

Radiation-induced cation disorder in the spinel MgAl_2O_4

Raju P. Gupta

Service de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif sur Yvette cedex, France

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Abstract

There is some controversy in the literature concerning the nature of radiation-induced cation disorder and phase transformation in the spinel MgAl_2O_4 . Attempts have been made to interpret the experimental data either in terms of a pure inversion involving the exchange between the Mg and Al atoms, or the disordering of the cation sublattice leading to a change in crystallographic symmetry to a defective NaCl-type lattice. We have performed first principles electronic structure calculations in order to examine the nature of this cationic disorder. We find that at low energies an exchange between the Mg and Al atoms is more favourable leading to an inversion in the spinel. With further increase in energy, the cations can be displaced from the tetrahedral sites to the unoccupied octahedral sites in the lattice, both in the normal and inverse spinels. In the case of the inverse spinel, such a displacement leads to a spontaneous change in the value of the u parameter of the oxygen lattice to the ideal value, and thus to an ideal defective NaCl-type lattice. On the other hand, in the case of a normal spinel, the displacement of Mg atoms to the unoccupied octahedral sites leads initially to a pseudo-cubic arrangement which then transforms later with further energy to an ideal defective NaCl-type structure. Thus in both cases a defective NaCl-type structure is obtained as the final structure. We find that the total energy barrier for obtaining this structure is the same in both cases.

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1. Introduction

The spinel MgAl_2O_4 is an important ceramic material in nuclear applications since it is considered to be radiation resistant, and thus highly suitable for the disposal of minor actinide elements Am, Cm, Np with very long life times. It crystallises in a diamond-type cubic spinel structure with space group $Fd\bar{3}m$ (No. 227). The general formula for the compounds crystallizing in the spinel-type structure is AB_2O_4 , where A is usually a divalent metallic element and B is a trivalent metallic element. The oxygen atoms

form a face-centred-cubic (fcc) lattice, and in a normal spinel, such as MgAl_2O_4 , the A atoms are located at the 8a tetrahedral sites in the lattice while the B atoms are located on the 16d octahedral sites. Not all the compounds with the spinel type structure are normal, and a certain degree of inversion may exist. In this case a certain fraction of the tetrahedral sites are occupied by the trivalent atoms and an equivalent number of octahedral sites by the divalent atoms. These are mixed spinels but when all the tetrahedral sites are occupied by the trivalent atoms and half of the octahedral sites by the divalent atoms, the spinel is completely inverse. A well known example of such an inverse spinel is Fe_3O_4 where Fe atoms exist in both divalent and trivalent

E-mail address: rgupta@cea.fr

ionic states and almost all of the divalent Fe ions occupy the octahedral sites while the trivalent Fe ions are evenly divided between the tetrahedral and octahedral sites. The space group of the mixed or completely inverse spinels is not affected by the degree of inversion since the space group is determined exclusively by the site occupancies of the 8a tetrahedral and 16d octahedral sites and not by the valence of the ions occupying these sites.

The oxygen sublattice in the MgAl_2O_4 spinel remains quite rigid under irradiation despite the lower atomic mass of the oxygen atoms relative to the metal atoms, and energies of more than 60 eV are required to displace an oxygen atom [1,2]. The metal atoms (cations) have much lower displacement energies (~ 20 eV for Mg and Al) and are thus the ones that are the most easily affected by the irradiation [1,2]. There has been a debate [3–6] in the literature concerning the nature of cationic displacement in MgAl_2O_4 . There are various possibilities that can be envisaged for metal atom displacements. The first and the easiest possibility is that, while the MgAl_2O_4 spinel is a completely normal spinel, there is a site exchange between the Mg and Al atoms so that some Mg atoms occupy the octahedral sites and an equivalent number of Al atoms occupy the tetrahedral sites that they normally do not occupy. Such a site exchange has been observed under neutron irradiation [7]. However, if this is the only disorder created by irradiation, this makes the spinel mixed or at best completely inverse but does not lead to any change in the crystallographic symmetry or the lattice parameter. It should be noted that the thermodynamically stable ground state of the MgAl_2O_4 is the normal spinel, and hence energy is required to disorder it in the inverse form. Some experimental data has also been interpreted in terms of the cation displacements that require a change in the crystallographic space group and leading to a division of the lattice parameter of the cubic lattice by a factor of two [2,6]. Such displacements and the change in the crystallographic symmetry are not obvious at first glance and further clarifications are necessary. We have, therefore, performed *ab initio* electronic structure calculations to elucidate the energetics of various metal atom displacements and the resulting change in crystallographic symmetry.

2. Computational details

The calculations presented here were performed within the density functional theory (DFT) using

the local density approximation (LDA) and employing the Hedin–Lundqvist [8] treatment for the exchange and correlation terms. We have used the FPLAPW (Full Potential Linearised Augmented Plane Wave) method [9] in our calculations. This is a first principles method and requires no adjustable parameters. The starting crystal potential is constructed from the atomic charge densities of the constituent elements which are obtained from an atomic program where only the atomic number Z of the elements enters as a parameter. The crystal potential is iterated to self-consistency with wavefunctions and energy eigenvalues obtained from the resolution of the Schrödinger equation. This is a general potential method and no shape approximations are required in the construction of the crystal potential. The values of 1.9, 1.9, and 1.52 a.u. were used for the muffin-tin radii of Mg, Al, and O atoms in all our calculations. Approximately 9800 plane waves were included in the expansion of the crystal potential and charge densities, and approximately 1200 plane waves were included in the expansion of the wave functions. The unit cell was treated with lower symmetry of the orthorhombic type to permit distinction between different octahedral sites. We included 108 special k -points in the irreducible portion of the Brillouin zone and the total energy was converged to better than 1 meV per formula MgAl_2O_4 . Both the lattice parameter a and the internal parameter u of the oxygen atoms were determined by energy minimization. We have used the conventional unit cell in our calculations that contains two formula units of MgAl_2O_4 , but all energy values presented in this paper correspond to one formula MgAl_2O_4 .

3. Results and discussion

The lattice parameter of the cubic MgAl_2O_4 spinel lattice found in our calculation is 15.2752 a.u. ($=8.083 \text{ \AA}$), in good agreement with the experimental value [2–5]. The value of the internal parameter of the oxygen sublattice u found in our calculation is $u = 0.387$, also in good agreement with experiment [3–5]. This value departs from the ideal value of $u = 0.375$ for the ideal tetrahedral or octahedral coordination of the metal atoms by the oxygen atoms. As will be shown below the value of this internal parameter has some consequences in the interpretation of the experimental data on irradiation.

The crystallographic structure of the spinel compounds is quite complex, and these are not compact

materials. Indeed, apart from the 8a tetrahedral and the 16d octahedral sites, there is another set of 8b tetrahedral and 16c octahedral sites that are not normally occupied in the spinel structure. These sites are empty due to the constraints imposed by the occupation of the 8a tetrahedral and 16d octahedral sites in a spinel. (We should note that in a spinel structure one can occupy either the 8b tetrahedral and 16c octahedral sites or the 8a tetrahedral and 16d octahedral sites but not both.) This is because the 16c sites are located midway between the two tetrahedral 8a sites, and thus the simultaneous occupation of both the 8a tetrahedral and 16c octahedral sites is not possible since it will lead to much too short interatomic distances. Similarly, the 16d octahedral sites lie in between the two 8b tetrahedral sites, and thus one can occupy either the 8b sites or the 16d sites but not both. The coordinates of these sites are given in Tables 1 and 2 for convenience and clarity.

This brings an alternative scenario for metal atom displacements in the lattice apart from inversion. As discussed above, one cannot occupy both the 8a and 16c sites simultaneously but the displacement of the atoms from the 8a tetrahedral sites to the 16c octahedral sites imposes no constraints of symmetry or interatomic distances. Again one should note that such a displacement does not require a change of space group to which the spinel structure belongs although the original lattice of the metal atoms of the compound is now different. This case is different from the case of the simple inversion of the spinel.

There are thus two possibilities that can be envisaged for the metal atom displacements into the octahedral sites. The first possibility is that the Mg atoms from the 8a tetrahedral sites are directly displaced

Table 1

Atomic coordinates of the cations in the 8a, 16d, 8b, and 16c positions in the spinel structure

Site	Coordinates
8a	(0 0 0) (1/4 1/4 1/4)
16d	(5/8 5/8 5/8) (5/8 7/8 7/8) (7/8 5/8 7/8) (7/8 7/8 5/8)
8b	(1/2 1/2 1/2) (3/4 3/4 3/4)
16c	(1/8 1/8 1/8) (1/8 3/8 3/8) (3/8 1/8 3/8) (3/8 3/8 1/8)
32e	(3/8 3/8 3/8) (3/8 1/8 1/8) (1/8 3/8 1/8) (1/8 1/8 3/8) (7/8 7/8 7/8) (7/8 1/8 1/8) (1/8 7/8 1/8) (1/8 1/8 7/8)

The coordinates of the oxygen atoms in the 32e positions with the ideal value 0.375 of the u parameter are also given. All coordinates are in units of the lattice constant a of the cubic spinel lattice.

Table 2

Atomic coordinates of the cations at the 16d and 16c sites and the oxygens at the 32e sites with the origin shifted to the oxygen site (3/8 3/8 3/8) in Table 1

Site	Coordinates
16d	(1/4 1/4 1/4) (1/4 1/2 1/2) (1/2 1/4 1/2) (1/2 1/2 1/4)
16c	(-1/4 - 1/4 - 1/4) (-1/4 0 0) (0 - 1/4 0) (0 0 - 1/4)
32e	(0 0 0) (0 - 1/4 - 1/4) (-1/4 0 - 1/4) (-1/4 - 1/4 0) (1/2 1/2 1/2) (1/2 - 1/4 - 1/4) (-1/4 1/2 - 1/4) (-1/4 - 1/4 1/2)

All coordinates are in units of the lattice constant a of the cubic spinel lattice.

into the 16c octahedral sites so that no tetrahedral sites are occupied and only the 16d and half of the 16c octahedral sites are now occupied. The second possibility is the cation exchange between the Mg and Al atoms. We consider here for convenience only the complete exchange between the Mg and Al atoms in such a way that all of the Mg atoms from the 8a tetrahedral sites are displaced to the 16d octahedral sites and simultaneously half of the Al atoms from the octahedral 16d sites are displaced into the 8a tetrahedral sites so that the tetrahedral sites are now fully occupied by the Al atoms leading to a complete inversion of the spinel. We find, as shown in Table 3, that there is a slight decrease in the lattice parameter to $a = 15.25$ a.u. ($=8.07 \text{ \AA}$), and also the u parameter decreases to $u = 0.3815$. The total energy of the crystal with a complete inversion of the spinel MgAl_2O_4 is only slightly higher, by 0.62 eV per formula MgAl_2O_4 , with respect to the normal spinel. This is an endothermic exchange and quite expected since, as mentioned above, the equilibrium thermodynamic state of this spinel is a normal spinel and not inverse. We should

Table 3

Lattice parameter values a (in \AA), the oxygen parameter u , and the change in energy (in eV) per formula MgAl_2O_4 with respect to the normal spinel

	Site occupation	a	u	Energy change
Normal spinel	Mg at 8a 2 Al at 16d	8.083	0.387	0.00
	Mg at 16c 2 Al at 16d	8.083	0.386	1.13
	Mg at 16c 2 Al at 16d	8.017	0.375	2.16
Inverse spinel	Al at 8a 1 Mg at 16d	8.070	0.3815	0.62
	+1 Al at 16d			
	Al at 16c 1 Mg at 16d	8.017	0.375	2.16
	+1 Al at 16d			

Note that all energies are positive and thus represent barriers for transformations.

mention here that these lattice relaxations play an important role in determining the true value of the energy barrier to inversion of the spinel. Without the inclusion of relaxations an energy barrier value of 1.21 eV per formula MgAl_2O_4 is obtained. This process can be followed by a further displacement of the Al atoms from the 8a tetrahedral sites towards the 16c octahedral sites. The lattice parameter decreases again to $a = 15.15$ a.u. ($=8.017$ Å) and the u parameter spontaneously takes the ideal value $u = 0.375$. There is an increase in the energy of the crystal by 1.54 eV per formula MgAl_2O_4 with respect to the inversion. Thus this process in which only the octahedral sites are occupied but in a way that 16d sites are half occupied by Mg atoms and half by Al atoms and half of the 16c sites are occupied by the Al atoms requires a total energy of 2.16 eV per formula MgAl_2O_4 with respect to the normal spinel.

The scenario in which the Al atoms remain at the 16d octahedral sites of the normal spinel and the Mg atoms are displaced directly from their 8a tetrahedral sites into the vacant 16c octahedral sites does not lead to a change in the lattice parameter from its original value of the normal spinel, according to our calculations, and there is only a marginal decrease in the value of the u parameter to $u = 0.386$. There is an increase in the energy by 1.13 eV per formula MgAl_2O_4 . This change in energy is much larger than that was found for the case of complete inversion. This is consistent with the fact that the spinels are either normal, inverse, or mixed and there is no occupation of the vacant interstitial sites in the spinel structure. Our calculations confirm the fact that the occupation of such sites is not favourable compared to inversion. We notice that in this displacement the u parameter does not take the ideal value $u = 0.375$ as was obtained in the case with inversion. In this particular case, the distorted coordination of the oxygen atoms around the metal atoms has a lower energy than the ideal arrangement. The ideal arrangement of the oxygen atoms is achieved through an endothermic reaction with an energy barrier of 1.03 eV per formula MgAl_2O_4 . This again gives a total energy barrier of 2.16 eV per formula MgAl_2O_4 with respect to the normal spinel. We again obtain a reduced value of the lattice parameter $= 15.15$ a.u. ($=8.017$ Å), as expected, and as obtained in the case of inversion.

The displacement of the metal atoms into the vacant octahedral sites has important consequences

concerning the interpretation of the experimental data. First one should note that since all the sites 8a, 16d, and 16c belong to the same space group Fd3m, the half occupation of the 16c octahedral sites at the expense of the complete depopulation of the 8a tetrahedral sites does not change the space group or the lattice parameter since the space group is not determined by partial or full occupation of certain sites. But it does alter the arrangement of the cations which is now no longer the same as in the original spinel lattice, and thus can no longer be identified with the crystal structure of the spinel. The arrangement where the u parameter is not ideal is really a pseudo cubic arrangement of the anions. For the case of an arrangement with an ideal value of the u parameter, $u = 0.375$, the structure can be alternatively re-interpreted, as discussed below, in terms of a defective NaCl-type lattice with a cubic lattice parameter which is half that of the spinel lattice. In Table 1, we have shown the positions of the oxygen atoms in the spinel lattice with the ideal value of the u parameter. In Table 2, we have given the positions of the Mg, Al and the oxygen atoms with respect to the origin shifted to the oxygen atom at $(3/8, 3/8, 3/8)a$, in terms of the lattice parameter a of the spinel lattice.

It is immediately clear from Table 2 that all the atomic coordinates can be easily expressed in terms of a lattice parameter $a_0 = a/2$, where a and a_0 are, respectively, the lattice parameters of the spinel lattice and the new lattice to be identified. It can be easily seen that the new lattice formed by Mg, Al, and O atoms belongs to the space group 225 and is of the NaCl-type with a lattice parameter a_0 in which only 75% of the metal atoms sites are occupied. The case of inversion followed by the displacement of the Al atoms to the 16c sites results in an ideal value of the u parameter, as discussed above. This leads to an ideal but defective rock salt structure in which 75% of the metal atom sites are randomly occupied. When the Mg atoms at 8a sites in the normal spinel are displaced directly to 16c sites, we see that in the absence of relaxation of the oxygen lattice, the resulting structure can be considered to be pseudo-cubic since the oxygen atoms do not have the perfect arrangement of an fcc lattice. But with further energy, it achieves the same arrangement as with inversion. It is interesting to note that the total energy required to achieve the final rock salt structure is the same for both normal and inverse spinels from the ground state of the normal spinel. Thus, although, we have only treated the

cases of fully normal or fully inverse spinels, our conclusions regarding the total energy change to achieve the phase transformation to the rock salt structure are unlikely to be changed for the case of a mixed spinel since the cation distribution in the rock salt structure is completely random.

4. Conclusions

In conclusion, our *ab initio* electronic structure calculations show that the radiation-induced cation disorder in the spinel MgAl_2O_4 depends on the nature of irradiation. For low energies, the exchange between the Mg atoms at the tetrahedral sites and the Al atoms on the octahedral sites is more favourable since it requires less energy and this disorder leads to simple inversion of the spinel. The original spinel structure is preserved in this disorder. At this stage there is no crystallographic transformation or a division of the lattice parameter by a factor of two. At higher energies the cations at the tetrahedral sites in this inverse spinel can be displaced to previously unoccupied 16c octahedral sites. This displacement spontaneously leads to an ideal value of the u parameter of the oxygen sublattice. This new arrangement can be easily identified as a change in the crystal structure to a defective NaCl-type lattice in which 25% of the metal atom positions are vacant

and 75% of the metal atom positions are occupied. In the case where the Mg atoms at the tetrahedral sites are directly displaced to the unoccupied 16c sites, the resulting structure is a pseudo-cubic structure, and can be indexed with the original space group $Fd\bar{3}m$. However, with further irradiation this pseudo-cubic structure also transforms to an ideal defective cubic NaCl-type structure as with inversion. The total energy required for transformation to the defective NaCl-type structure is the same, 2.16 eV, in both processes.

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