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THERMODYNAMIC BEHAVIOR OF Ga^{3+}, Al^{3+} AND Fe^{3+} DISTRIBUTIONS IN GARNETS[1]

ROBERT F. MUELLER AND SUBRATA GHOSE
Goddard Space Flight Center, Greenbelt, Maryland 20771

ABSTRACT

Data on the distribution of Ga^{3+}, Al^{3+} and Fe^{3+} among the tetrahedral (*d*) and octahedral (*a*) sites in certain garnets were examined in terms of a thermodynamic model which yields the following expression for the distribution constant K°:

$$K^\circ = \frac{X_d(1 - X_a)\phi_{da}}{X_a(1 - X_d)\phi_{ad}}$$

Here the X's are site occupancy fractions and the ϕ's are equivalent to activity coefficient products factors. It is shown that for the elements discussed $(\phi_{da}/\phi_{ad}) \approx 1$, corresponding to ideal mixing on the individual sites. Thus we obtain

Garnet	X_d, X_a	K°	T, °K
$Y_3Ga_xFe_{5-x}O_{12}$	$Ga^{3+}/(Ga^{3+} + Fe^{3+})$	6.71	1643
$Y_3Ga_xAl_{5-x}O_{12}$	$Ga^{3+}/(Ga^{3+} + Al^{3+})$	~2.24	—
$Eu_3Ga_xFe_{5-x}O_{12}$	$Ga^{3+}/(Ga^{3+} + Fe^{3+})$	~4.46	—

where x ranges from zero to five.

With the presently available precision the calculated temperature sensitivity of K° is such that variations of several hundred degrees in the sintering temperature should be apparent.

It is stressed that this form of ideal mixing on the individual sites corresponds to nonideal mixing of the component end members $Y_3Fe_5O_{12}$ and $Y_3Ga_5O_{12}$ when referred to their mole fractions and mean molar volumes. This is consistent with the apparent positive deviation of the mean molar volume from a straight line.

INTRODUCTION

Nearly all crystalline materials are of a nonstoichiometric character and at the same time have crystal structures in which each atom or ion is distributed over two or more nonequivalent structural positions. In the garnets Ga^{3+}, Al^{3+} and Fe^{3+} are distributed among two different crystallographic sites with octahedral (*a*) and tetrahedral (*d*) coordinations of the O^{2-} ions. The nature of the distributions or order-disorder relations between these positions are functions of the total crystalline composition, the temperature and the pressure in the equilibrium state. In a disequilibrium state the distributions are also dependent on the previous history of the sample and on the time and provide an interesting application of chemical kinetics.

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The first comprehensive treatment of the thermodynamic theory for order-disorder phenomena was provided by Bragg and Williams (1934) for the simple binary alloys. Analogous treatments were subsequently given by others for the spinels. Especially noteworthy contributions were made by Néel (1950), Smart (1954) and by Callen, Harrison and Kriessman (1956). Recently Borghese (1967) interpreted the magnetic properties of certain spinels and garnets in terms of the model in which mixing on the individual lattice sites has the character of ideal solutions. Analogous equilibrium equations were also derived for the distribution of Mg^{2+} and Fe^{2+} among the nonequivalent structural sites of pyroxenes and amphiboles (Mueller, 1962). As distinguished from the previous treatments of metallic alloys, spinels and garnets, the latter equations were formulated in terms of the atomic fractions (site occupancy fractions) of the cations on the individual sites, a procedure which will be adopted in this paper also. This formulation has the advantage of yielding more simplified data plots.

Although the effect of temperature on the intracrystalline distributions forms an important part of the problem and is implicit in all the theoretical treatments, this aspect of the problem has not been sufficiently appreciated in much of the experimental work on garnets so that more often than not the temperature of preparation of the specimens is not given. We shall attempt here to analyse the character of the solid solutions and to calculate the effect of temperature on the distribution isotherms.

OBSERVED DISTRIBUTIONS

There are five sets of experimental data for the distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of the garnet $Y_3Ga_xFe_{5-x}O_{12}$, where x can in theory range from zero to five, corresponding to complete substitution of Ga^{3+} for Fe^{3+}. These data were obtained from the analysis of residual magnetic moments (Lüthi and Henningsen, 1964; Geller, Cape, Espinosa and Leslie, 1966); nuclear magnetic resonance (Streever and Uriano, 1965); X-ray and neutron diffraction (Fischer, Hälg, Stoll and Segmüller 1966); and by Mössbauer spectroscopy (Çzerlinsky, 1969). These data may for convenience be separated into two groups, one constituting the magnetic data and the other those data collected by other means. Distributions determined from the latter group are presented in Figure 1 and the distribution from magnetic data are presented in Figure 2. These figures are plotted in terms of the atomic fraction $Ga^{3+}/(Ga^{3+}+Fe^{3+})$ (where the chemical symbol represents the number of moles) of gallium in the tetrahedral and octahedral sites of the total $Ga^{3+}+Fe^{3+}$ on each site.

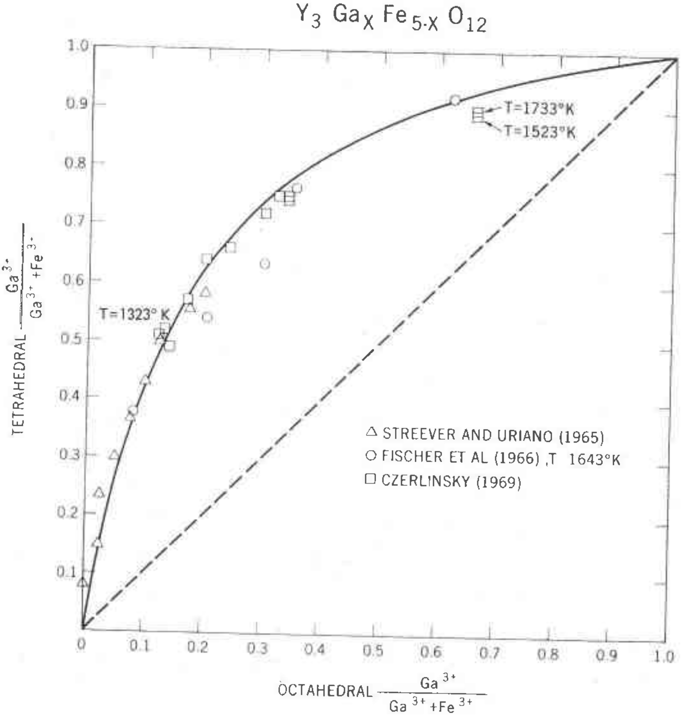

FIG. 1. Distribution, exclusive of magnetic data, of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Y_3Ga_xFe_{5-x}O_{12}$. The curve is fitted to the data of Fischer, *et al.* and corresponds to ideal mixing on the individual sites with an equilibium constant of 6.71.

Data for the distribution of Al^{3+} and Ga^{3+} in $Y_3Al_x\,Ga_{5-x}\,O_{12}$ available from X-ray diffraction experiments (Marezio, Remeika, and Dernier, 1968) are given in Table 1.

Distribution for Al^{3+} and Fe^{3+} from magnetic data by Geller, Williams, Espinosa and Sherwood, (1964) for $Y_3Al_xFe_{5-x}O_{12}$ and as discussed by Borghese (1967) are shown as points in Figure 3.

Finally some experimental points obtained for the distribution of Ga^{3+} and Fe^{3+} in the garnet $Eu_3Ga_xFe_{3-x}O_{12}$ by Mössbauer spectroscopy are shown in Figure 4.

Unfortunately it is not possible to evaluate some major uncertainties in the experimental site occupancy fractions because of lack of information on the conditions of sample preparation. However, according to Fischer *et al.* (1966) the X-ray and neutron diffraction data embody probable errors of about 4–5 percent of the measured values. It should also be borne in mind that the actual site occupancy fractions plotted

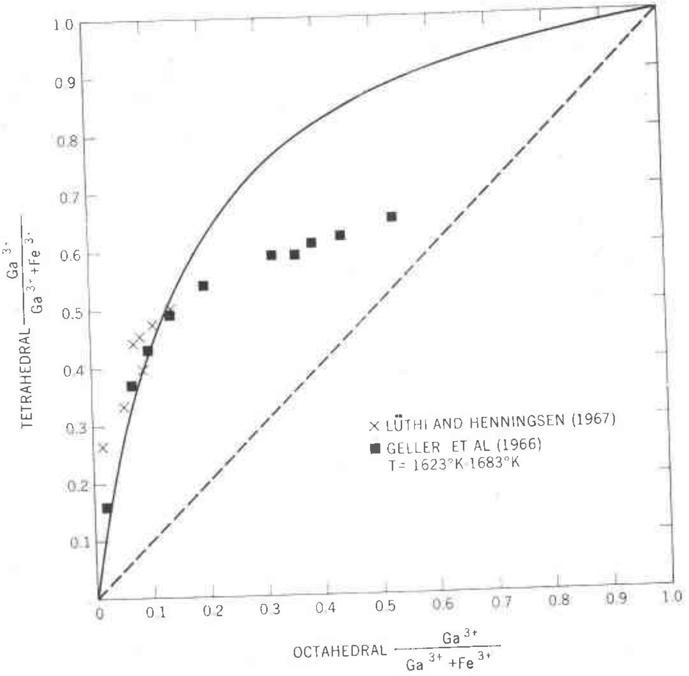

FIG. 2. Distribution based on magnetic data and the model of Geller *et al.* of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Y_3Ga_xFe_{5-x}O_{12}$. The curve is the same as in Fig. 1.

in the figures have usually been derived from the raw data through the use of a model which contains some assumptions about the distributions. We shall see that in the case of the magnetic data in particular, where the site occupancy fractions are derived from magnetic moments, the derived points are highly dependent on the model.

TABLE 1. DISTRIBUTION OF Ga^{3+} AND Al^{3+} IN $Y_3Ga_xAl_{5-x}O_{12}$ AND THE CORRESPONDING EQUILIBRIUM CONSTANT OF EXCHANGE
Data are taken from Marezio *et al.*(1968)

$Ga^{3+}/(Ga^{3+}+Al^{3+})$		K°
Tetrahedral (*d*)	Octahedral (*a*)	
0.290	0.080	4.69
0.491	0.223	3.36
0.653	0.470	2.12
0.863	0.744	2.17

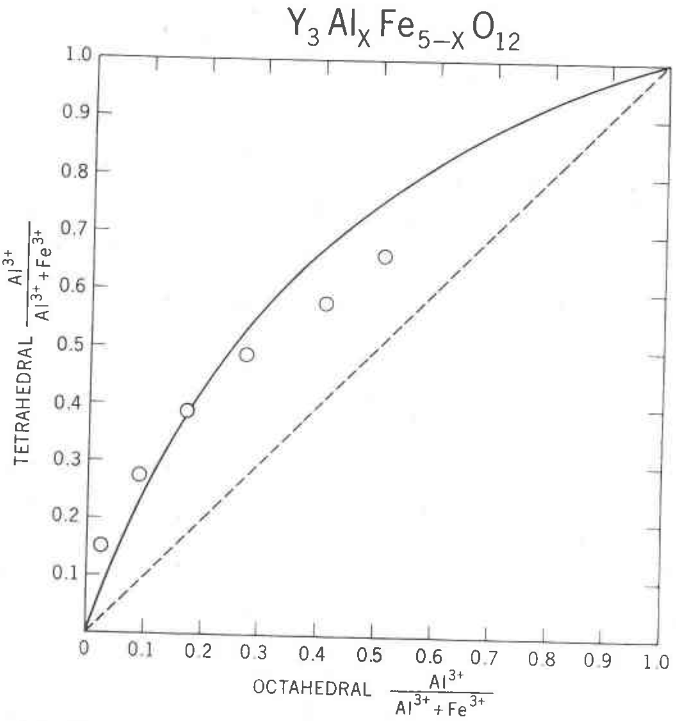

FIG. 3. Distribution of Al^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Y_3Al_xFe_{5-x}O_{12}$. The points are derived from magnetic data and the model of Geller *et al.* (1964). The curve is based on ideal mixing on both sites and corresponds to a distribution constant of 3 (Borghese, 1967).

Although the curve drawn through the data of Figure 1 is a quite good fit it is important to point out that because of the temperature effect on the distribution coefficients (to be discussed later), not all these points can be represented by one curve. The curve shown has been fitted to the data of Fischer *et al.* which represents a temperature of about 1643°*K*. We shall see that the other distributions established at known temperatures should bear definite relations to the curve. Unfortunately little is known of the thermal history of the other data shown in Figure 1. Again, although the thermal histories of most of the samples of Figure 2 are known, we shall see that this information has little meaning when the model from which these points were derived is considered.

VARIATION OF THE MEAN MOLAR VOLUME WITH COMPOSITION

The variation of the unit cell volume of $Y_3Ga_xFe_{5-x}O_{12}$ with $Ga^{3+}/(Ga^{3+}+Fe^{3+})$ is shown in Figure 5. These data, which have a

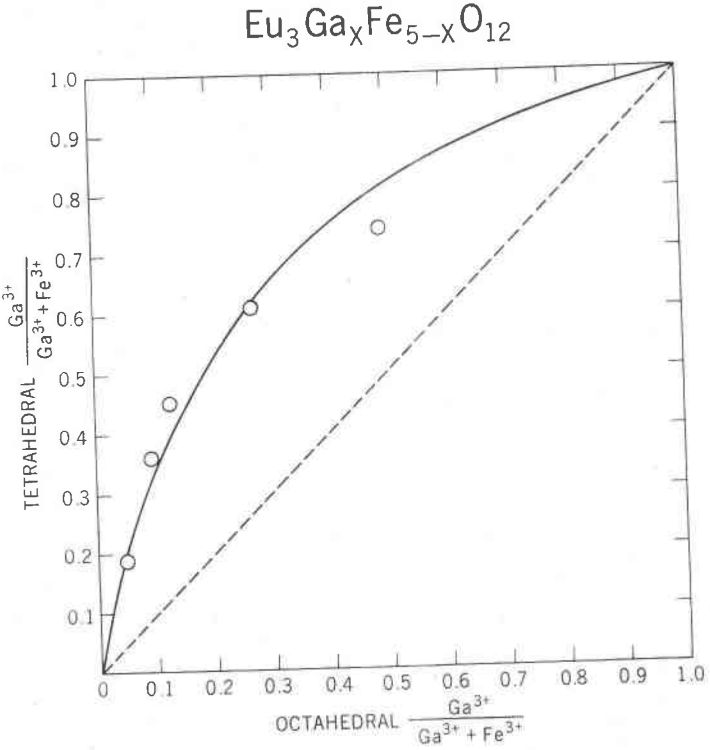

FIG. 4. Distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral **sites of** $Eu_3Ga_xFe_{5-x}O_{12}$ (Nowik and Ofer, 1967). The curve is based on the model for ideal **mixing** on both sites and corresponds to a distribution constant of 4.46.

direct bearing on the thermodynamic interpretation of the distribution data, are taken from the work of Gilleo and Geller (1958), Espinosa (1964), Geller *et al.* (1964), Euler and Bruce (1965), and Fischer *et al.* (1966). The chief interest here is in the possible deviation from a straight line between the molar volumes of $Y_3Ga_5O_{12}$ and $Y_3Fe_5O_{12}$ since adherence of the data to such a line would be required for an ideal solid solution between these macroscopic components. Unfortunately the uncertainties in the cell volume data do not allow this question to be answered unambiguously. However, it is clear that even if a straight line were drawn through the highest volume point (that of Euler and Bruce) for $Y_3Ga_5O_{12}$, most of the intermediate points would still lie above this line. From the most probable straight line (drawn as dashed) this result is even clearer. If this is the true picture, it is clear that there is a positive excess molar volume and that the garnet solid solutions as a whole is non-ideal in character.

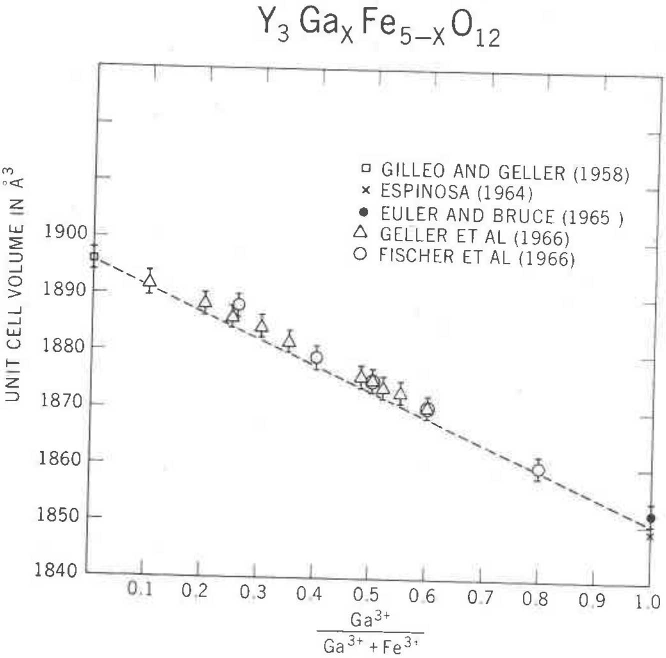

FIG. 5. Cell volume (in Å^3) as a function of the composition in $Y_3Ga_xFe_{5-x}O_{12}$. The cell volumes are proportional to the mean molar volumes.

THERMODYNAMIC CHARACTER OF THE SOLID SOLUTIONS

If the dependence on composition of the free energy of exchange between the nonequivalent lattice sites is largely confined to the entropy of mixing terms, it is convenient to write (Mueller, 1967) the following expression for a quasibinary crystal such as a garnet:

$$K^\circ = \frac{X_d(1 - X_a)\phi_{da}}{X_a(1 - X_d)\phi_{ad}} \tag{1}$$

Here the X's are the site occupancy fractions of one of the two exchangable species on the octahedral (a) and tetrahedral (d) sites, K° is the equilibrium constant and the ϕ factors are analogous to activity coefficient products and are derived from kinetic formulas. By definition K° is a function only of the temperature and the pressure (or volume) while the ϕ's are also functions of the total composition. However, only the temperature dependency is significant for these condensed systems at low to intermediate pressures.

The site occupancy fractions are related to the total mole fraction X_t of a given end member (such as $Y_3Ga_5O_{12}$) as

$$X_t = \tfrac{3}{5}X_d + \tfrac{2}{5}X_a \tag{2}$$

The simplest and most convenient form of equation (1) is one for which $(\phi_{da}/\phi_{ad})=1$, and in which all compositional dependency is confined to the entropy of mixing on the individual *a* and *d* sites. This is a form of "ideal" solution, which is, however, sharply differentiated from the ideal solution of the crystal as a whole in which the activity a_t of a component end member (such as $Y_3Ga_5O_{12}$) is set equal to X_t. The activity of this "ideal" solution (normalized to 1/5 $Y_3Ga_5O_{12}$) is

$$a_t = X_d^{3/5}X_a^{2/5} \tag{3}$$

Obviously (2) and (3) can be equal only if $X_d = X_a$ when $K^\circ = 1$. However in the model under discussion $K^\circ \neq 1$ even at the highest temperatures except as a limiting case since, unlike the nonequivalant sites in metallic alloys, the tetrahedral and octahedral sites always retain their identities.

Figure 3 shows the analogous curve as derived from equation (1) with X_d and X_a equal to the atomic fraction $Al^{3+}/(Al^{3+}+Fe^{3+})$ on the tetrahedral and octahedral sites of $Y_3Al_xFe_{3-x}O_{12}$. This curve corresponds to an equilibrium constant $K^\circ = K_2^\circ = 3$ as derived by Borghese (1967).

The plotted points in Figures 2 and 3 were derived from the experimental data by Geller *et al.* (1964, 1966) by utilizing a highly idealized model which linked the site distributions to observed magnetic moments. Their curves, which give the fraction of various ions in the tetrahedral site as a function of x, indicate that at $x \to 0$ all Al is the tetrahedral site. It may be shown however that such a result is inconsistent with the observed distribution coefficient and with any form of equation (1).

The data of Figures 1 and 3 should be directly related to those of Marezio *et al.* as given in Table 1 if certain simplifying assumptions are introduced, for we have the following related exchange reactions and equilibrium constants:

$$\mathrm{Ga}(a) + \mathrm{Fe}(d) \rightleftarrows \mathrm{Ga}(d) + \mathrm{Fe}(a) \quad K_1^\circ$$

$$\mathrm{Al}(a) + \mathrm{Fe}(d) \rightleftarrows \mathrm{Al}(d) + \mathrm{Fe}(a) \quad K_2^\circ$$

$$\mathrm{Ga}(a) + \mathrm{Al}(d) \rightleftarrows \mathrm{Al}(a) + \mathrm{Ga}(d) \quad K_3^\circ$$

in which *a* and *d* refer to the octahedral and tetrahedral sites. If we now assume that the mixing properties of the ions are invariant with respect to which other ion is present we obtain

$$\frac{K_1^\circ}{K_2^\circ} = K_3^\circ = 2.24$$

Table 1 shows the values of K° as derived from the data of Marezio *et al.* (1968). Although the correspondence with $K_3{}^\circ = 2.24$ is quite good for several specimens, the others differ considerably from this value. It is not known if these differences are attributable to the uncertainties in the data such as arise from the conditions of sintering or to a failure of the assumptions employed in the model.

The distribution curve and the corresponding equilibrium constant $K_4{}^\circ$ for the distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Eu_3Ga_xFe_{5-x}O_{12}$ are shown in Figure 4. In this case the curve gives a quite good fit with $K_4{}^\circ = 4.46$ if the most Ga-rich sample is disregarded. It is clear from a comparison of these data with Figure 1 that the substitution of europium for yttrium tends to favor Fe^{3+} in the tetrahedral site. However here again it must be remembered that the effect of the thermal history is unknown.

Taken together, Figures 1 and 5 point up an interesting feature of the thermodynamics. If the data of Figure 1 truely correspond to the simplified model with $(\phi_{da}/\phi_{ad}) = 1$, the system is a form of ideal solution in which the only compositional dependence of the free energy comes from the entropy of mixing on the individual sites as given by equation (3). However, this result in turn implies non-ideal mixing between the macroscopic components $Y_3Ga_5O_{12}$ and $Y_3Fe_5O_{12}$ in which the sites are not distinguished. The apparent positive deviation from a straight line of the mean molar volume in Figure 5 is compatible with this interpretation.

EFFECT OF TEMPERATURE

Of primary interest is the determination of the effect of temperatures of annealing on the equilibrium constants. This effect could of course be evaluated directly if ΔH° the standard enthalpy of exchange were known, since

$$\frac{\partial \ln K^\circ}{\partial T} = \frac{\Delta H^\circ}{RT^2}.$$

However, in the absence of independent knowledge of ΔH° we can estimate ΔG°, the Gibbs free energy of exchange from the distribution data of Figure 1 for which the annealing temperature is known, since

$$\Delta G^\circ = -RT \ln K^\circ \tag{4}$$

According to Fischer *et al.* (1966), the temperature of sintering for their specimens was 1643°K, and since $K_1{}^\circ = 6.71$, we obtain $\Delta G_1{}^\circ = -6220$ cal. Also we have the general relation

$$\frac{\partial \Delta G_1^\circ}{\partial T} = -\Delta S_1^\circ,$$

where ΔS° is the standard entropy of exchange.

Now we have reason to suspect that ΔS_1° will be small since the system is condensed and no large volume changes are involved. Also, this anticipation has recently been substantiated for the case of the order-disorder relations of Fe^{2+} and Mg^{2+} in $(Mg,Fe)SiO_3$ (orthopyroxene) (Virgo and Hafner, 1969), which represents a situation closely parallel to the garnets.

Thus if $\Delta S_1^\circ \simeq 0$ we have

$$\Delta H_1^\circ \simeq \Delta G_1^\circ,$$

and the temperature effect can be estimated directly for equation (4). This has been done for five isotherms in Figure 6.

If Figure 6 is valid indication of the temperature sensitivity of K_1°, it

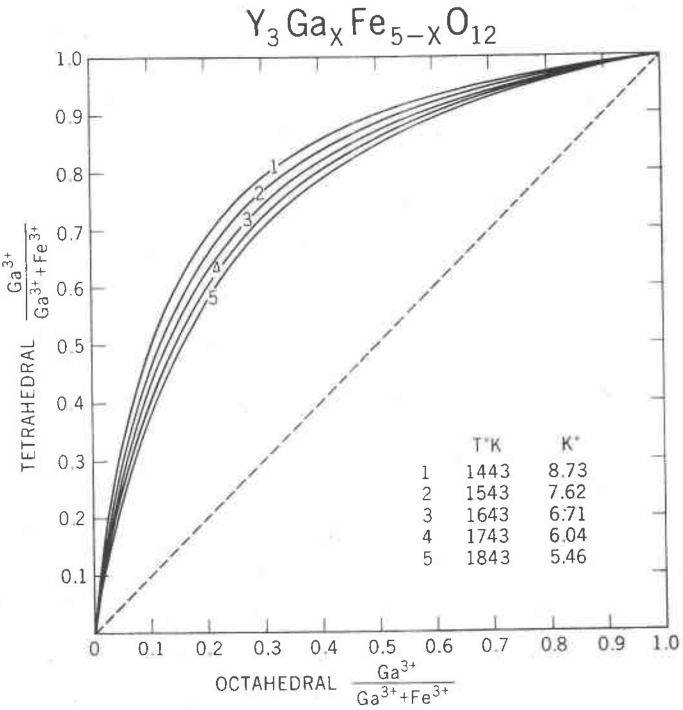

FIG. 6. Calculated isotherms for different (hypothetical) temperatures from the mode which assumes ideal mixing on the individual sites of $Y_3Ga_xFe_{5-x}O12$.

is clear that from the amount of scatter shown in Figure 1 variations of several hundred degrees in sintering temperatures should be detectable. It is unfortunate that the thermal histories of most of the specimens are unknown. Unfortunately probable systematic errors, differences between the different investigations, as well as lack of sufficient data on the thermal histories of the samples, make it impossible to evaluate the effect of temperature precisely. However, it is clear that the 1323°K and 1733°K points of Czerlinsky are in harmony with the data of Fischer and with equation (4).

Equation (4) and the isotherms of Figure 6 can also be used to estimate deviations from ideal mixing on the individual sites from systematic deviations of the data from the isotherms. The excess free energy contributions for such a source should have the same effect proportionally as temperature variations. It is possible that some of the deviations from the data points from the isotherm of Figure 1 are attributable to this source, but the uncertainties in the data preclude any quantitative estimate of the effect at this time.

DEVIATION OF THE DISTRIBUTION FROM MAGNETIC DATA

The model utilized by Geller, *et al.* (1964, 1966) to determine site occupancies from magnetic data has already been discussed (Czerlinsky, 1969). It is an assumption of this model that the intrasublattice and intersublattice interactions are independent of the nature of the non-magnetic ions. However, we already know that such independence does not exist with respect to thermodynamic properties. Each exchangable ion confers its unique thermodynamic properties on the distribution coefficients and these directly influence the magnetic properties. The result is that the model of Geller *et al.* yields distributions which are inconsistent with thermodynamic theory and, indeed, with the results of other methods as shown particularly by Figure 1. The deviation becomes increasingly marked as the quantity of non-magnetic ion is increased. These two sets of data thus provide an interesting illustration of the value of thermodynamic models in guiding the interpretation of experimentally determined distribution data.

EQUATION OF THE EXCHANGE KINETICS

Although no kinetic data exist for the exchange reactions in garnets, it is interesting to write down the phenomenological form of the rate equations. This may be done if we assume as did Dienes (1955) that the rate controlling process is the exchange rather than some other process such as nucleation. Thus, if C_0 is the concentration (in moles or particles per cm^3) of the total tetrahedrally and octahedrally coordinated ions, we obtain the following equation (Mueller, 1967) for the rate of change of concentration of one of the ions on the tetrahedral site:

$$-\frac{dX_{\mathrm{d}}}{dt} = \frac{2}{5} C_{\mathrm{O}} K_{\mathrm{da}} \phi_{\mathrm{da}} X_{\mathrm{d}}(1 - X_{\mathrm{a}}) - \frac{2}{5} C_{\mathrm{O}} K_{\mathrm{ad}} \phi_{\mathrm{ad}} X_{\mathrm{a}}(1 - X_{\mathrm{d}}). \quad (5)$$

This is related to rate of change on the other site as

$$\frac{3}{2}\frac{dX_{\mathrm{a}}}{dt} = -\frac{dX_{\mathrm{d}}}{dt}.$$

K_{ad} and K_{da} are the specific rate constants for exchange in the two directions. It is apparent that when $(dX_{\mathrm{d}}/dt) = 0$, equation (5) reduces to equation (1). The important point to be made here is that although $\phi_{\mathrm{da}}/\phi_{\mathrm{ad}}$ may approach unity with essentially ideal mixing on the stable lattice sites, the individual ϕ's may deviate widely from unity. The reason for this is that these factors embody the thermodynamic properties of the transitional state, and mixing in this state might be far from ideal. Of course, if mixing were also ideal in the transitional state, the ϕ's would reduce to unity and equation (5) would assume its simplest form.

ACKNOWLEDGMENTS

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NOTE ADDED IN PROOF

Since our paper was submitted for publication, Czerlinsky and McMillan (1970) have shown that in the $Y_3Al_xFe_{5-x}O_{12}$ garnets, the Al-Fe distribution in equilibrated samples cannot be represented by a single constant $K°$. However, for compositions, $x<1$, the cation distribution follows the ideal solution model as shown in this paper and by Borghese (1967) and *not* the distribution curve implied from magnetic measurements by Geller *et al.* (1964).

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