

ORDER-DISORDER IN  $MgAl_2O_4$ . THE SYSTEMS:  
 $MgAl_2O_4$ - $LiAl_5O_8$ ,  $MgAl_2O_4$ - $NiCr_2O_4$ ,  $MgAl_2O_4$ - $NiAl_2O_4$ ,  
 AND  $NiAl_2O_4$ - $ZnAl_2O_4$

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ABSTRACT

Serious question has been raised about merely classifying  $MgAl_2O_4$  as a normal spinel. Infrared spectra, the appearance of extra X-ray diffraction peaks, change of the lattice parameter ( $8.076 \pm 0.002 \text{ \AA}$  at  $1200^\circ\text{C}$  and  $8.084 \pm 0.001 \text{ \AA}$  at about  $2100^\circ\text{C}$ ), the nature of crystalline solutions with  $LiAl_5O_8$  and  $NiAl_2O_4$ , etc., all point to the fact that although at high temperature  $MgAl_2O_4$  may tend to be a normal spinel, there is appreciable change in the distribution of cations in the tetrahedral and octahedral sites with temperature. The possibility of a first-order transition near  $1240^\circ\text{C}$  is mooted.

INTRODUCTION

The mineral spinel,  $MgAl_2O_4$  has given its name to a large class of isostructural (face-centered, cubic) compounds of space group  $O_h^7$  ( $Fd3m$ ). The crystal chemistry of spinel has been extensively dealt with by other authors (Gorter, 1954a).

The unit cell of a spinel contains  $A_8B_{16}O_{32}$ , or eight  $AB_2O_4$  "molecules". The 32 oxygen ions are arranged in a cubic close-packed arrangement. Such an arrangement gives rise to 64 tetrahedral (four-coordinated) and 32 octahedral (six-coordinated) holes as possible sites for cations, of which only eight tetrahedral and 16 octahedral positions are occupied. Barth and Posnjak (1932), on the basis of the cation distribution in these sites, suggested the idea of normal, inverse and intermediate (random) spinels. In case of normal spinels, the four- and six-coordinated positions are occupied by 8 ions of element A and 16 ions of element B, respectively. In inverse spinels, 8 ions of element B occupy the tetrahedral positions, whereas 8 ions of element A and the remaining B ions together occupy the octahedral positions. In case of random or intermediate spinels, ions of elements A and B are distributed in both octa- and tetrahedral sites. The ionic distributions involved in various spinels can be expressed as follows:

Normal spinel:  $A^{(4)}B_2^{(6)}O_4$

Inverse spinel:  $B^{(4)}(AB)^{(6)}O_4$

Random spinel:  $(A_{1-x}B_x)^{(4)}(B_{2-x}A_x)^{(6)}O_4$

The numeral superscripts in parentheses indicate the coordination of the cations.  $x$  is a measure of the partition of the cations in the tetra- and octahedral positions. Normal and inverse spinels can be considered as two limiting cases where  $x$  is equal to 0 and 1, respectively.

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Barth and Posnjak (1932) assumed a random distribution of ions inside each type of these cation sites. In some spinels the following three types of long-range order have since been found to occur in one of these cation sites.

1. 1:1 order in the tetrahedral sites (Braun, see Gorter, 1954b)
2. 1:1 order in the octahedral sites (Verwey and Haayman, 1941; Blasse, 1964)
3. 1:3 order in the octahedral sites (Braun, 1952)

These types of order are accompanied by a change in the space group and may be considered as superstructure formation in spinels. In addition to these types of order-disorder, it should be recalled that only 1/2 of the available octahedral sites and only 1/8 of the tetrahedral sites are occupied. Clearly, another type of disorder would result if a fraction of the cations were to occupy the other interstices (usually unoccupied) in the close-packed layers. The fact that the possible long-range orders can be observed only in a few cases has been ascribed by De Boer *et al.* (1950) to the amount of energy involved. The ordering energies for the above-mentioned superstructures are large compared to the energy of thermal motion available at the transition temperatures. Nevertheless, the possibility of a fairly large amount of short-range order or disorder<sup>1</sup> in an inverse or intermediate spinel, where the cations randomly exchange their positions between the tetra- and octahedral positions with change in temperature, cannot be ruled out. The energy required for such exchange of positions is in the order of several kcal/gm atomic weight (Miller, 1959).

It is now experimentally established that the distribution of cations among various sites in certain spinels such as  $NiAl_2O_4$ ,  $Ni_2GeO_4$ ,  $MgGa_2O_4$ , etc., is an *equilibrium* function of temperature, pressure and composition (Datta and Roy, 1961a, 1961b, 1963a, 1967; see also Schmalzried, 1961).  $MgAl_2O_4$  is *generally* (see later) accepted to be an ideally normal spinel where  $Mg^{2+}$  and  $Al^{3+}$  ions occupy the tetra- and octahedral positions, respectively (Verwey and Heilman, 1947; Bacon, 1952; Wanmaker, *et al.*, 1968; Schmitz-Dumont, 1965), although no reference is usually made to the conditions of its syntheses. Further, due to the small difference in the X-ray scattering factors of  $Mg^{2+}$  and  $Al^{3+}$  ions, X-ray intensity studies fail to establish decisively the cation arrangement in  $MgAl_2O_4$  and its relation, if any, with temperatures. Nevertheless, the random nature of  $MgAl_2O_4$  spinel and the temperature dependence of the distribution of the cations in the tetra- and octahedral

<sup>1</sup> The same change in the positions of the cations can be viewed as order or disorder depending on the arrangement of the reference state.

sites can be indirectly inferred from many published reports such as the following:

Kordes (1931) reported a few very weak, low-angle diffraction lines corresponding to the reflections (210), (211), etc., which would indicate a superstructure of the cations. The N.B.S. X-ray data (Swanson *et al.*, 1953) list a dozen patterns with more than one showing such reflections which are not allowed for a face-centered cubic material like spinel. Miller (1959) from theoretical calculations involving Madelung, short-ranged and crystal field terms showed that the octahedral site-preference energies for  $Mg^{2+}$  and  $Al^{3+}$  in a spinel are  $-5.0$  and  $-2.5$  kcal/g-at. wt., respectively. The energy difference involved is seen to be small compared to the total lattice energy of  $MgAl_2O_4$  and to the available thermal energy at temperatures where  $MgAl_2O_4$  is prepared. Recently, disordered Mg/Al distribution and the temperature dependence of such disorder have been suggested from nuclear resonance (Braun and Hafner, 1962) and neutron-diffraction (Stoll, Fischer, Halg, and Maier, 1964) studies of synthetic and natural spinel,  $MgAl_2O_4$ . Hummel and Sarver (1964) attributed the two emission bands of  $Fe^{3+}$ -activated  $MgAl_2O_4$  under cathode-ray excitation to the distribution of  $Mg^{2+}$ ,  $Fe^{3+}$  and  $Al^{3+}$  ions among the tetra- and octahedral sites of the solid-solution phase  $MgFe_{0.002}Al_{1.998}O_4$ .

The present investigation aims to show further evidences for the presence of short- and long-range order and qualitatively establish the relationship between the cation arrangement and temperature in the spinel,  $MgAl_2O_4$ . The experimental part of the investigation involved two separate steps:

1. Preparation of polycrystalline  $MgAl_2O_4$  under widely different thermal conditions.
2. Measurement of those physical properties of the quenched samples which are most susceptible to cation distribution:
  - (a) Unit cell size, as revealed by X-ray diffraction analysis
  - (b) Infrared absorption spectra
  - (c) Subsolidus relations between  $MgAl_2O_4$  and other spinels of known cation arrangement.

#### EXPERIMENTAL

For the present study two sets of starting materials were used. One set consisted of nitrate gels prepared by mixing appropriate proportions of nitrate solutions, evaporating to dryness over a steam bath and finally dehydrating at  $600^\circ C$  for 24 hours (Roy, 1956); the second set comprised of mechanical mixtures of appropriate proportions of oxides and carbonates. To prevent any loss of  $ZnO$ ,  $NiO$  and  $Li_2O$  at higher temperatures, mechanical mixtures involving these oxides were first reacted hydrothermally (Roy and Tuttle, 1956) at  $600^\circ C$  (well above the maximum temperature at which hydrous phases are stable). The pre-reacted mixtures were then used as starting materials.

The starting materials were equilibrated at high temperatures under both dry and "hydrothermal-catalysis" conditions. All dry runs (above 930°C) were made in sealed platinum or gold tubes depending on the temperature of reaction. Below 920°C all runs were made in sealed (or unsealed) gold tubes under high water-vapor pressure (100–1000 bars). The catalysis by high water-vapor pressure of the subsolidus reactions in such systems is the only possible avenue known to us whereby one may hope to attain equilibrium in this temperature range. It should be clearly understood that the pressure here is too low to be an important factor in altering significantly the solid-solid equilibria, and further that since the water does not appear in the products or reactants of the net reaction, it cannot alter equilibria. Details of the furnaces, temperature control and X-ray investigation are given in the original dissertation by Datta (1961).

The products of the runs were identified mainly by X-ray diffraction patterns.  $CuK_{\alpha}$  radiation from a Norelco diffractometer with a nickel filter was used throughout. For precise determination of lattice constants, the patterns were run in the back-reflection region ( $2\theta \sim 130^\circ$ ) at low speed ( $\frac{1}{4}$  degree per minute). Reproducibility of measurement was within  $\pm 0.001 \text{ \AA}$  unless otherwise indicated. The relative integrated intensities of diffraction lines from powdered specimens were measured by weighing the corresponding peak area after it was carefully cut from the diffraction chart. To insure the reliability of this method, separate experiments were performed, and it was observed that equal areas of the diffraction-chart paper have equal weights within  $\pm 2$  percent. The width of the sample in the diffractometer was always made larger than the incident beam at all angles and was effectively of infinite thickness (Cullity, 1956). While measuring the relative intensities, only different orders of the same reflection, *e.g.*, (220), (440), etc., were considered, thereby unequivocally avoiding errors due to any preferred orientation. In addition, it should be noted that the relative intensities of these two reflections are a very good measure of the distribution of the cations between the tetra- and octahedral sites of a spinel (Datta and Roy, 1967). A Perkin-Elmer Double Beam (Model 21) infrared spectrometer with KBr prism was used to obtain absorption spectra in the 11–25 $\mu$  region. Techniques described by Stimson and O'Donnell (1952) were followed for the preparation of powdered (polycrystalline) samples. Usually 1–3 mgm of powdered sample and about 250 mgm of KBr were ground together and the mixture pressed to a transparent disc under low-vacuum.

## RESULTS AND DISCUSSION

One basic assumption runs through the entire work that is reported here. It is so major an assumption and its implication so far reaching that its mention has been usually neglected in similar work. All the data recorded herein were actually taken at room temperature, and it is assumed that the quenching (usually at rates between 200 and 2000°C/sec) is such as to perfectly retain the high temperature assemblages. This assumption of the "perfect quenching" in high temperature states is undoubtedly valid in many cases, such as in certain stable glass forming systems, and is known to be invalid in most halide and simple oxide cases. The validity of the assumption in cases such as the present one was periodically tested by X-ray work at elevated temperatures.

*Studies on  $MgAl_2O_4$ .* It has been mentioned before that the N.B.S. X-ray data (Swanson *et al.*, 1953) lists many patterns showing many unallowed

TABLE I. RESULTS OF HEATING  $MgO \cdot Al_2O_3$  GEL UNDER DIFFERENT CONDITIONS

| Conditions of heating | Temperature in C | Pressure   | Duration in days | Observed reflections in addition to those allowed by spinel space group | Cell size in Å $\pm 0.002$ |
|-----------------------|------------------|------------|------------------|---|----------------------------|
| Dry                   | 700              | 1 atm      | 3                | (210) (211) (431)   | 8.120                      |
| Dry                   | 650              | 1 atm      | 4                | (210) (211) (431) (332)   | 8.122                      |
| Dry                   | 800              | 1 atm      | 3                | (210) (211) (431)   | 8.120                      |
| Dry                   | 900              | 1 atm      | 3                | (210) (211)   | 8.115                      |
| Dry                   | 1000             | 1 atm      | .5               | (210) (211)   | 8.093                      |
| Dry                   | 1200             | 1 atm      | 1.5              | nil   | 8.076                      |
| Dry                   | 1540             | 1 atm      | 1                | nil   | 8.084                      |
| Dry                   | ~2200            | 1 atm      | (10 min.)        | nil   | 8.084                      |
| Wet                   | 650              | 15,000 psi | 2                | (210) (211)   | 8.112                      |
| Wet                   | 750              | 15,000 psi | 2                | (210) (211)   | 8.110                      |
| Wet                   | 800              | 7,000 psi  | 2                | (210) (211)   | 8.092                      |
| Wet                   | 850              | 5,000 psi  | 1.5              | (210) (211) (both indistinct)   | 8.092                      |
| Wet                   | 750              | 10,000 psi | 7                | nil   | 8.074                      |
| Wet                   | 650              | 15,000 psi | 10               | nil   | 8.074                      |

reflections, such as (210), (211), (510)<sup>1</sup>, etc., for the spinel  $MgAl_2O_4$ .

The present investigation showed that the unallowed reflections are definitely not present at the equilibrium state. However, such reflections along with varying lattice parameters were observed reproducibly whenever the gel was heated below 1000°C (both dry and wet, Table 1). They disappeared on heating either for a longer time or at higher temperatures and did not reappear on reheating (wet or dry) at lower temperatures. Nevertheless, the following observations taken together provide considerable evidence for the existence of various types of order-disorder in  $MgAl_2O_4$ , although the transitions may not always be reversible.

1. The extra reflections are definitely observed under certain conditions of formation.

2. Infrared absorption patterns of  $MgAl_2O_4$  (Fig. 1) synthesized at 600°C (1000 bars water vapor pressure, 12 days), and 1540°C and the one synthesized by quenching molten  $MgAl_2O_4$  from just above the melting point (2150°C) at 1500°C/sec differ in much the same way as in other phases where order-disorder is established (Laves and Hafner, 1956). The significance of these spectra will be discussed in a later section.

3. Molten  $MgAl_2O_4$  quenched very rapidly was found to be very well crystallized to X-rays showing no line broadening and giving all the back reflection peaks. The unit cell dimension measured, however, was 8.084 Å, compared with the value of  $8.074 \pm .002$  Å which is obtained on the hydrothermal samples. Indeed, it was found that using exactly the same composition the lattice constant of the phases *equilibrated* above 1300°C was always about 8.084 Å, whereas that of the samples quenched from 1200°C or below was about

<sup>1</sup> Many patterns in the list show unindexed reflections. The present authors indexed them using the cell dimension reported in the corresponding pattern.

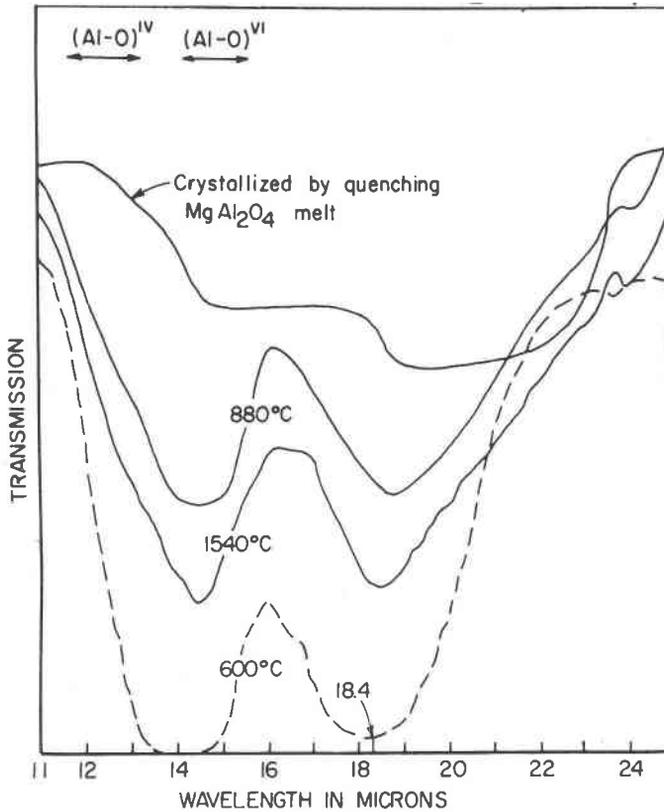


FIG. 1. Infrared spectra of  $MgAl_2O_4$  samples synthesized at different temperatures.

$8.074 \pm .002 \text{ \AA}$ .<sup>1</sup> The demonstration of the change of this lattice parameter with temperature of heat treatment (see Table I) now enables us to account for the spread of values reported by well-known investigators for the unit cell of  $MgAl_2O_4$  (see Swanson *et al.*, 1953). Phases with superstructure reflections (usually found at lower temperatures) give values as high as  $8.122 \text{ \AA}$ .

<sup>1</sup> One reviewer suggested that the apparent smaller unit cell of  $MgAl_2O_4$  synthesized from gels at lower temperatures (below  $1200^\circ\text{C}$ ) could be ascribed to incomplete reaction:



$MgO$  (gel) is amorphous to X-ray, and the unit-cell dimension of the spinel phase (solid-solution),  $MgAl_2O_4 \cdot Al_2O_3$ , is smaller than the stoichiometric spinel,  $MgAl_2O_4$ . However, many samples listed in Table I were studied under petrographic microscope and no amorphous material was observed. Besides, solubility of  $Al_2O_3$  in the  $MgAl_2O_4$  lattice at temperatures below  $1200^\circ\text{C}$  is too little to cause such contraction of the unit cell (Roy, Roy & Osborn, 1953).

High-temperature X-ray diffraction studies of  $\text{MgAl}_2\text{O}_4$  made at temperatures from 500–850°C showed an increase in the integrated intensity of the (220) reflection\* relative to that of the (440) reflection. Datta and Roy (1963a, 1967) showed that the ratio of the intensities of the (220) and (440) reflection of a spinel is very sensitive to the exchange of positions between the tetra- and octahedral sites by the cations, provided the cations involved have significantly different X-ray scattering factors. Since  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  have nearly identical X-ray scattering factors, the observed relative change in the  $I(220)$  of  $\text{MgAl}_2\text{O}_4$  cannot be attributed to the changes in the ionic distribution ( $x$ , see Introduction). However,  $I(220)$  of  $\text{MgAl}_2\text{O}_4$  also increases rapidly if the oxygen parameter ( $u$ ) changes from 0.375 to 0.390 (Barth and Posnjak, 1932). It has been found from theoretical calculations that a more normal arrangement of cations is favored when  $u > 0.379$  (in the case of  $\text{MgAl}_2\text{O}_4$ ) otherwise inverse or random arrangements are stabilized (De Boer *et al.*, 1948, 1950). Hence, the observed increase in the  $I(220)$  of  $\text{MgAl}_2\text{O}_4$  with temperature may be interpreted as due to gradual increase in  $u$  which in turn would cause  $\text{MgAl}_2\text{O}_4$  to become a more normal spinel at higher temperatures.

### BINARY SYSTEMS

From the general discussion presented in earlier papers, the essential variables determining the cation arrangement in spinels are: (1) the size and charge of the cations involved, (2) the lattice constant, (3) the oxygen parameter,  $u$ , (4) the distribution and degree of order among the ions in the tetra- and octahedral sites. A calculation of the Madelung constant shows some relationship between (2), (3) and (4) (De Boer *et al.*, 1948, 1950). A gradual change in the oxygen parameter and the lattice constant of a spinel is expected when the temperature and/or composition of a solid-solution spinel phase is gradually changed. This in turn may cause a continuous rearrangement of cations in their distribution in the two possible sites. Such rearrangement will be reflected in the X-ray intensities of a solid-solution series of spinels having cations of significantly different scattering factors. Furthermore, crystalline solutions of spinels in which no changes in cation distribution or in valence occur are supposed to be ideal (Romeijn, 1953), and Vegard's law is obeyed. However, deviation from Vegard's law can be interpreted as deviation from such ideal distribution of cations, and any variation in the extent of the deviation with temperature<sup>1</sup> can be explained as further change in the distribution of the cations in the solid-solution spinel phase with temperature. In addition, introduction of two or more cations in a spinel structure increases the possibility of ordering in one or more of the sublattices—at least at lower temperatures. Thus, a 50:50 mixture of  $\text{A}^{(4)}\text{B}_2^{(6)}\text{O}_4$  and  $\text{C}^{(4)}\text{D}_2^{(6)}\text{O}_4$  would, in case of a "regular" (Romeijn, 1953) solid solution, have a configuration of  $(\text{A}_{0.5}\text{C}_{0.5})^{(4)}(\text{BD})^{(6)}\text{O}_4$  with the possibility of 1:1 ordering in both tetra- and octahedral sites. For this

\* Abbreviated as  $I(220)$

<sup>1</sup> Temperature at which the crystalline solutions are synthesized.

reason, the subsolidus regions of a series of binary systems of spinels were studied with a view toward (1) interpreting the mutual crystalline solubility of various spinels as a function of temperature in terms of the type of cation distribution and (2) formulating the nature of the distribution of the cations as a function of temperature in the binary systems in which the cation distribution of one end member is well known, or in those cases in which the crystal field stabilization energy strongly favors a particular extreme distribution, such as  $Cr^{3+}$  in octahedral and  $Zn^{2+}$  in tetrahedral sites (Miller, 1959).

The significant observations of the present study together with very brief comments on the present and previous investigations are presented.

*The System  $LiAl_5O_8$ - $MgAl_2O_4$ .*  $LiAl_5O_8$  is a derivative of  $MgAl_2O_4$  where  $Li^+$  and  $Al^{3+}$  together substitute two  $Mg^{2+}$  ions (Kordes, 1935). It exists in two polymorphic forms. The high-temperature form with a spinel structure undergoes a first-order reconstructive (Buerger, 1951) transformation at  $1295 \pm 5^\circ C$  to an equilibrium low-temperature form with primitive cubic symmetry (Datta and Roy, 1963b). This transition is associated with a 1:3 ordering of  $Li^+$  and  $Al^{3+}$  ions in the octahedral sites of the low-temperature form, and this type of order reduces the space group from  $O_h^7$  (spinel) to  $O^7$  (Braun, 1952; Verwey and Heilman, 1947; White and DeAngelis, 1967). The ordered low-temperature form shows low-angle superstructure reflections, such as (210), (211), etc., under X-ray diffraction.

The results of the critical experiments on the temperature dependence of the phases present as obtained in the present investigation, are plotted in Figures 2 and 3. These are selected from a total of some 240 runs. Also shown in Figures 4 and 5 are the lattice spacing changes with composition at two different temperatures. Several features of the diagrams need comment. Figure 2 shows the existence of two virtually complete series of crystalline solution; the high-temperature form is a true spinel, whereas the low-temperature form has a primitive cubic symmetry. Although both forms occur in pure  $LiAl_5O_8$ , the low-temperature form has not yet been reversibly quenched in  $MgAl_2O_4$ . The intensities of the ordering or superstructure peaks decrease continuously with increase of  $MgAl_2O_4$  content and finally become undetectable when the composition has 90 mole percent of  $MgAl_2O_4$  or more. Figure 2 shows the phase diagram as prepared by heating gels in up-temperature direction only and, therefore, may not represent the true equilibrium conditions. The data in Figure 3 are obtained by heating crystalline phases in both up- and down-temperature directions and thus establish reversibility. A comparison of Figures 2 and 3 indicates that these two diagrams are

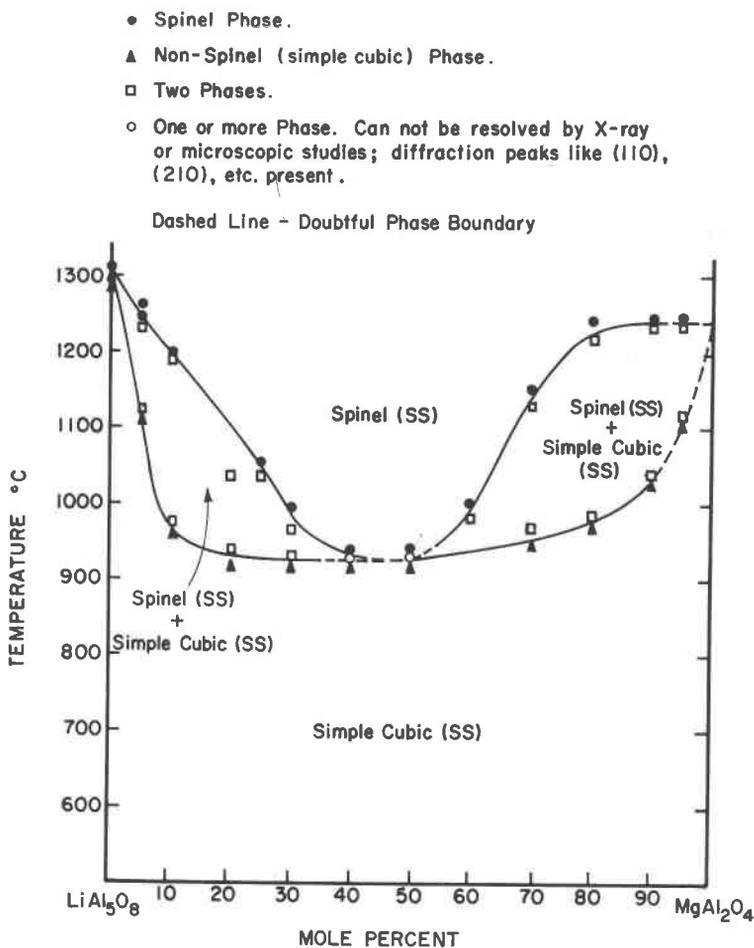


FIG. 2. The system  $\text{LiAl}_5\text{O}_8\text{-MgAl}_2\text{O}_4$ : Diagram obtained by heating gels in up-temperature direction.

essentially identical except for the data on compositions with 10 mole percent of  $\text{LiAl}_5\text{O}_8$ . This is rather difficult to explain. Further, Figure 2 shows a typical complete solid-solution relationship with a first-order transition in the end-members. The significant aspect is the fact that the data extrapolate clearly to a transition in pure  $\text{MgAl}_2\text{O}_4$  at about  $1240^\circ\text{C}$ , although this has never been proved. Indications of its existence are indirectly obtained from the anomalous appearance of the superstructure reflections in the low-temperature  $\text{MgAl}_2\text{O}_4$  runs and from the lattice constants (see Table I). Moreover, its presence in essentially pure  $\text{MgAl}_2\text{O}_4$  raises questions about the ascription of the transition in  $\text{LiAl}_2\text{O}_8$

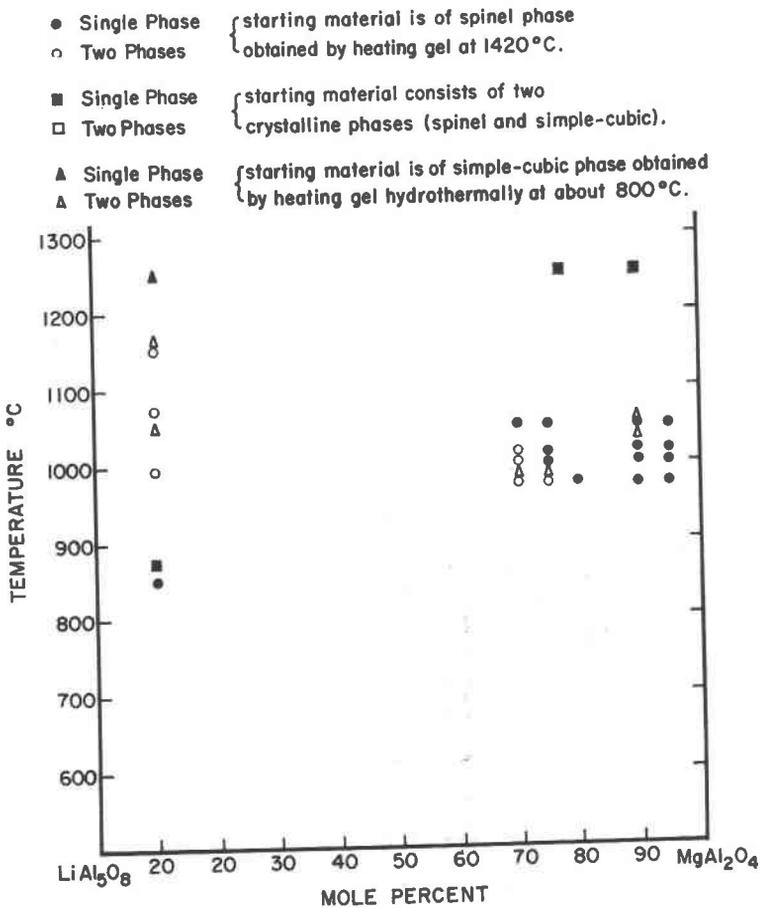


FIG. 3. The system  $LiAl_5O_8$ - $MgAl_2O_4$ : Diagram shows the number of coexisting phases as revealed by equilibrium heating and cooling of crystalline phases.

to disorder of  $[LiAl_3]$  on the octahedral sites (Verwey and Heilman, 1947). The failure of the few magnesia rich mixtures (see Fig. 3) to exsolve may be reasonably ascribed to:

- (1) the nonavailability of transition energy at the annealing temperature, or
- (2) the fact that the two-phase region in the magnesia-rich side is metastable.

However, it can be clearly seen that the two structures can be prepared under equilibrium conditions with as little as about 10 mol percent of  $LiAl_5O_8$ .

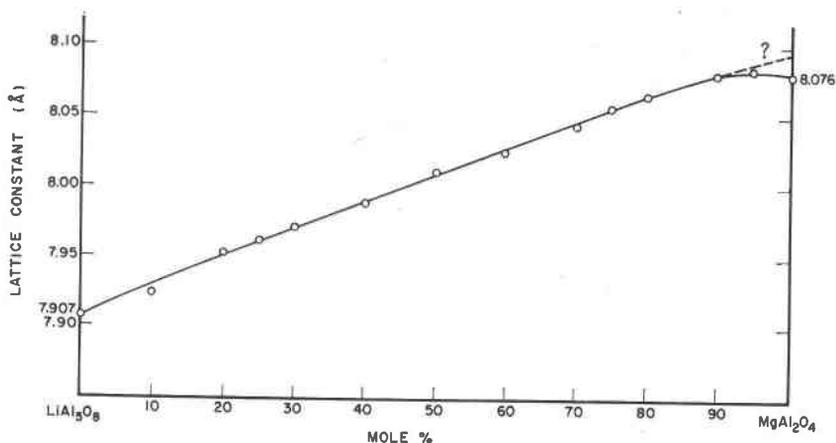


FIG. 4. Lattice parameter versus composition diagram of the system  $\text{LiAl}_5\text{O}_8\text{-MgAl}_2\text{O}_4$ . Lattice constants were determined from the (844) and (440) reflections of the phases quenched from  $750^\circ\text{C}$ .

*The System  $\text{MgAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  and  $\text{NiAl}_2\text{O}_4\text{-ZnAl}_2\text{O}_4$ .* Investigation in the one component systems showed "typical"  $\text{NiAl}_2\text{O}_4$  to be a spinel with varying degrees of normality depending on the temperature of equilibration in the range  $600\text{-}1500^\circ\text{C}$ , whereas  $\text{ZnAl}_2\text{O}_4$  remains strictly a normal spinel. The concentration of nickel in the tetrahedral sites (*i.e.* normality) increases with temperature. At  $600$  and  $1550^\circ\text{C}$  the cation arrange-

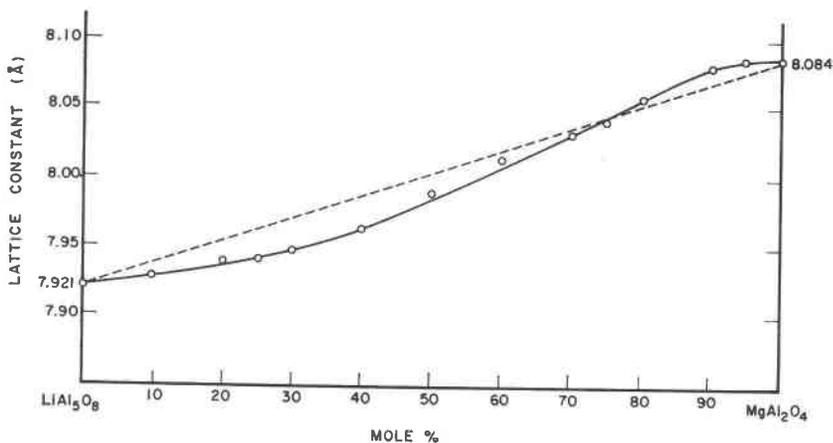


FIG. 5. Lattice parameter versus composition diagram of the system  $\text{LiAl}_5\text{O}_8\text{-MgAl}_2\text{O}_4$ . Lattice constants were determined from the (844) and (440) reflections of the phases quenched from  $1420^\circ\text{C}$ . The dashed line shows the expected results for ideal solution.

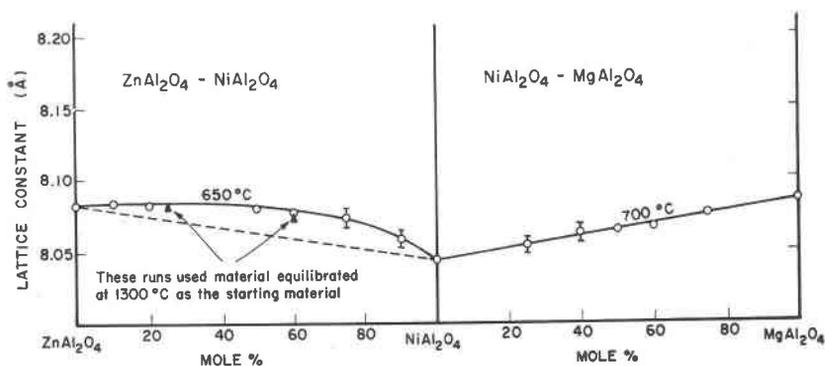
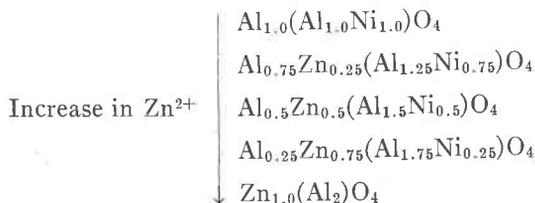


FIG. 6. Lattice parameter versus composition diagram for the systems  $NiAl_2O_4$ - $ZnAl_2O_4$  ( $650^\circ C$ ) and  $NiAl_2O_4$ - $MgAl_2O_4$  ( $700^\circ C$ ). Lattice constants were measured from the (844) and (751) reflections. The dashed line indicates the case for ideal solution.

ments in  $NiAl_2O_4$  are  $(Al)^{(4)}(NiAl)^{(6)}O_4$  and  $(Ni_{0.25}Al_{0.75})^{(4)}(Al_{1.25}Ni_{0.75})^{(6)}O_4$ , respectively (Datta and Roy, 1963a, 1967). Both  $ZnAl_2O_4$  and  $MgAl_2O_4$  are completely miscible with  $NiAl_2O_4$  within the temperature range of 650 ( $700$  bars) to  $1370^\circ C$ . The variation of lattice constant with composition for these two systems is shown in Figures 6 and 7. In the case of the  $MgAl_2O_4$ - $NiAl_2O_4$  system, an ideal mixing is closely followed at all temperatures, whereas the  $ZnAl_2O_4$ - $NiAl_2O_4$  system shows markedly different degrees of positive deviation at different temperatures (Figs. 6 and 7). Since  $NiAl_2O_4$  tends toward the inverse arrangement at lower temperatures, being almost completely inverse at  $650^\circ C$  (Datta and Roy, 1967), the substitution of  $ZnAl_2O_4$  in the  $NiAl_2O_4$  lattice at  $650^\circ C$  probably proceeds according to the following scheme:



The ions in parentheses are in the octahedral sites. Contraction of the lattice parameter due to replacement of the octahedral  $Ni^{2+}$  ( $r=0.78 \text{ \AA}$ )<sup>1</sup> by  $Al^{3+}$  ( $r=0.57 \text{ \AA}$ ) appears to be overcompensated by the substitution of the tetrahedral  $Al^{3+}$  by  $Zn^{2+}$  ( $r=0.83 \text{ \AA}$ ). At higher temperatures ( $1370^\circ C$ ), a part of nickel of  $NiAl_2O_4$  is present in the tetrahedral sites. So,  $Zn^{2+}$  replaces both  $Al^{3+}$  and  $Ni^{2+}$  ions in tetrahedral positions and,

<sup>1</sup> Throughout this paper Goldschmidt's values for ionic radii have been used.

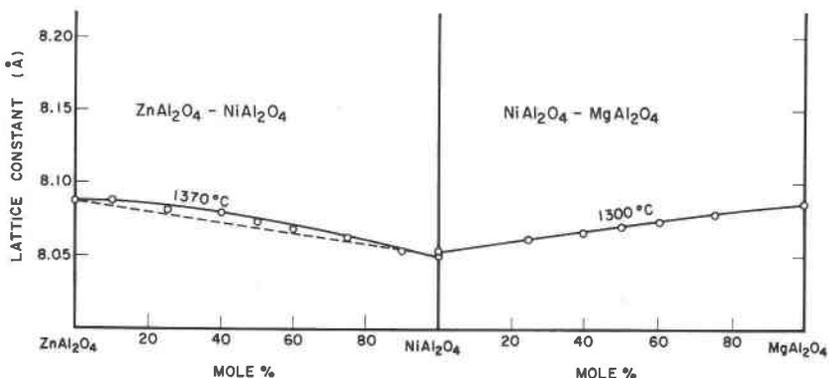


Fig. 7. Lattice parameter versus composition diagram for the systems  $\text{NiAl}_2\text{O}_4\text{-ZnAl}_2\text{O}_4$  ( $1370^\circ\text{C}$ ) and  $\text{NiAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$  ( $1300^\circ\text{C}$ ). Lattice constants were measured from the (844) and (751) reflections.

therefore, the positive deviation is somewhat subdued. Due to the poor crystallinity of the nickel-rich spinels synthesized at lower temperatures, the reproducibility of lattice parameter measurements is only with  $\pm 0.003 \text{ \AA}$ . Nevertheless, a stronger positive deviation is quite obvious (Fig. 6). As the intensity of the (220) reflection in the X-ray diffraction pattern is only determined by the ions at the tetrahedral sites (Datta and Roy, 1967), sharp increase in the intensity of the (220) reflection of  $\text{NiAl}_2\text{O}_4$  phases with increase in  $\text{ZnAl}_2\text{O}_4$  content indicates that all zinc ions go to the tetrahedral sites, whereas  $\text{Ni}^{2+}$  ions prefer octahedral sites (Fig. 8).

The ideal relation in the  $\text{MgAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  system (Figs. 6, 7) can be explained by two alternatives:

1.  $\text{Mg}^{2+}$  ( $r=0.78 \text{ \AA}$ ) randomly replaces  $\text{Ni}^{2+}$  ( $r=0.78 \text{ \AA}$ ) in both tetra- and octahedral sites which  $\text{Ni}^{2+}$  has been shown to occupy at  $1300^\circ\text{C}$ . Such a scheme would again point to the presence of some randomization of cations in  $\text{MgAl}_2\text{O}_4$ .
2. Substitution is the same as in the  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  system with  $\text{MgAl}_2\text{O}_4$  completely "normal." This time the contraction of lattice parameter due to replacement of octahedral  $\text{Ni}^{2+}$  by  $\text{Al}^{3+}$  is exactly compensated by the replacement of  $\text{Al}^{2+}$  by  $\text{Mg}^{2+}$  in the tetrahedral sites.

However, the relative intensities of the (220) and (440) reflections of the system remain fairly constant throughout the series (Fig. 8) supporting the former alternative that  $\text{Ni}^{2+}$  ions are replaced randomly by  $\text{Mg}^{2+}$  in the tetrahedral and octahedral sites. Hence, it can be suggested that the distribution of the cations in  $\text{MgAl}_2\text{O}_4$  is between the normal arrangement of  $\text{ZnAl}_2\text{O}_4$  and the random arrangement of  $\text{NiAl}_2\text{O}_4$ . Like  $\text{NiAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$  becomes more normal with increase in temperature. In other

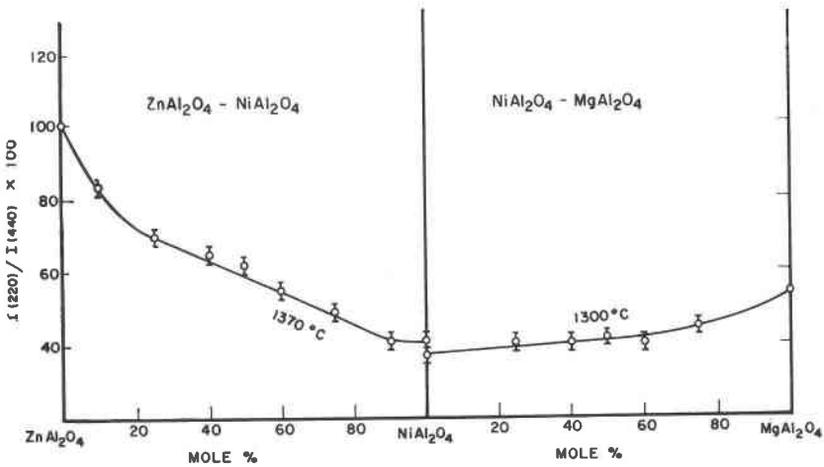


FIG. 8. Relative integrated X-ray intensities of the (220)/(440) reflections versus composition diagram for the systems  $ZnAl_2O_4$ - $NiAl_2O_4$  and  $NiAl_2O_4$ - $MgAl_2O_4$ . The temperatures from which the samples were quenched are shown.

words, the cation arrangement in  $MgAl_2O_4$  can be expressed by the general formula  $(Mg_{1-x}Al_x)^{(4)}(Al_{2-x}Mg_x)^{(6)}O_4$  where  $x$  decreases with increase in temperature.

*The System  $MgAl_2O_4$ - $NiCr_2O_4$ .* The observations in the preceding pages have already appeared to produce evidence for a random arrangement of cations in  $MgAl_2O_4$ . Complete or partial miscibility with marked deviation from ideality in the subsolidus region of the system  $MgAl_2O_4$ - $NiCr_2O_4$  would further substantiate the concept of a partly random  $MgAl_2O_4$  (Romeijn, 1953). This is because all chromites ( $A^{2+}Cr_2^{3+}O_4$ ) are supposed to be normal spinels due to the strong affinity of  $Cr^{3+}$  for octahedral sites (Miller, 1959).

Nine compositions (gel) in the system  $NiCr_2O_4$ - $MgAl_2O_4$  were heated in noble-metal tubes within the temperature range of 600 (750 bars) to 1300°C. It has been found that these spinels are entirely miscible within this range of temperature. The changes in the lattice constant with composition at 700 and 1200°C are given in Figures 9 and 10, respectively. Although Vegard's law is obeyed at high temperature, a positive deviation is observed at 700°C, indicating again that a measurable change in the cation distribution with temperature must have occurred. Since  $NiCr_2O_4$  is very stable in the normal arrangement within a wide temperature range, the change must be due to  $MgAl_2O_4$ . Furthermore, the direction of the change would then also be analogous to that in  $NiAl_2O_4$ , *i.e.*

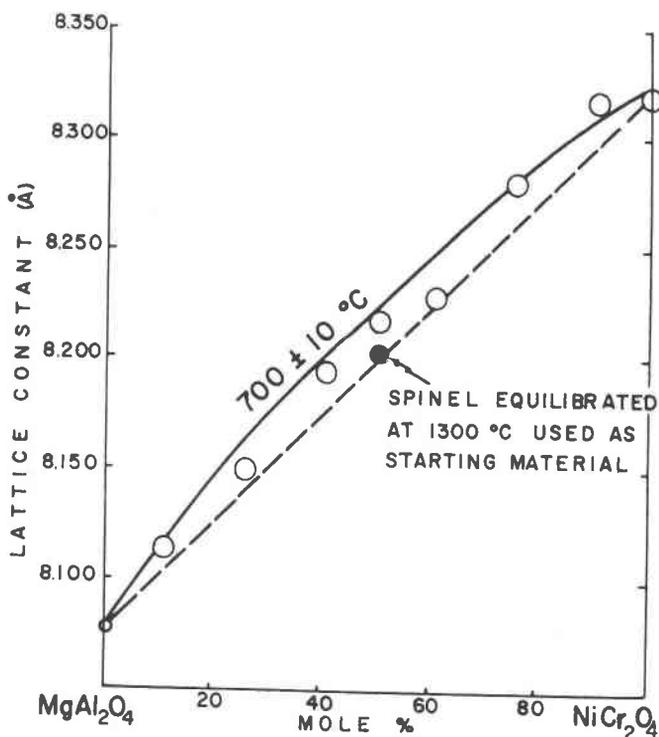


FIG. 9. Lattice parameter versus composition diagram for the system  $\text{MgAl}_2\text{O}_4$ - $\text{NiCr}_2\text{O}_4$ . Cell parameters were measured from the (731), (533) and (440) reflections of the phases quenched from  $700 \pm 10^\circ\text{C}$ . The dashed line shows the case for ideal solution.

from a more inverse type spinel at lower temperatures to a more normal type spinel at higher temperatures.

*Infrared spectra.* From the infrared spectra of known compounds (Stubican and Roy, 1961; White and Roy, 1964), the (Al-O) bands due to tetrahedral and octahedral  $\text{Al}^{3+}$  are assigned to Figure 1. The spectra show two main bands at about  $14$  and  $18\mu$  regions. Of these only the former shows relative shifts with temperatures, indicating that any disorder involves the relative amount of  $\text{Al}^{3+}$  in four- and six-fold positions. Thus at lower temperature ( $600^\circ\text{C}$ ) when  $\text{Al}^{3+}$  is present in both four- and six-coordinating positions, (Al-O)<sup>(4)</sup> and (Al-O)<sup>(6)</sup> bands are superimposed. With increase in temperature,  $\text{MgAl}_2\text{O}_4$  becomes more normal and therefore the (Al-O)<sup>(6)</sup> band is prominent at  $1540^\circ\text{C}$ . The spectrum given by the sample obtained by quenching molten  $\text{MgAl}_2\text{O}_4$  from just above the melting point ( $2150^\circ\text{C}$ ) at  $2000^\circ\text{C}/\text{sec}$  is remarkably different. This can

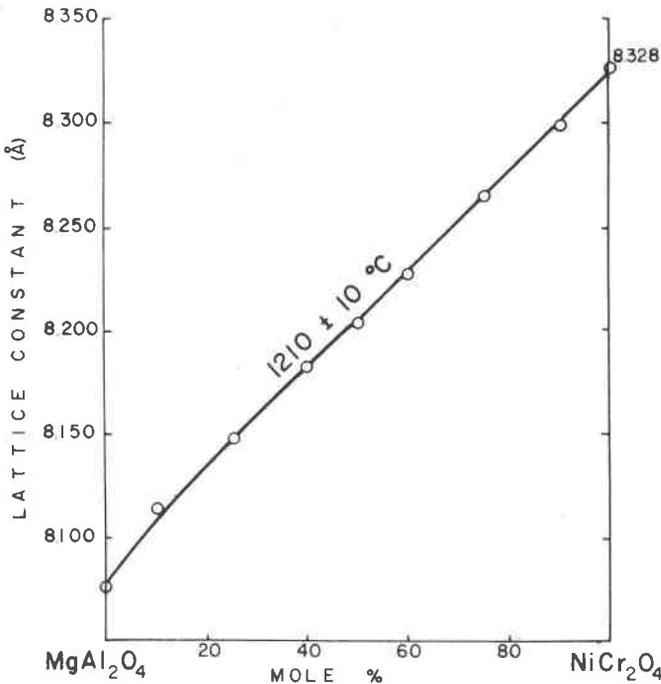


FIG. 10. Lattice parameter versus composition diagram for the system  $MgAl_2O_4$ - $NiCr_2O_4$ . Cell parameters were measured from the (731), (533) and (440) reflections of the phases quenched from  $1210 \pm 10^\circ C$ .

be explained as due to an increase of  $Al^{3+}$  in 6-coordination (new absorption near  $15-16\mu$ ), decrease of  $Al^{3+}$  in 4-coordination (weakening of band at  $14\mu$ ) and possibly introduction of substantial amount of  $Mg^{2+}$  in 4-coordination (new band at about  $22\mu$ ). The latter band could also be a Mg-O-Al type stretching, but its assignment to (Mg-O)<sup>(4)</sup> in the spinel is not unreasonable in view of the (Mg-O)<sup>(6)</sup> band of periclase at  $23\mu$  (Stubican and Roy, 1961).

The above considerations indicate that the infrared spectra and the unit-cell dimensions of natural spinels could possibly be used as geologic thermometers. Two transparent single crystals (2-3 mm in size) of natural spinels which belong to two different geologic settings in Ceylon and Sweden were obtained from commercial sources. The spinel from Sweden occurs in contact limestone, whereas the one from Ceylon occurs in alumina-rich gneiss. The powdered samples of these two spinels, in spite of their essentially identical composition (99.9% pure)<sup>1</sup>, gave different

<sup>1</sup> Spectrographically analyzed.

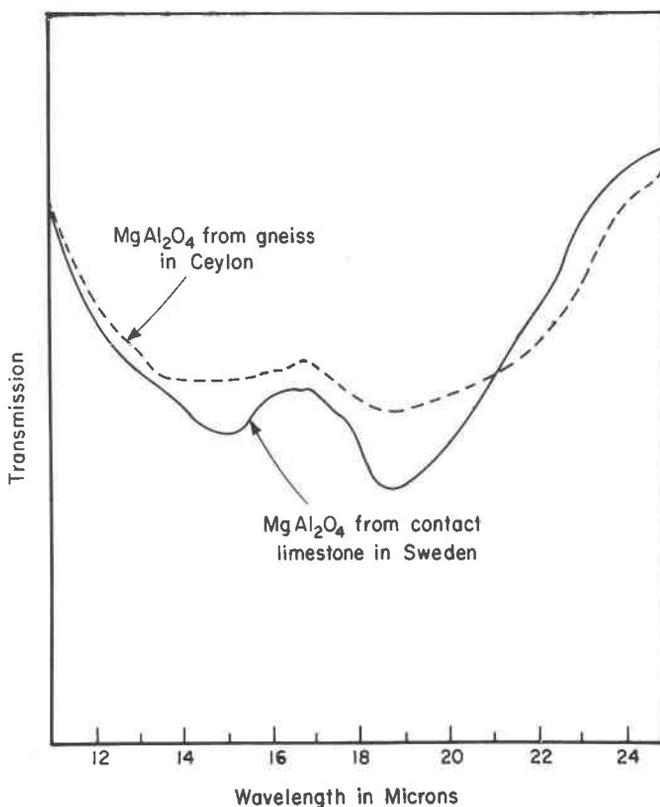


FIG. 11. Infrared spectra of natural  $MgAl_2O_4$  samples obtained from different geological settings.

cell dimensions and infrared spectra (Fig. 11). The cell dimensions of the samples obtained from Ceylon and Sweden were found to be 8.078 and  $8.071 \pm 0.001$  Å, respectively, indicating a higher temperature of formation for the former. The same conclusion can be obtained by comparing the infrared spectra of these samples with those obtained from heating  $MgAl_2O_4$  at different temperatures (Fig. 1).

#### REVERSIBILITY AND THE NATURE OF THE TRANSITION

The investigations of the binary systems presented earlier can be interpreted in terms of (1) a possible superstructure (long-range order) in  $MgAl_2O_4$  at temperatures below  $1240^\circ C$  and (2) a temperature-dependent, random distribution of  $Mg^{2+}$  and  $Al^{3+}$  in the tetra- and octahedral sites at higher temperatures.

The superstructure or the order has been observed only when  $MgAl_2O_4$  *gel* is heated at temperatures below  $1240^\circ C$  and is most likely to be irreversible under equilibrium conditions.

In general, the reversibility of the disordering transitions involving the distribution of the cations between the tetra- and octahedral sites is demonstrated in the cell dimension versus composition or temperature diagrams studied. Diffusion of the cations from tetrahedral to octahedral positions and vice versa in the system  $MgAl_2O_4-NiCr_2O_4$  was found to be unusually sluggish and reversion could not be achieved at all. When oxide mixtures were used as starting materials, heating even up to  $1200^\circ C$  for 15 hours showed unreacted oxides. In the present investigation, the 50:50 composition quenched at  $1250^\circ C$  was reheated hydrothermally at  $700^\circ C$  for two weeks (Fig. 9) without any change in cell dimension. An attempt to prove the reversibility of the transitions was also made by noting the change in the  $I(220)$  of annealed samples in the system  $MgAl_2O_4-NiCr_2O_4$ . Although the intensity change could not be reversed completely, the reversible nature and the direction of equilibrium were unequivocally established by the direction of the changes. Hence, a gradual reversible equilibrium change in the coordination of cations in  $MgAl_2O_4$  and its solid-solution phases with change in temperature (over a range of several hundred degrees) has been established. Since during such a process each spinel maintains its crystallographic characteristics (space group is unchanged), these transitions can be classified as second order changes (Buerger, 1951) of positional disorder.

#### SUMMARY AND CONCLUSION

Due to the small difference in their X-ray scattering factors, intensity calculations fail to show any ordering of Mg and Al in the spinel  $MgAl_2O_4$ . Published results on cell dimensions, powder diffraction patterns, and the infrared spectra obtained in the present investigation indicate a temperature dependence of the distribution of the cations in the tetra- and octahedral sites. In addition, other lines of evidence from subsolidus studies of selected systems reveal the following facts.

1. The  $LiAl_5O_8-MgAl_2O_4$  system indicates the possible existence of two cubic structures for  $MgAl_2O_4$ , a spinel form at high temperature and a simple-cubic form at lower temperature.

2.  $MgAl_2O_4$  and  $NiCr_2O_4$  (ideally normal spinel within the range of  $600-1400^\circ C$ ) are completely miscible within a temperature range of  $600$  (750 bars)— $1300^\circ C$ . Although Vegard's law is obeyed at higher temperatures, a positive deviation is observed at  $700^\circ C$  suggesting a change in the distribution of the cations in  $MgAl_2O_4$  with temperature.

3. Both  $ZnAl_2O_4$  (normal spinel) and  $MgAl_2O_4$  are completely miscible

with  $\text{NiAl}_2\text{O}_4$  (usually random spinel with varying degrees of normality with change in temperature) within a temperature range of 650 (750 bars)—1370°C. In the system  $\text{MgAl}_2\text{O}_4$ - $\text{NiAl}_2\text{O}_4$ , Vegard's law is closely followed at all temperatures, whereas the  $\text{ZnAl}_2\text{O}_4$ - $\text{NiAl}_2\text{O}_4$  system shows different degrees of positive deviation at different temperatures. The relative intensity measurement of the (220) and (440) reflections and comparison with the calculated values further indicate the temperature dependence and the random distribution of the cations between the tetrahedral and octahedral sites of  $\text{MgAl}_2\text{O}_4$ . The concentration of  $\text{Mg}^{2+}$  in the tetrahedral sites gradually increases with increase in temperature.

## ACKNOWLEDGMENT

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