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TITLE: **DEFECTS AND METASTABLE STRUCTURES OF $MgAl_2O_4$**

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DEFECTS AND METASTABLE STRUCTURES OF $MgAl_2O_4$

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INTRODUCTION

The $MgAl_2O_4$, which crystallizes in spinel structure, were usually found to be very resistant to the radiation induced swelling and transformation at room and elevated service temperatures. Yet recently, Yu et al [1,2] have found that under low temperature conditions (100K) a single crystal of $MgAl_2O_4$ spinel can be amorphized by irradiation of Xe atoms through an intermediate metastable phase. This intermediate phase has a higher Young's modulus, while the amorphous phase has a lower Young's modulus than the spinel structure [2]. The diffraction pattern of the metastable structure shows the reduction of the lattice parameter by approximately a factor of two, while the cubic symmetry along [001] zone is maintained. Several cubic structures have been proposed for the metastable phase of $MgAl_2O_4$ [1,3, 4].

In this paper, we present the calculated results of properties in normal spinel and inverse spinel structures of this material, as well as properties of point defects in the spinel structure. These results provide important information for further studying and understanding the possible metastable states of this material. The calculated properties of the "amorphous" structure are also presented in this paper. We have also calculated properties of several proposed metastable states of $MgAl_2O_4$ and the results can be found in [5]. The interionic interactions are described by Coulombic long range and the Buckingham short range potentials which incorporate the shell model [6] to account for ionic polarization of ions. The short range potentials were taken from [7]. The structural relaxations were performed by using GULP program [8].

RESULTS

Fig.1 shows the normal spinel structure of $MgAl_2O_4$, in which the O^{2-} ions form a f.c.c. sublattice, the Mg^{2+} ion occupies one out of eight tetrahedral interstitial sites, and the Al^{3+} ions take two out of four octahedral interstitial sites within the O^{2-} based f.c.c. unit cell. In an alternate structure, inverse spinel, the Mg^{2+} ions and half of the Al^{3+} ions are on octahedral interstitial sites, and half of the Al^{3+} ions are on the tetrahedral interstitial sites.

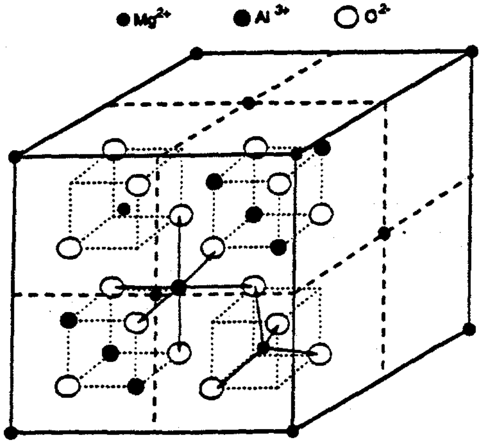

Fig.1 The structure of the spinel.

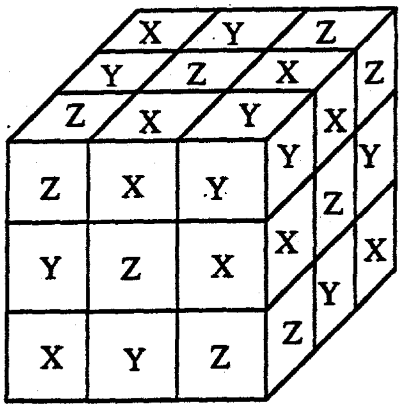

Fig.2. The building block of the "amorphous" state.

Table 1 summarizes the calculated equilibrium properties of $MgAl_2O_4$ in the normal and inverse spinel structures, in the proposed rock salt structure, and in the "amorphous" structure. They include the lattice energy, E_L, lattice volume V, lattice constants a, b, and c, structural symmetry, and the Young's modulus, E. For the spinel structure, the calculated lattice constant 8.1439Å is very close to the experimental measured value of 8.08Å, and the cubic symmetry is remained after the relaxation. The internal variable x, which represents the position of O^{2-} ion, was found to be 0.387 from the calculation, which is the same as the value from experiments. The Young's modulus, calculated as the average value based on the Voigt and Reuss assumptions [9], is 328 GPa for $MgAl_2O_4$. in normal spinel. While the experimental measured value is 277 GPa, the calculated value is overestimating by about 18%. This is because in the fitting of the potentials the accuracies in energies and crystal structures are emphasized at the expense of the accuracy of the moduli. Therefore, the values of moduli can only be used as guide lines instead of the absolute values. As for the inverse spinel, the calculations show higher lattice energy than the normal spinel, indicating its structure is less favorable. The relaxed structure of the inverse spinel has the near tetragonal symmetry, with one of the angles equals 88.59° while the other two equal 90.00°.

Table 2 summarizes the calculated energies of several point defects in $MgAl_2O_4$ spinel structure. It can be seen that the site exchange between an Mg^{2+} ion and an Al^{3+} leads to the smallest energy increase of 0.92eV/atom, while all the other point defects lead to much larger energy increases. This suggests that the most likely point defects to be formed under irradiation is the disordering between cations, and the metastable structures can be formed afterwards. Among all the Frenkel defects, Mg^{2+} ion has the smallest Frenkel defect energy, which is

4.59eV/atom. Even through, this energy is larger than the energy increased by creating a Schottky defect, consisting of one vacancy on Mg site, two vacancies on Al sites and four vacancies on O sites, with energy increase of 3.71eV/atom. This suggests that in $MgAl_2O_4$ the formation of Frenkel defects is more difficult than the formation of Schottky defect and the exchange of cations.

Table 1. Calculated properties for several structures of $MgAl_2O_4$..

Structures	E_L (eV)	V ($Å^3$)	a,b,c (Å)	symmetry	E (GPa)
normal spinel	-200.51	67.52	8.1439	cubic	328
inverse spinel	-199.22	66.32	8.1122 8.1122 8.0652	near tetragonal	352
"rock salt"	-193.03	63.40	4.1199 4.1199 3.7354	tetragonal	420
"amorphous"	-200.09	88.56	---------	triclinic	152

Table 2. Calculated energies of several point defects in $MgAl_2O_4$ spinel structure.

Defect	Energy (eV)	Defect	Energy (eV)
Mg'_{Al}	30.40	$Al^{\bullet}_{Mg}$	-28.56
$V''_{Mg}+Mg^{\bullet\bullet}_i$	9.18	$V'''_{Al}+Al^{\bullet\bullet\bullet}_i$	12.74
$V^{\bullet\bullet}_O+O''_i$	10.57	$V''_{Mg}+2V'''_{Al}+4V^{\bullet\bullet}_O$	25.94

The proposed rock salt structure of $MgAl_2O_4$ is the one in which the four O^{2-} ions form a f.c.c. unit cell, the Mg^{2+} ion and two Al^{3+} ions distribute randomly on the four octahedral interstitial sites within the f.c.c. unit cell. The calculated properties of this structure are summarized in Table 1. This structure has less binding energy, smaller volume, and higher Young's modulus than those in the normal structure. The structure possesses tetragonal symmetry after relaxations, and the direction of the c-axis depends on how the Mg^{2+} ion and two Al^{3+} ions distribute on the four octahedral interstitial sites. An "amorphous" state of $MgAl_2O_4$ was created by building up a structure with the unit cell consisting of 27 mixed rock salt structural units, as shown in the schematic plot in Fig.2. The small units denoted as x, y, or z represent the rock salt unit cells with the c axis points in x, y or z directions, respectively. The unit cell for the "amorphous" state was built in the way such that each unit is neighbored by other units with different orientations, e.g., each x unit is neighbored by y and z units. The equilibrium properties of the relaxed amorphous state are given in Table 1. The lattice energy increases by only 0.2%, and the volume increases by 31% comparing with the spinel structure. This small increase in the binding energy is not very significant and it does indicate that when the spinel is heavily irradiated it is energetically favorable to transform to the amorphous phase. Also, the expansion of the "amorphous" phase of 31% is consistent in sign with the irradiation experiment but no quantitative information is available at the moment. Furthermore, the calculated Young's modulus of the "amorphous" structure is smaller than that of the spinel structure by 54%, which agrees qualitatively with results from indentation experiments.

Figs.3(a-c) show the coordination environments within 4Å around the Mg^{2+}, Al^{3+} and O^{2-} ions in the normal spinel structure, respectively. The Mg^{2+} and Al^{3+} ions are coordinated by four and six O^{2-} ions at the distance 1.93Å and 1.94Å, respectively, while the O^{2-} ion is coordinated by one Mg^{2+}, and three Al^{3+} ions. Fig.4 shows the average coordination numbers around each Mg^{2+}, Al^{3+} and O^{2-} ions in the "amorphous" state of $MgAl_2O_4$, in which X-Y represents the number of Y neighbors around each X atom. The most significant feature in the amorphous structure is the wide range of values for all the bond lengths between ions. For example, around each Mg^{2+} ion the O^{2-} neighbors distributed in the range from 1.76Å to 2.24Å, and similar for the Al^{3+} ion and O^{2-} ions. Such a wide range of the bond lengths indicates that the diffraction pattern would show glass-like or amorphous-like halos instead of the sharp crystalline diffraction spots or rings, and this is consistent with the experimental observations [1]. Table 2 summarizes the average bond length between ions in the "amorphous" state. It can be seen that on average, the Mg-O, O-O and Al-Al bond lengths become larger, and Al-O and Mg-Al bond lengths become smaller than those in the spinel structure.

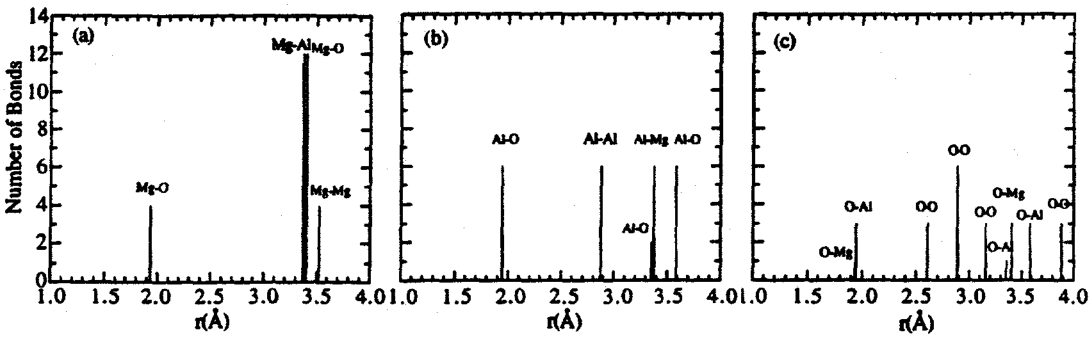

Fig.3. Number of bonds around (a) Mg^{2+} ions, (b) Al^{3+} ions and (c) O^{2-} ions in $MgAl_2O_4$ spinel structure

Table 2. The average bond length between ions in the "amorphous" state of $MgAl_2O_4$.

Mg-O	Al-O	O-O	Mg-Al	Al-Al
2.00 A	1.79 A	3.00 A	3.06 A	3.25 A

CONCLUSIONS

We have found, from atomistic simulations, that in $MgAl_2O_4$ spinel structure the exchange of an Mg^{2+} ion with an Al^{3+} ion has the lowest energy

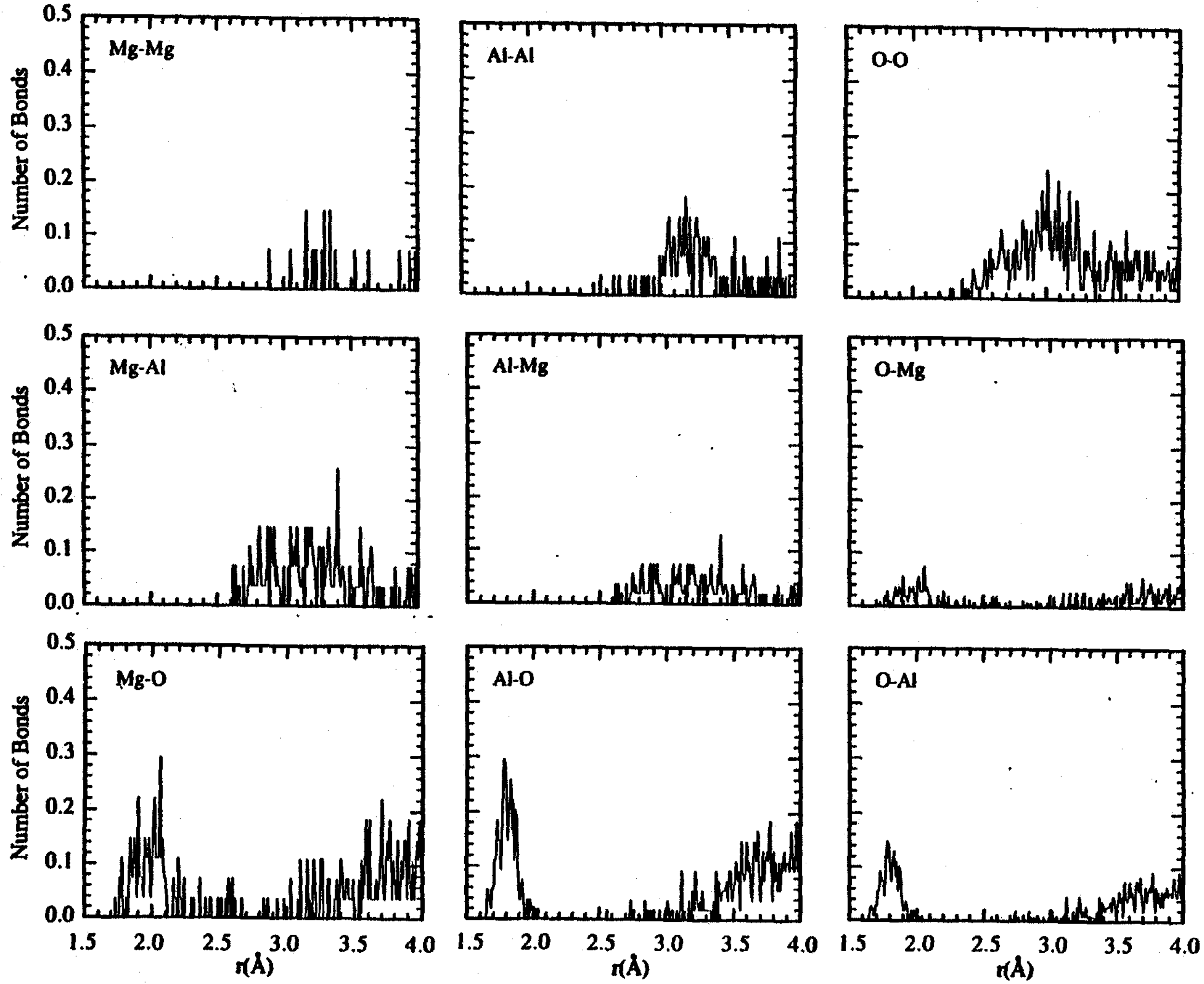

Fig.4. Average number of bonds around ions in the "amorphous" state of $MgAl_2O_4$ within the distance of 4Å

increase, 0.92eV/atom. The Schottky defect increases the energy by 3.71eV/atom. The formation of Frenkel defects is the most difficult, which increases the energy at least 4.59eV/atom for the Mg^{2+} Frenkel defect. The proposed rock salt structure of $MgAl_2O_4$ has smaller volume and larger Young's modulus, and the amorphous state has larger volume and smaller Young's modulus than those in the $MgAl_2O_4$ spinel structure.

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REFERENCES

1. N. Yu, K. E. Sickafus and M. Nastasi, *First Observation of Amorphization in Single-Crystal $MgAl_2O_4$ Spinel*, Philo. Mag. Lett. 70, 235 (1994).
2. N. Yu, K. E. Sickafus and M. Nastasi, *Temperature Effects on Ion Irradiation Damage in $MgAl_2O_4$ Spinel Single Crystals,* in Microstructure of Irrated Materials, (edited by I. M. Robertson, S. J. Zinkle, L. E. Rehn and W. J. Phythian), Mat. Res. Soc. Proc. Symp., Vol. 373, (1995).
3. L. M. Wang, W. L. Gong, N. Bordes, R. C. Ewing and Y. Fei, in Microstructure of Irrated Materials (edited by I. M. Robertson, S. J. Zinkle, L. E. Rehn and W. J. Phythian), Mat. Res. Soc. Proc. Symp., Vol. 373, (1995).
4. R. Devanathan, N. Yu, K. E. Sickafus and M. Nastasi, *The Structure of the Metastable State in Ion-Irradiated $MgAl_2O_4$ Spinel*, submitted to Philo. Mag. Lett. (1995).
5. S. P. Chen, M. Yan, J. Gale, R. W. Grimes, S. Vyas, R. Devanathan, K. E. Sickafus, N. Yu and M. Nastasi, *Atomistic Study of Defects, Metastable and "Amorphous" Structure of $MgAl_2O_4$,* in preparation for Philo. Mag. A. (1995).
6. B. G. Dick and A. W. Overhauser, *Theory of the Dielectric Constants of Alkali Halide Crystals*, Phys. Rev. 112, 90 (1958).
7. T. S. Bush, J. D. Gale, C. R. A. Catlow and P. D. Battle, *Self-consistent Interatomic Potentials for the Simulation of Binary and Ternary Oxides*, J. Mater. Chem. 4, 1 (1994).
8. J. D. Gale, GULP-General Utility Lattice Program, Royal Institution of Great Britain, (1994).
9. D. H. Chung and W. R. Buessem, *The Elastic Anisotropy of Crystals,* in Anisotropy in Single Crystal Refractory Compounds (edited by F. W. Vahldick and S. A. Mersol), Plenum Press, (1968).