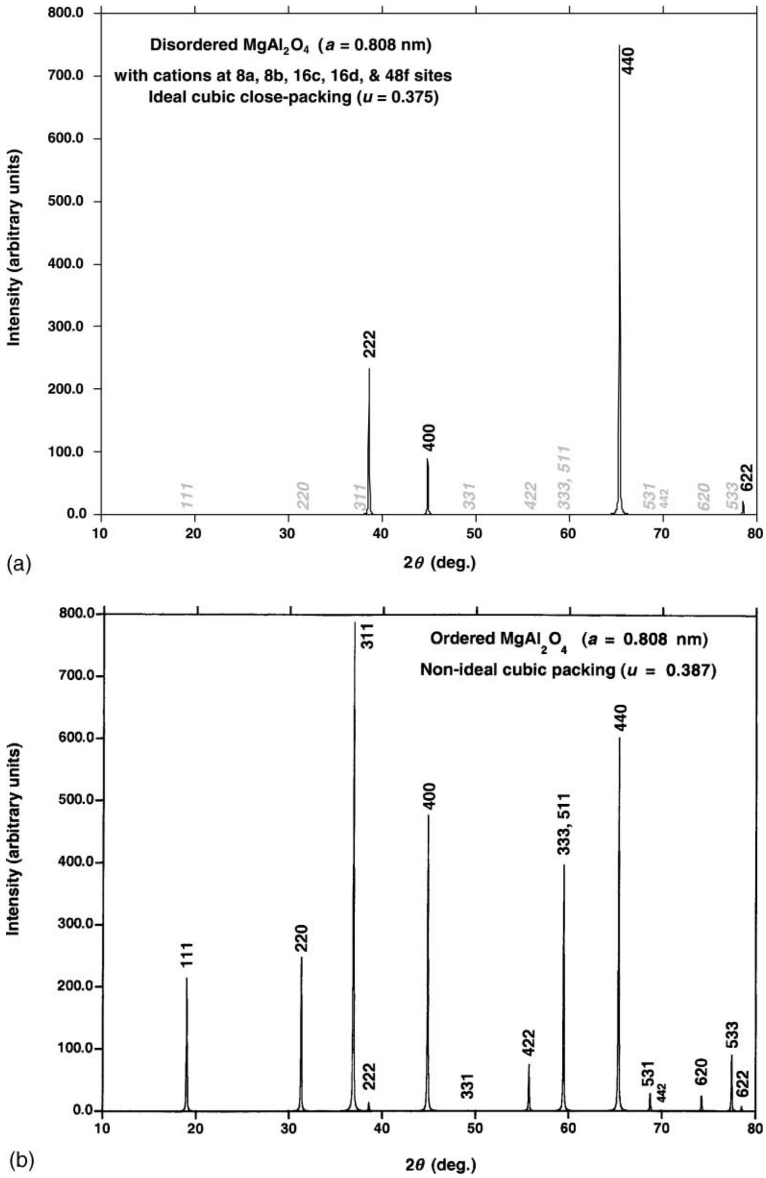


Fig. 1. Simulated X-ray powder diffraction patterns for different model $MgAl_2O_4$ structures: (a) a fully ordered spinel cation sublattice (cations on 8a and 16d Wycoff equipoints in space group Fd$\bar{3}$m), along with an 'ideal' fcc anion sublattice ($a = 0.808$ nm, $u = 0.375$). (The $\{4\,4\,2\}$ reflection is shown in gray because it is extinct in this hypothetical spinel model. The only contribution to the structure factor at this reciprocal lattice position is from the anion sublattice. When the ideal fcc anion model is invoked, no intensity is obtained at this 2θ position. The reason for this is that, with respect to the ideal anion sublattice, the assumption of $a = 0.808$ nm for the unit cell of spinel doubly redundant. The correct description for the anion sublattice is Fm$\bar{3}$m, $a = 0.404$ nm. Thus, all $\{h\,k\,l\}$ indices for anion-sublattice-only scattering in Fd$\bar{3}$m should be divided by two to get the correct $\{h\,k\,l\}$ notation for the anion sublattice. But then, a $\{4\,4\,2\}$ reflection becomes $\{2\,2\,1\}$, which is a forbidden reflection in Fm$\bar{3}$m); (b) a fully ordered spinel cation sublattice (cations on 8a and 16d Wycoff equipoints in space group Fd$\bar{3}$m), along with a non-ideal anion sublattice ($a = 0.808$ nm, $u = 0.387$); (c) a fully disordered spinel cation sublattice (cations on 8a and 16d Wycoff equipoints in space group Fd$\bar{3}$m), along with an 'ideal' fcc anion sublattice ($a = 0.808$ nm, $u = 0.375$) (the $\{4\,4\,2\}$ reflection is shown in gray because it is extinct as in (a)); (d) a fully disordered spinel cation sublattice (cations on 8a and 16d Wycoff equipoints in space group Fd$\bar{3}$m), along with a non-ideal anion sublattice ($a = 0.808$ nm, $u = 0.383$); (e) a fully disordered spinel cation sublattice (cations on 8a and 16d Wycoff equipoints in space group Fd$\bar{3}$m), along with a non-ideal anion sublattice ($a = 0.808$ nm, $u = 0.387$); (f) a metastable 'rocksalt-like' structure consisting of a disordered cation sublattice in space group Fm$\bar{3}$m with cations randomly arranged on the 4a Wycoff equipoint, along with an 'ideal' fcc anion sublattice ($a = 0.404$ nm); (g) a metastable 'sphalerite-like' structure consisting of a disordered cation sublattice in space group F$\bar{4}$3m with cations

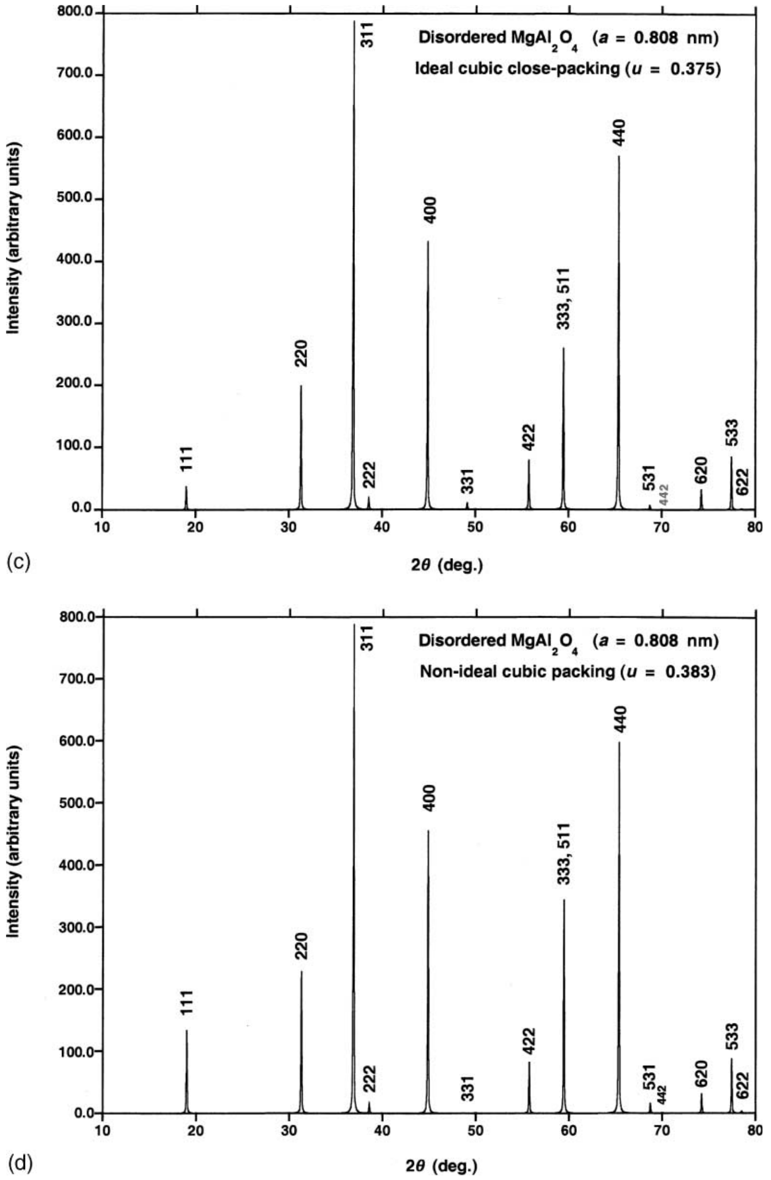
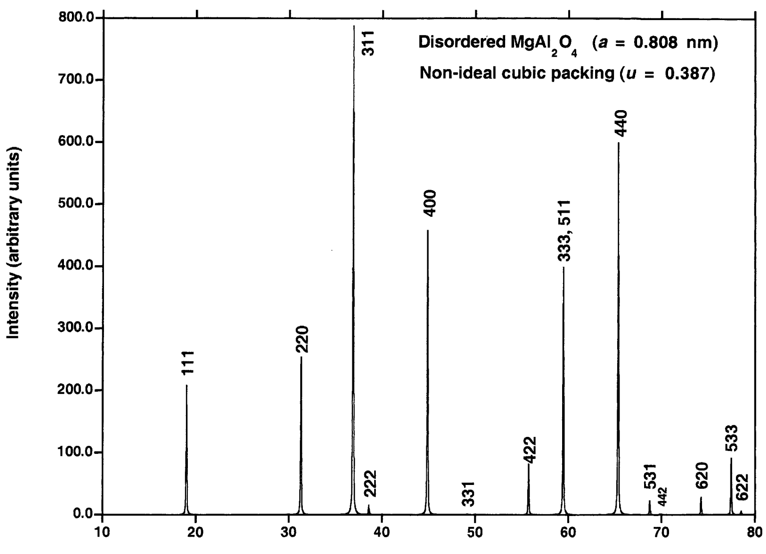
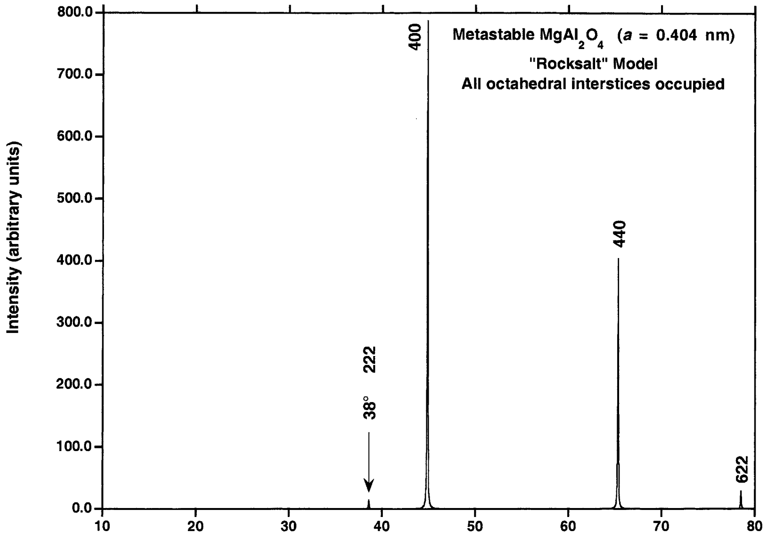


Fig. 1 (*continued*) randomly arranged on the 4c Wycoff equipoint, along with an 'ideal' fcc anion sublattice ($a = 0.404$ nm); (h) a metastable 'anti-fluorite-like' structure consisting of a disordered cation sublattice in space group Fm$\bar{3}$m with cations randomly arranged on the 8c Wycoff equipoint, along with an 'ideal' fcc anion sublattice ($a = 0.404$ nm); (i) a metastable '1/2 octahedral/all tetrahedral' structure consisting of a disordered cation sublattice in space group F$\bar{4}$3m with cations randomly arranged on the 4b and 4c Wycoff equipoints, along with an 'ideal' fcc anion sublattice ($a = 0.404$ nm); (j) a metastable 'all interstices' structure consisting of a disordered cation sublattice in space group Fm$\bar{3}$m with cations randomly arranged on the 4b and 8c Wycoff equipoints, along with an 'ideal' fcc anion sublattice ($a = 0.404$ nm); (k) a metastable 'accidental extinction' structure consisting of a disordered cation sublattice in space group Fd$\bar{3}$m with cations randomly arranged on 8a, 8b, 16c, 16d, and 48f Wycoff equipoints, along with an 'ideal' fcc anion sublattice ($a = 0.808$ nm, $u = 0.375$); (l) a metastable structure consisting of a disordered cation sublattice in space group Fd$\bar{3}$m with cations randomly arranged on 8a, 8b, 16c, 16d, and 48f Wycoff equipoints, along with a non-ideal anion sublattice ($a = 0.808$ nm, $u = 0.383$).

Upon irradiation, atoms are displaced from their lattice sites and the spinel structure takes on a disordered appearance. Many researchers have observed that the lattice parameter of the irradiated spinel is



(e)



(f)

Fig. 1 (*continued*)

reduced by a factor of two ($a_{\mathrm{irrad}} = 0.404$ nm). Simeone et al. interpreted their diffraction observations from the irradiation-induced 'disordered' spinel as an 'order-disorder phase transition mixing of the A and B cations in AB_2X_4 spinels'. Simeone et al. go on to say 'In the case of $MgAl_2O_4$, an extinction appears as in KCl due to similarities between atomic for {m} factors of these ions i.e., Mg and Al, leading to a division by two of the unit cell'. This analogy between spinel and KCl is invalid, as can be appreciated by performing diffraction structure factor calculations.

Fig. 1 shows simulated powder X-ray diffraction patterns for a fully ordered $MgAl_2O_4$ spinel (Fig. 1(a) and (b)), as well as for a hypothetical fully disordered $MgAl_2O_4$ spinel in which the Mg and Al cations occupy randomly the 8a and 16d equipoints in the $Fd\bar{3}m$ unit cell (Fig. 1(c)–(e)). Oxygen ions in spinel are situated at equipoint 32e. The fractional coordinates of this equipoint are dependent on a single parameter known as the oxygen or u parameter. For the fully ordered spinel structure factor calculations reported here, values of $u = 0.375$ (Fig. 1(a)) and 0.387 (Fig. 1(b)) were used (assuming a setting for the SG with origin at $\bar{4}3m$), while for the fully disordered spinel calculations, values of $u = 0.375$ (Fig. 1(c)), 0.383 (Fig. 1(d)), and 0.387 (Fig. 1(e)) were used (same SG setting). The oxygen para-

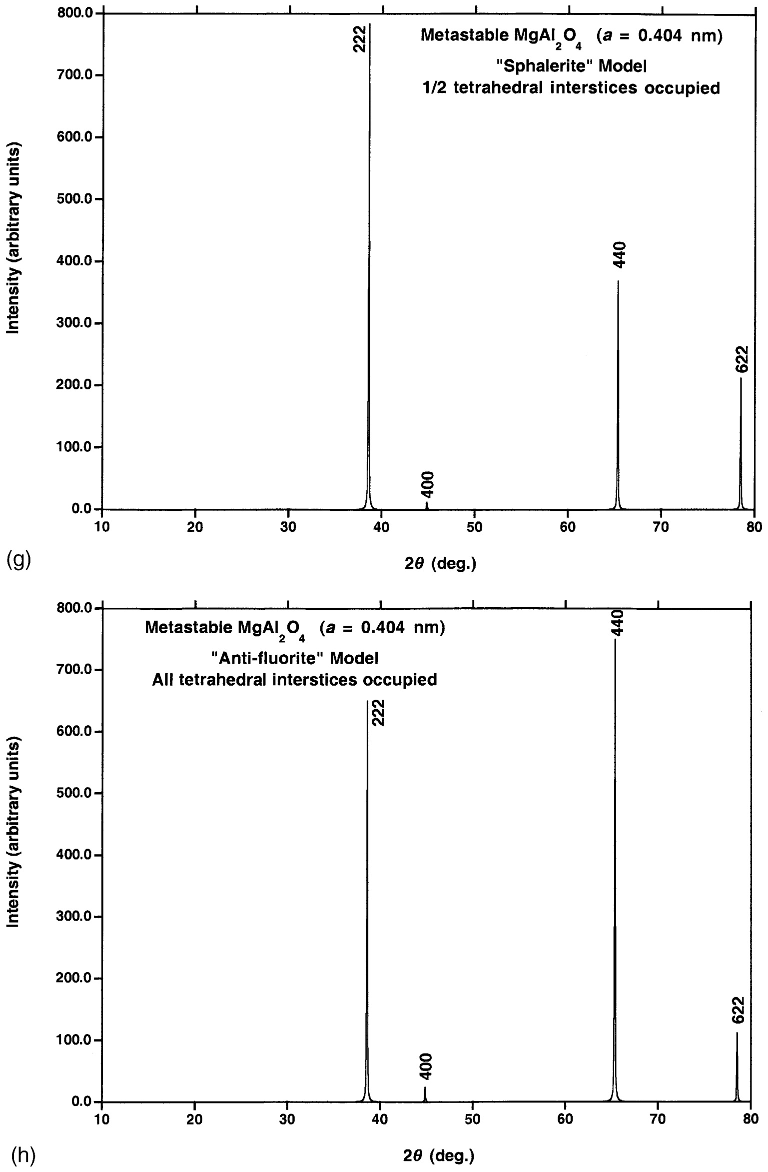


Fig. 1 (*continued*)

meter $u = 0.375$ is a hypothetical value for a so-called 'ideal' spinel crystal in which all octahedral and tetrahedral interstices are regular. When u deviates from the ideal value, the structure is referred to as non-ideal, because the octahedral and tetrahedral interstices are irregular, and there are three O–O first neighbor bonding distances instead of one (in ideal spinel, an oxygen ion is surrounded by 12 equidistant first nearest neighbor oxygen ions). The additional oxygen parameter values considered in this report, namely $u = 0.387$ and 0.383, were chosen to be consistent with measured values for ordered and disordered spinel structures, respectively [7]. The quantitative predicted intensities for the diffraction patterns in Fig. 1(a)–(e) are shown in Table 1. The diffraction simulation results for ordered spinel ($u = 0.387$) (Fig. 1(b) and Table 1) are in good agreement with published powder diffraction data for $MgAl_2O_4$ spinel (see, for instance JCPDS file 21–1152 [8]). The X-ray diffraction simulations in Fig. 1 and Table 1 were performed assuming CuK_α radiation ($\lambda = 1.542$ Å). The structure factors and the corresponding diffracted intensities were calculated based on a powder X-ray experiment, such that the scattered intensity, I_{hkl}, from Bragg planes $\{h,k,l\}$ is given by

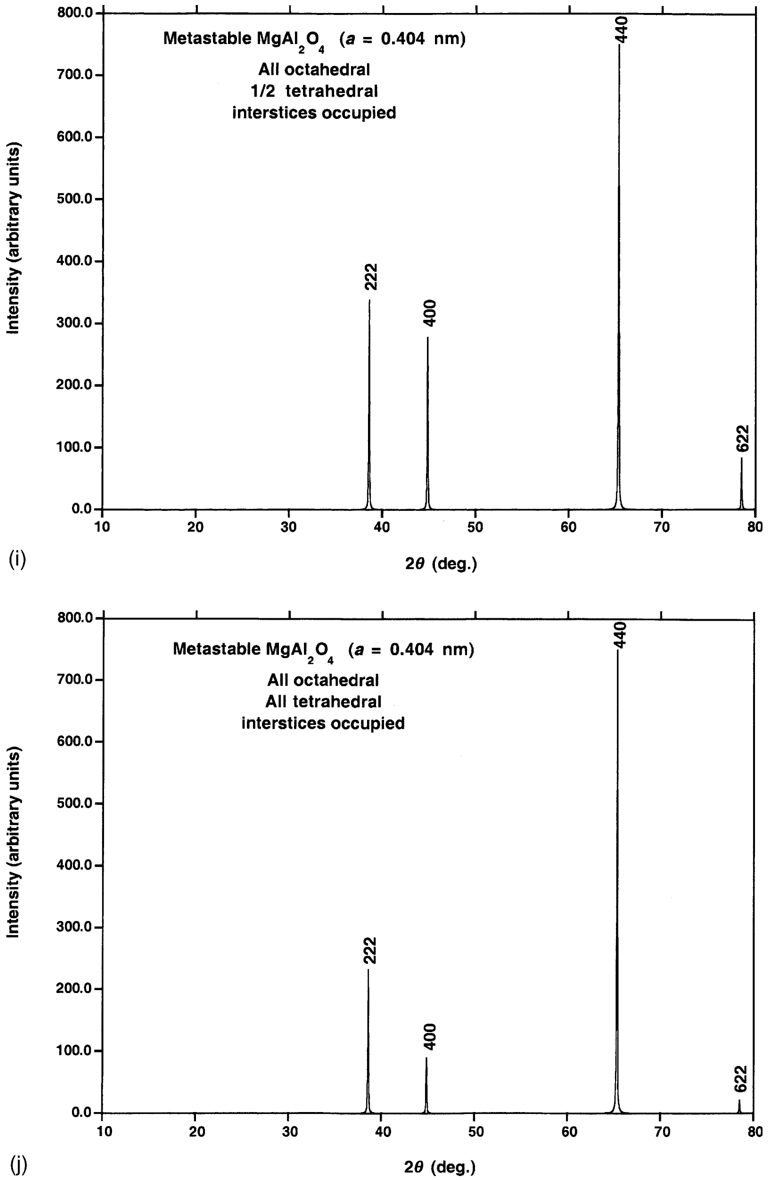


Fig. 1 (*continued*)

$I_{hkl} = |F_{hkl}^2| m_{hkl}((1+\cos^2 2\theta_{hkl})/\sin^2\theta_{hkl}\cos\theta_{hkl})$, where F_{hkl} is the structure factor for Bragg reflection $\{h,k,l\}$, given by $F_{hkl} = \sum_n^{\text{unit cell}} f_n e^{2\pi i(hx_n+ky_n+lz_n)}$; f_n is the atomic form factor for atom n; (x_n, y_n, z_n) are the fractional coordinates of the nth atom in the unit cell; m_{hkl} is the *multiplicity* of reflection $\{h,k,l\}$; and $(1+\cos^2 2\theta_{hkl})/\sin^2\theta_{hkl}\cos\theta_{hkl}$ is the Lorentz polarization factor for scattering at angle θ_{hkl}. The scattering angle θ_{hkl} is determined from Bragg's equation, $\lambda = 2d_{hkl}\sin\theta_{hkl}$, where lattice spacing $\{h,k,l\}$ for a cubic unit cell is given by $d_{hkl}^{\text{cube}} = a_{\text{cube}}/\sqrt{h^2+k^2+l^2}$. The X-ray atomic form factors, f_n, for Mg, Al, and O were obtained from the International Tables for Crystallography, vol. C, Table 6.1.1.4 [9]. The form factors in this table are based on an analytical fit to atomic form factors calculated using a Hartree–Fock formalism [10]. In the diffraction simulations presented here, form factors for Mg^{2+}, Al^{3+}, and O^- were used (a calculated form factor for O^{2-} is not available). For the diffraction patterns, a pseudo-Voigt peak shape function was applied to the normalized diffracted intensities for the hkl reflections (from Table 1) [9]. The pseudo-Voigt profile used here was one-half

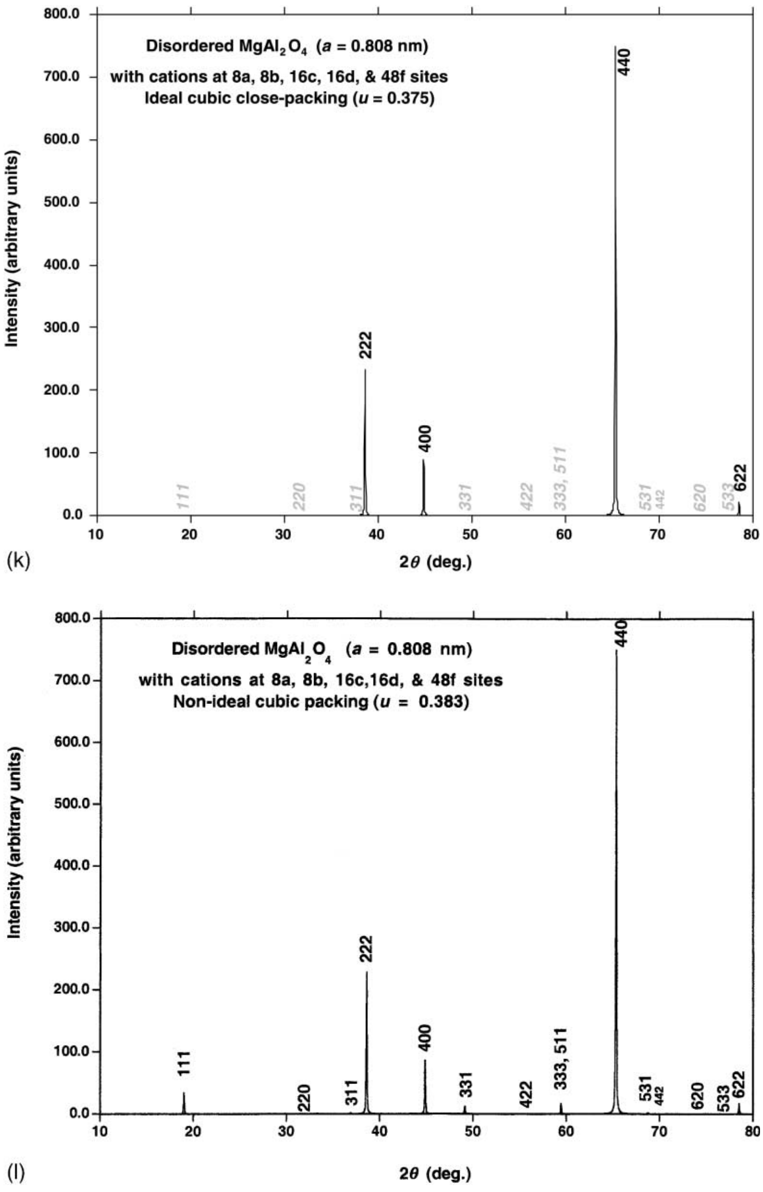


Fig. 1 (*continued*)

Gaussian and one-half Lorentzian. The diffraction peaks were assumed to have a full width at half maximum (FWHM) given by FWHM = 0.10°. [1]

In light of the simulation results described above, the first point for consideration is that a randomization of Mg and Al cations on 8a and 16d equipoints does not change the crystal symmetry of spinel or the lattice parameter. The structure remains SG $Fd\bar{3}m$, $a \sim 0.8$ nm. Simeone et al. pointed out that the X-ray atomic form factors for Mg and Al are quite similar. But even if these form factors were identical, so long as cations occupy 8a and 16d equipoints, spinel remains $Fd\bar{3}m$, $a \sim 0.8$ nm. In fact, if one examines the quantitative diffracted intensities presented in Table 1, one finds that the oxygen parameter has a far more profound effect on the predicted diffraction intensities than any cation disorder effects (so long as cations are confined to 8a and 16d sites). This situation is little different than that of the spinel-structured mineral magnetite, Fe_3O_4, wherein Fe^{2+} and Fe^{3+} ions with nearly identical form factors occupy both 8a and 16d sites. Once again, the space group for magnetite corresponds to $Fd\bar{3}m$ with $a \sim 0.8$ nm. The $Fd\bar{3}m$ space group of $MgAl_2O_4$ and Fe_3O_4

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[1] Calculations performed using Mathematica v. 4.0 [11].

Table 1
Simulated powder X-ray diffraction intensities for various $MgAl_2O_4$ lattices

#	*hkl*		*d* (nm)	2θ (°)	Intensity (normalized; % of maximum peak intensity)											
					Fully ordered spinel ($u = 0.375$) (Fig. 1(a))	Fully ordered spinel ($u = 0.387$) (Fig. 1(b))	Fully disordered spinel ($u = 0.375$) (Fig. 1(c))	Fully disordered spinel ($u = 0.383$) (Fig. 1(d))	Fully disordered spinel ($u = 0.387$) (Fig. 1(e))	Metastable 'Rocksalt' spinel (MX) (all octahedral interstices occupied by cations (Fig. 1(f)))	Metastable 'Sphalerite' spinel (MX) (1/2 tetrahedral interstices occupied by cations (Fig. 1(g)))	Metastable 'Anti-Fluorite' spinel (M_2X) (all tetrahedral interstices occupied by cations (Fig. 1(h)))	Metastable spinel (M_2X) (all octahedral/ 1/2 tetrahedral interstices occupied by cations (Fig. 1(i)))	Metastable spinel (M_3X) (all octahedral/all tetrahedral interstices occupied by cations (Fig. 1(j)))	Metastable 'Accidental Extinction' $Fd\bar{3}m$ structure (M_3X) with 8a, 8b, 16c, 16d, and 48f sites occupied by cations ($u = 0.375$) (Fig. 1(k))	Metastable $Fd\bar{3}m$ structure (M_3X) with 8a, 8b, 16c, 16d, and 48f sites occupied by cations ($u = 0.383$) (Fig. 1(l))
	$a = 0.808$ (nm)	$a = 0.404$ (nm)			$a = 0.808$ (nm), $Fd\bar{3}m$					$a = 0.404$ (nm), $Fm\bar{3}m$	$a = 0.404$ (nm), $F\bar{4}3m$	$a = 0.404$ (nm), $Fm\bar{3}m$	$a = 0.404$ (nm), $F\bar{4}3m$	$a = 0.404$ (nm), $Fm\bar{3}m$	$a = 0.808$ (nm), $Fd\bar{3}m$	$a = 0.808$ (nm), $Fd\bar{3}m$
1	1 1 1		0.4665	19.03	5.01	27.19	4.75	16.96	26.47							4.31
2	2 2 0		0.2857	31.32	25.47	32.43	26.13	29.81	33.20							0.03
3	3 1 1		0.2436	36.90	100.00	100.00	100.00	100.00	100.00							0.20
4	2 2 2	1 1 1	0.2332	38.60	2.26	1.72	2.46	2.27	1.91	**1.84**	100.00	82.84	43.13	29.71	29.71	29.13
5	4 0 0	2 0 0	0.202	44.88	57.18	60.53	55.00	57.77	58.14	100.00	1.52	3.08	35.27	11.39	11.39	10.93
6	3 3 1		0.1854	49.16	1.70	0.08	1.31	0.01	0.19							1.54
7	4 2 2		0.1649	55.74	9.66	9.90	10.43	10.82	10.73							0.01
8	3 3 3, 5 1 1		0.1555	59.45	32.90	50.52	33.09	43.70	50.70							2.15
9	4 4 0	2 2 0	0.1428	65.34	76.44	80.36	76.06	79.66	79.94	53.81	49.31	100.00	100.00	100.00	100.00	100.00
10	5 3 1		0.1366	68.74	1.38	3.75	0.92	2.14	2.91							0.27
11	4 4 2		0.1347	69.85		0.15		0.03	0.15							0.04
12	6 2 0		0.1278	74.24	3.75	3.22	4.21	4.07	3.69							0.02
13	5 3 3		0.1232	77.47	10.69	11.58	10.80	11.20	11.69							0.01

14	622	311	0.1218	78.54	0.30	1.02	0.18	0.40	0.78	3.78	28.06	14.76	10.89	2.81	2.81	2.22
15	444	222	0.1166	82.77	8.55	8.19	7.74	7.74	7.34	16.35	1.04	2.12	4.11	0.75	0.75	0.58
16	551, 711		0.1131	85.91	0.80	3.38	0.48	1.73	2.84							0.98
17	642		0.108	91.13	4.21	5.91	4.88	5.82	6.75							0.02
18	553, 731		0.1052	94.27	19.72	18.19	19.98	18.60	18.46							1.07
19	800	400	0.101	99.52	11.61	11.47	11.55	11.77	11.41	8.17	7.49	15.18	15.18	15.18	15.18	14.78
20	733		0.0987	102.71	0.31	0.29	0.17	0.12	0.46							0.76
21	644		0.098	103.79		0.04		0.01	0.04							0.01
22	822, 660		0.0952	108.13	2.46	3.67	2.92	3.56	4.25							0.03
23	555, 751		0.0933	111.45	12.89	15.89	13.10	15.14	16.12							0.33
24	662	331	0.0927	112.58	0.30	1.17	0.18	0.45	0.91	2.33	14.80	7.25	5.79	1.22	1.22	0.75
25	840	420	0.0903	117.18	16.11	13.87	14.12	13.43	11.92	30.28	2.13	4.31	7.35	1.24	1.24	0.74
26	753, 911		0.0887	120.76	0.96	2.51	0.51	1.22	1.92							0.73
27	842		0.0882	121.98		0.36		0.08	0.36							0.10
28	664		0.0861	127.05	1.72	0.83	2.08	1.63	1.11							0.06
29	931		0.0847	131.08	12.54	21.96	12.76	18.91	22.25							0.50
30	844	422	0.0825	138.43	55.86	51.98	55.58	55.04	51.71	39.32	36.03	73.08	73.08	73.08	73.08	69.09
31	755, 771, 933		0.0812	143.40	1.39	2.35	0.71	1.18	1.84							1.13
32	862, 1020		0.0792	153.36	9.01	10.30	11.02	11.86	12.55							0.06
33	773, 951		0.0781	161.53	44.75	78.44	45.62	66.71	79.43							8.93
34	666, 1022	333, 511	0.0777	165.17	0.86	6.58	0.40	1.89	5.07	9.02	68.14	36.12	26.44	6.98	6.98	3.53

The parameters for the calculations are described in the text. It should be noted that the cation:anion (M:X) ratio for $MgAl_2O_4$ is fixed at 3:4. The M:X stoichiometries of the metastable structures shown below represent the ideal compound stoichiometries. When $MgAl_2O_4$ assumes one of these compound structures, it is cation deficient. For an MX compound, the cation site occupancy for $MgAl_2O_4$ is 3/4; for M_2X it is 3/8; for M_3X, it is 1/4. Also, since the Mg:Al cation ratio in $MgAl_2O_4$ is 1:2, the 'average atom' atomic form factor for the cations in the disordered 'metastable' compounds is assumed to be $(1/3)f_{\mathrm{Mg}} + (2/3)f_{\mathrm{Al}}$ (i.e., we assume fully disordered cation sublattices).

derives from the special arrangement of cations on tetrahedral 8a sites and octahedral 16d sites (or equivalently the absence of atoms on tetrahedral 8b and 48f interstices, and octahedral 16c interstices). The 'flavor' of the atoms occupying 8a and 16d sites has no effect on the space group or the lattice parameter of spinel. [2]

But the most important point to be raised in this discussion is that observed diffraction patterns obtained from ion-irradiated metastable spinel structures (e.g., see Ref. [1], Fig. 6) bear little resemblance to any of the predicted diffraction patterns in Fig. 1(a)–(e). Based on the fact that all first-order reflections appear to be missing in the observed diffraction patterns, we surmise that a reduced lattice parameter model is necessary to explain the ion-induced metastable phase of spinel.

On the contrary, Simeone et al. suggested that the extinctions observed in irradiated $MgAl_2O_4$ are the result of an 'accidental extinction' effect, much like what occurs in KCl. The effect referred to may be summarized as follows: KCl is a cubic compound consisting of two interpenetrating simple cubic (SC) sublattices. The space group is $Pm\bar{3}m$ with Cl on the 1a equipoint and K on the 1b equipoint. Under X-ray diffraction conditions, since K^+ and Cl^- have very similar X-ray atomic form factors, the structure appears as if it is a body-centered cubic (bcc) lattice corresponding to SG $Im\bar{3}m$, but with the same lattice parameter. This false identification of space group is purely an artifact of the technique used to analyze the structure. [3] Neutron diffraction reveals the correct unit cell for KCl, because the cation and anion neutron atomic form factors are well distinguished.

But the issue we raise in this report relates to structural analysis of a compound in which we presume that cations are randomly arranged on whatever specific sites they occupy. The average form factor for each cation site in a disordered AB_2O_4 compound is given by $(1/3)f_A + (2/3)f_B$ modified by a site occupancy factor that is model dependent (see Table 1). In this situation, the structure will look the same whether it is analyzed by X-rays, neutrons, electrons, etc. The analogy to KCl invoked by Simeone et al. is simply invalid for any possible fully disordered spinel model. We can summarily dispose with this erroneous analogy for the remainder of our discussion.

The next point to consider is that the SG symmetry of the irradiated spinel must change from $Fd\bar{3}m$ if the lattice repeat unit is reduced from $a = 0.808$ nm to $a_{\mathrm{irrad}} = 0.404$ nm upon irradiation. The easiest way to understand this is to consider the oxygen sublattice. For irradiated spinel, a cubic unit cell with repeat unit $a_{\mathrm{irrad}} = 0.404$ nm can only contain four oxygen atoms. But SG $Fd\bar{3}m$ has no equipoint with multiplicity less than 8. There is no possibility to place four oxygen atoms on an equipoint in SG $Fd\bar{3}m$ without invoking partial site occupancy, which is physically non-intuitive. The oxygen sublattice is presumed to be virtually unaltered under irradiation. It is always assumed (even by Simeone et al.) that the oxygen sublattice remains pseudo-cubic-close-packed. But if, during irradiation, the oxygen sublattice relaxes to the ideal structure, $u = 0.375$, then the Bravais lattice of the oxygen sublattice becomes face-centered cubic (fcc) and the repeat unit of the oxygen sublattice becomes $a_{\mathrm{oxygen}} = 0.404$ nm, and in addition, we obtain the requisite four oxygen atoms per (conventional cubic, non-primitive) unit cell. But the space group must necessarily be altered from $Fd\bar{3}m$. It appears that we require two features in the metastable phase of spinel: (1) the oxygen sublattice must relax to an ideal fcc configuration; and (2) the cation sublattice must transform to a new atomic configuration that is compatible with a periodicity equal to 1/2 the periodicity of the ordinary $MgAl_2O_4$ lattice. [4]

Two space groups that satisfy this criterion are SGs $Fm\bar{3}m$ and $F\bar{4}3m$. In both of these space groups, an fcc arrangement of oxygen atoms can be accommodated on a 4a equipoint (four oxygen atoms per unit cell). The cell parameter is now the reduced cell, $a_{\mathrm{irrad}} = 0.404$ nm. With this condition, there are then five possible 'disordered' cation arrangements (compatible with SGs $Fm\bar{3}m$ and $F\bar{4}3m$), four of which were presented in a previous study by Sickafus et al. [5]. [5] Before elucidating the five

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[2] Magnetite, Fe_3O_4, is a nearly inverse spinel with Fe^{3+} ions occupying tetrahedral 8a sites and, at ambient temperature, a random mixture of Fe^{2+} and Fe^{3+} ions occupying octahedral 16d sites. Below ~120 K, Fe^{2+} and Fe^{3+} ions order on the 16d sites and the overall space group symmetry is reduced compared to $Fd\bar{3}m$ [12]. But for room temperature diffraction measurements, an average form factor, i.e., $1/2(f_{Fe^{2+}} + f_{Fe^{3+}})$, is an appropriate representation for scattering from an average 16d site in magnetite.

[3] If one were to completely disorder cations and anions on 1a and 1b sites in a KCl (CsCl-type) lattice, the lattice actually transforms to body-centered cubic and the space group changes to $Im\bar{3}m$. The lattice parameter remains unchanged by this disorder reaction. This transformation is observed in many irradiated CsCl-structured intermetallics (see, e.g., Ref. [13]).

[4] Another way to explain the incompatibility between the irradiation-induced structure and SG $Fd\bar{3}m$, is to consider the most prominent diffraction peak (at $2\theta \sim 45°$) observed by Simeone et al. in irradiated $MgAl_2O_4$ (Ref. [1], Fig. 6). When one attempts to index the observed peaks in this experimental diffraction pattern, the only possibility is to assume a cubic lattice with $a_{\mathrm{irrad}} = 0.404$ nm and then the principal peak at $2\theta \sim 45°$ indexes as a $\{200\}$ reflection. But a $\{200\}$ reflection is forbidden in SG $Fd\bar{3}m$, as dictated by the presence of a 4_1 screw axis operation in this space group. Thus, the space group of the irradiated $MgAl_2O_4$ phase must be other than $Fd\bar{3}m$.

[5] We assume that only tetrahedral and octahedral interstices may be occupied by cations. We ignore all coordinations with anions other than four- and sixfold.

possible cation arrangements, it is important to review the arrangement of interstices for possible cation occupation within a cubic-closed packed (fcc) anion lattice.

An fcc anion lattice is most easily recognized as a cubic lattice with four anions per unit cell. Given this lattice, there are eight tetrahedrally coordinated interstices per unit cell, which form a simple cubic lattice with $1/2$ the periodicity of the anion sublattice, and four octahedrally coordinated interstices per unit cell, which form an fcc lattice that interpenetrates the fcc oxygen sublattice with equivalent dimensions. Under these conditions, the following model disordered spinel structures can be defined:

(1) a 'rocksalt-like' structure consisting of an fcc oxygen sublattice with all (i.e., 4) octahedral interstices occupied (cations on equipoint 4b in SG $Fm\bar{3}m$);
(2) a 'sphalerite-like' structure consisting of an fcc oxygen sublattice with $1/2$ (i.e., 4) tetrahedral interstices occupied (cations on equipoint 4c in SG $F\bar{4}3m$);
(3) an 'anti-fluorite-like' structure consisting of an fcc oxygen sublattice with all (i.e., 8) tetrahedral interstices occupied (cations on equipoint 8c in SG $Fm\bar{3}m$);
(4) a structure consisting of an fcc oxygen sublattice with all (i.e., 4) octahedral and $1/2$ (i.e., 4) tetrahedral interstices occupied (cations on equipoints 4b and 4c in SG $F\bar{4}3m$);
(5) an 'all-interstices' structure consisting of an fcc oxygen sublattice with all (i.e., 4) octahedral and all (i.e., 8) tetrahedral interstices occupied (cations on equipoints 4b and 8c in SG $Fm\bar{3}m$).

The predicted structure factors and predicted powder X-ray diffraction patterns for these model structures are shown in Table 1 and in Fig. 1(f)–(j), respectively. Note that the general features of the simulated diffraction patterns for these disordered (so-called 'metastable') spinel structures are profoundly different from the patterns corresponding to $Fd\bar{3}m$ spinel (Fig. 1(a)–(e)). Of these metastable structures, the rocksalt model has been identified by Ishimaru et al. [3] as the most plausible model for the irradiation-induced spinel structure.

Highlighted in bold in the rocksalt model column in Table 1 is the $\{1\,1\,1\}$ reflection ($a_{\mathrm{irrad}} = 0.404$ nm; equivalent to $\{2\,2\,2\}$, $a = 0.808$ nm) at $2\theta = 38.6°$. This reflection was a subject of considerable attention in the report by Simeone et al., due to its apparent absence in the experimental diffractogram obtained from an irradiated $MgAl_2O_4$ sample (Ref. [1], Fig. 6). Simeone et al. pointed out that while this reflection was missing in their diffraction pattern, it is a 'non-null peak' in the simulated diffraction pattern for the rocksalt model (#(1) above, also Table 1 and Fig. 1(f)). Simeone et al. claimed that this discrepancy rules out the rocksalt model for consideration. However, it should be noted that using the rocksalt model, the predicted intensity for the $\{1\,1\,1\}$ reflection at $2\theta = 38°$, is less than 2% of the most intense peak in the simulated diffraction pattern (Table 1). In the report by Simeone et al. (see Ref. [1], Fig. 6), there is a broad peak due to scattering from an amorphous phase that overlaps the region $2\theta = 38°$. This scattering probably masks the small $\{1\,1\,1\}$ peak predicted in the rocksalt model (Fig. 1(c)). Because of this interference, the apparent absence of a peak at this position (experimentally, that is) certainly does not rule out the validity of the rocksalt model. Probably more significant is the fact that of the various metastable phase models, the rocksalt model predicts that the most prominent diffracted intensity occurs at $2\theta \sim 45°$ (corresponding to a $\{2\,0\,0\}$ reflection, $a_{\mathrm{irrad}} = 0.404$ nm), which is in agreement with observed diffraction patterns for ion irradiated spinel (e.g., Ref. [1], Fig. 6).

Simeone et al. went on to perform a Rietveld crystal structure refinement in which they fit their diffraction data to a model based on SG $Fm\bar{3}m$ with cations randomly arranged on 4a and 8c equipoints. This apparently is our 'all-interstices' model (#(5) above, also Table 1 and Fig. 1(j)). Simeone et al. claim a good fit for this structure with their observations. However, a good fit with the simulated structure factor for the all-interstices model presented here is not possible because significant intensity (approximately 30% of the maximum diffracted intensity) is predicted at the $\{1\,1\,1\}$ reflection position ($2\theta = 38.6°$), but Simeone et al. observed no crystalline diffracted intensity at this position. If the all-interstices model is correct, this reflection should have been detected experimentally, in spite of the amorphous-phase scattering in this region. It is unclear at present what, in fact, was the precise nature of the atomic model used by Simeone et al. in their crystal structure refinement. They claim that they used a spinel cation distribution with a lattice parameter reduced by two. However, as described earlier, a spinel cation distribution is only possible in SG $Fd\bar{3}m$, but a reduced lattice parameter is incompatible with $Fd\bar{3}m$.

To further elucidate the subtleties associated with the metastable phase of spinel, it is interesting to consider a situation in which 'accidental extinctions' could arise in a disordered compound like $MgAl_2O_4$ in SG $Fd\bar{3}m$. Table 1 and Fig. 1(k) show results for diffraction calculations using a hypothetical, metastable $Fd\bar{3}m$ spinel structure that results in accidental extinctions for many $\{h\,k\,l\}$ reflections that ordinarily should be allowed in SG $Fd\bar{3}m$. For this structure, we assume that anions occupy the 'ideal' fcc lattice ($u = 0.375$), while Mg^{2+} and Al^{3+} cations are randomly arranged on 8a, 8b, and 48f tetrahedral sites, and 16c and 16d octahedral sites. In other words, this is an 'all interstices' model, much like the 'all interstices' model in Fig. 1(j), but with twice the lattice parameter, $a = 0.808$ nm. It should also be noted that cations in 48f tetrahedral interstices are assumed to be located at special, 'ideal' positions, such that the generalized $\{x, 0, 0\}$ definition for the 48f site is given by $\{1/4, 0, 0\}$ in our model. Table 1 reveals that every all-odd-indice reflection is absent in this model (e.g., {1 1 1}, {3 1 1}, {3 3 1}, and so forth; these absent reflections are indicated in italicized gray in Fig. 1(k)). The reasons for these extinctions become apparent when we analyze the structure factor in detail. Consider, for instance, the intensity diffracted by one set of {1 1 1}-type planes in $\mathrm{Fd\bar{3}m}$ spinel, which is given by $2(4\sqrt{2}f_{16c} - 4\sqrt{2}f_{16d} + 4f_{8a} - 4f_{8b})^2$. Clearly, if we assume the validity of an 'all-interstices', ion-induced cation disorder reaction, the atomic form factors on all sites become identical, i.e., $f_{8a} = f_{8b} = f_{16c} = f_{16d} = f_{48f} = (1/4)(1/3f_{Mg} + (2/3)f_{Al})$ (the factor 1/4 arises from the distribution of 24 cations on 96 interstices). Thus, diffraction at the {1 1 1} position in diffraction space is null (note that cations on the 48f equipoint and anions on the 32e equipoint do not contribute to diffraction at the {1 1 1} reciprocal lattice position, assuming $x = 1/4$ and $u = 0.375$). It turns out that the 'accidental extinctions' for all-odd-indice reflections in this model are due to cancellations of atomic form factor contributions to the structure factor on 16c and 16d octahedral sites, as well as cancellations on 8a and 8b tetrahedral sites. Incidentally, some all-even-indice reflections are also made null in this model when a fully disordered metastable phase is achieved. For instance, the intensity diffracted by one set of {2 2 0}-type planes in $\mathrm{Fd\bar{3}m}$ spinel is given by $(-16f_{48f} + 8f_{8a} + 8f_{8b})^2$. Since $f_{48f} = f_{8a} = f_{8b} = (1/4)((1/3)f_{Mg} + (2/3)f_{Al})$, when a fully disordered structure is achieved, {220} reflections become extinct in this model for disordered spinel. The result is that the predicted diffraction pattern for this $\mathrm{Fd\bar{3}m}$ model structure is identical to that for the metastable 'all-interstices' model, based on an $\mathrm{Fm\bar{3}m}$ structure with reduced lattice parameter, $a_{irrad} = 0.404$ nm (Table 1, Fig. 1(j)). But the 'accidental extinctions' found in this model are a consequence of the erroneous choice of a doubly redundant unit cell, rather than a fortuitous coincidence of atomic form factors. The correct unit cell for this structure is that presented in model #(5) (presented earlier) for $a_{irrad} = 0.404$ nm.

Lastly, it is important to note that if oxygen sublattice distortions were to persist in the presence of metastable cation rearrangements, then the validity of the $\mathrm{Fd\bar{3}m}$, $a_{irrad} = 0.8048$ nm, is finally validated. Fig. 1(l) (also Table 1) shows results of such a calculation in which an 'all-interstices' cation sublattice (as described above) is combined with a dilated anion sublattice, $\mathrm{Fd\bar{3}m}$, $u = 0.383$. Now, the structure factor is consistent with $\mathrm{Fd\bar{3}m}$: both all-even and all-odd indice reflections are permissible (though {0 0 2}, {0 0 6}, {0 0 10}, etc., reflections are forbidden due to the presence of the 4_1 screw axis operation, and {0 2 4}, {0 2 8}, {0 4 6}, {0 4 10}, etc. reflections are forbidden due to the presence of the *d*-glide operation in this space group). Reflections such as {1 1 1} become permissible in this model because the intensity diffracted by one set of {1 1 1}-type planes is given by $2(4\sqrt{2}f_{16c} - 4\sqrt{2}f_{16d} - k\Delta f_{32e} + 4f_{8a} - 4f_{8b})^2$, where k is approximately a constant equal to 212, and Δ represents the deviation from 'ideal' oxygen packing (for $u = 0.383$, $\Delta = 0.008$; for $u = 0.387$, $\Delta = 0.012$). So, even though perfect cancellation occurs between structure factor contributions from 8a, 8b, 16c, and 16d sites, the dilation of the oxygen sublattice (32e) results in non-forbidden reflections. For the purposes of this report, it is critical to state that the numerous, albeit weak, reflections predicted by this last model (Fig. 1(l)) need to be observed in diffraction experiments in order to validate the assumption that the space group and lattice parameter are unchanged by irradiation, and the structure remains $\mathrm{Fd\bar{3}m}$, $a_{irrad} = 0.808$ nm. Alternatively, one could employ an experimental technique such as extended X-ray absorption fine-structure (EXAFS), i.e., a technique that is sensitive to local atomic environment, in order to analyze nearest neighbor bond lengths, and possibly to demonstrate that the first-order O–O bond in ion-irradiated spinel is triply degenerate. This would prove that the irradiated structure is $\mathrm{Fd\bar{3}m}$, $a_{irrad} = 0.808$ nm. Nevertheless, if one invokes this model, one still needs a cation sublattice model that produces diffracted intensities in agreement with observations. The most probable cation arrangement for this sublattice is a rocksalt-like structure (anion sublattice effects will simply produce weak, additional reflections).

Simeone et al. concluded their report with the following statement: 'The analysis of Rietveld refinement on these two spinels clearly shows an order–disorder transition under irradiation without any modification of their space group'. This is probably not the case, based on the diffraction simulations and discussion presented here. Spinel most likely succumbs to a phase transformation under irradiation that involves a profound change in the arrangement of cations in the lattice. The space group is modified by the transformation and most experiments indicate that the transformation is to the rocksalt structure described here [3]. In fact, the diffraction data of Simeone et al. (Ref. [1], Fig. 6) look remarkably similar to the predictions in Fig. 1(f) for the rocksalt model. It should be further noted that rocksalt-like structures have been observed in other spinel compounds, due to chemically induced rearrangements entirely unrelated to radiation damage. For instance, the compound $Li_4Ti_5O_{12}$, a spinel-structured titanate being considered for lithium battery applications, has been found to transform to a rock-salt-like structure when excess lithium is incorporated into the compound [14]. Thus, there seem to be several indications that the spinel and rocksalt structures have close physical ties. For the most recent report on this topic (see [15]).

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