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journal homepage: [www.elsevier.com/locate/jssc](http://www.elsevier.com/locate/jssc)Thermodynamics of  $\text{CoAl}_2\text{O}_4$ – $\text{CoGa}_2\text{O}_4$  solid solutionsKristina I. Lilova<sup>a,\*</sup>, Alexandra Navrotsky<sup>a,1</sup>, Brent C. Melot<sup>b,2</sup>, Ram Seshadri<sup>b,2</sup><sup>a</sup> Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis, CA 95616, USA<sup>b</sup> Materials Department and Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA

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## ABSTRACT

$\text{CoAl}_2\text{O}_4$ ,  $\text{CoGa}_2\text{O}_4$ , and their solid solution  $\text{Co}(\text{Ga}_z\text{Al}_{1-z})_2\text{O}_4$  have been studied using high temperature oxide melt solution calorimetry in molten  $2\text{PbO} \cdot \text{B}_2\text{O}_3$  at 973 K. There is an approximately linear correlation between lattice parameters, enthalpy of formation from oxides, and the Ga content. The experimental enthalpy of mixing is zero within experimental error. The cation distribution parameters are calculated using the O'Neill and Navrotsky thermodynamic model. The enthalpies of mixing calculated from these parameters are small and consistent with the calorimetric data. The entropies of mixing are calculated from site occupancies and compared to those for a random mixture of Ga and Al ions on octahedral site with all Co tetrahedral and for a completely random mixture of all cations on both sites. Despite a zero heat of mixing, the solid solution is not ideal in that activities do not obey Raoult's Law because of the more complex entropy of mixing.

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## 1. Introduction

The study of transition metal oxides, particularly spinels, is of great importance from both fundamental and applied research points of view. Spinels are important in many applications because of their high thermal stability and catalytic, electronic, and optical properties. They are commonly used in semiconductor and sensor technology, as magnetic storage media, as well as in heterogeneous catalysis [1–8]. Studies of cation distribution and thermodynamics of spinels are of interest in solid state chemistry, because they provide better understanding of the correlations between structure and physical and chemical properties, which depend on the octahedral and tetrahedral site occupancy by transition metal ions.

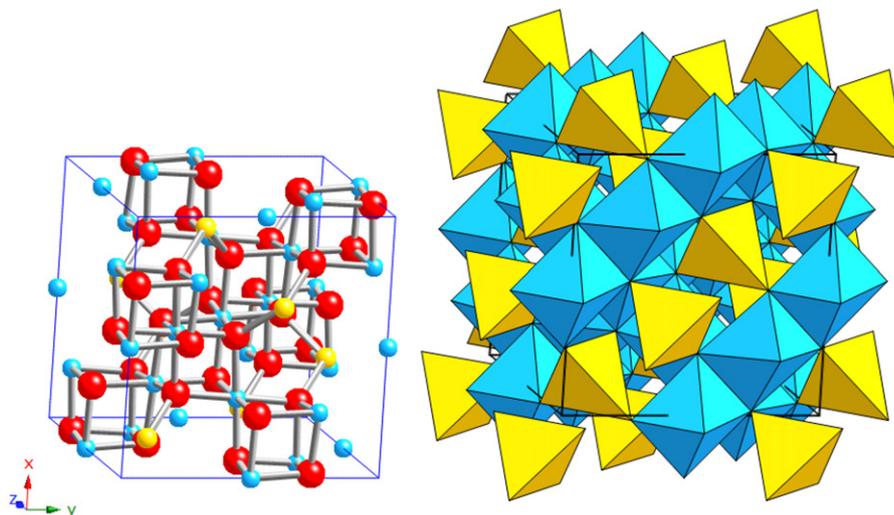
Among this class of materials, cobalt aluminate ( $\text{CoAl}_2\text{O}_4$ ) is a thermally and chemically stable pigment of intense blue color, known as Thénard's blue [9,10]. Early uses of cobalt blue were limited to ceramic applications. Later, the cobalt blues were involved in artists' colors [11]. The coloring performance of cobalt pigments strongly depends on their thermal stability, chemical reactivity, and coordination of  $\text{Co}^{2+}$  ions [12]. Another application of cobalt aluminate is selective catalytic reduction of  $\text{NO}_x$  with hydrocarbons [8].

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Many interesting physical and chemical properties of spinels arise from their ability to distribute the cations amongst the available tetrahedral and octahedral sites. This so-called cation distribution is described as an equilibrium function of temperature, pressure, and composition. A spinel of general formula  $\text{AB}_2\text{O}_4$  contains one cation of type A and two of type B, and has one tetrahedral and two octahedral sites per four oxygen atoms. The normal cation distribution places the A ions tetrahedrally and B ions octahedrally (Fig. 1); the inverse distribution places one B ion tetrahedrally and the remaining B and A ions octahedrally. The inversion parameter,  $x$ , represents the fraction of tetrahedral sites occupied by B cations and ranges from zero (normal) to one (inverse) with  $x=2/3$  representing a random distribution.

Cation distributions of end-members  $\text{CoAl}_2\text{O}_4$  and  $\text{CoGa}_2\text{O}_4$  [13–22] and particularly the temperature dependence of the inversion parameter [23,24] have been studied extensively. In general,  $\text{CoAl}_2\text{O}_4$  is approximately normal and  $\text{CoGa}_2\text{O}_4$  is partially inverse. The normality in  $\text{CoAl}_2\text{O}_4$  is easy to understand because of the site preference energies of  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  cations: 12.6 kJ/mol tetrahedral preference for cobalt and 44.4 kJ/mol octahedral preference for aluminum [14]. According to O'Neill [23] the inversion parameter of  $\text{CoAl}_2\text{O}_4$  quenched samples increases almost linearly with increasing annealing temperature between 973 and 1373 K, but above 1373 K  $x$  has a nearly constant value of 0.24–0.25, strongly suggesting that the additional disorder expected at higher temperature cannot be quenched due to rapid equilibration above 1373 K. On the other hand,  $\text{Ga}^{3+}$  and



**Fig. 1.** Crystal lattice of a normal spinel of general formula  $AB_2O_4$ . A ions on tetrahedral sites are presented in yellow, B ions and octahedral sites in blue, and the oxygen atoms in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$Co^{2+}$  ions show similar tetrahedral site preference energies: 12.6 and 14.6 kJ/mol [14], which explains the higher inversion parameter of  $CoGa_2O_4$ , which has been reported to have  $x=0.575$  [20], 0.72 [25], or 1 [18]. Experimental conditions have a large effect on the inversion parameters. Values for rapidly quenched and slowly cooled samples with the same annealing temperature are in most cases inconsistent due to the difference in the effective equilibrium temperature. Additionally, an inversion parameter of 0.575 is obtained for a single crystal grown by cooling from 1473 K to room temperature in  $PbF_2$  flux [20]. More inverse samples have been synthesized hydrothermally at 703 K,  $x=1$  [18] or quenched from 1473 K,  $x=0.72$  [25].

Porta and Anichini [25] investigated the cobalt ion distribution and its dependence on temperature and composition in  $Co(Ga_zAl_{1-z})_2O_4$  spinel solid solutions. Their results show the inversion parameter increases when the preparation temperature is increased from 853 to 1473 K.

Melot et al. [26] attempted to tune the degree of frustration in Co magnetic spinels by controlling interatomic spacings through  $Al^{3+}$  with  $Ga^{3+}$  substitution on the non-magnetic B-sites of spinels  $CoGa_yAl_{2-y}O_4$ . Such substitution steadily increase the distance between Co atoms, which decreases the degree of magnetic frustration. However the change toward a more random cation distribution, which means more  $Co^{2+}$  on octahedral sites with increasing Ga content (and increasing lattice parameter), complicates the interpretation.

A few thermodynamic data for end-members  $CoAl_2O_4$  and  $CoGa_2O_4$  are available but no investigations of solid solution thermodynamics have been reported. The molar enthalpies of formation from oxides at 970 K of  $CoAl_2O_4$  and  $CoGa_2O_4$  were measured by solution calorimetry in molten  $9PbO \cdot 3CdO \cdot 4B_2O_3$  by Navrotsky and Kleppa [27]. The purpose of the present work is to obtain enthalpies of formation of end-members and solid solutions, as well as enthalpies of mixing. The data are discussed in terms of the effect of cation distribution and cation size.

## 2. Experimental

### 2.1. Samples

End-members  $CoAl_2O_4$  and  $CoGa_2O_4$  and  $Co(Ga_zAl_{1-z})_2O_4$  solid solutions are the same samples synthesized, characterized, and used by Melot et al. [26].

**Table 1**

Average drop solution enthalpies ( $\Delta H_{ds}$ ) at 973 K; enthalpies of formation from oxides ( $\Delta H_{f,oxides}$ ) and enthalpies of mixing of  $CoGa_zAl_{2-z}O_4$ . Uncertainties are two standard deviations of the mean. The drop solution enthalpy of  $Al_2O_3$  is an average of the values measured over 5 years in the Peter A. Rock Thermochemistry Laboratory. The drop solution enthalpy of CoO is obtained by Wang and Navrotsky [35] and  $z$  is the mole fraction of  $CoGa_2O_4$ .

$z$	$\Delta H_{ds}$ (kJ/mol)	$\Delta H_{mix}$ (kJ/mol)	$\Delta H_{f,oxides}$ (kJ/mol)
0	$200.16 \pm 1.17$	0	$-35.35 \pm 1.68$
0.2	$198.44 \pm 1.34$	$0.67 \pm 2.44$	$-33.33 \pm 1.97$
0.4	$197.73 \pm 1.45$	$0.33 \pm 2.57$	$-32.24 \pm 2.04$
0.6	$196.30 \pm 1.76$	$0.70 \pm 2.69$	$-30.58 \pm 2.27$
0.8	$195.02 \pm 1.63$	$0.93 \pm 2.61$	$-29.00 \pm 2.17$
1	$194.90 \pm 1.67$	0	$-28.58 \pm 2.07$
$Al_2O_3$	$107.45 \pm 0.76$		
$Ga_2O_3$	$108.84 \pm 0.79$		
CoO	$57.48 \pm 0.93$		

### 2.2. High temperature calorimetry

High temperature oxide melt solution calorimetry was performed using a Tian Calvet twin calorimeter described in detail by Navrotsky [28,29]. Samples in the form of pellets (around 5 mg) were dropped from room temperature (298 K) into a molten  $2PbO \cdot B_2O_3$  solvent at 973 K in a platinum crucible in the calorimeter. The heat effect measured, the heat of drop solution, represents the sum of heat content of the sample from 298 to 973 K and its heat of solution in the oxide melt. The samples dissolved readily and no difficulties were encountered. The calorimeter was calibrated using the heat content of 5 mg  $\alpha-Al_2O_3$  samples.

## 3. Results

### 3.1. Enthalpy of formation from oxides and enthalpy of mixing of the solid solutions

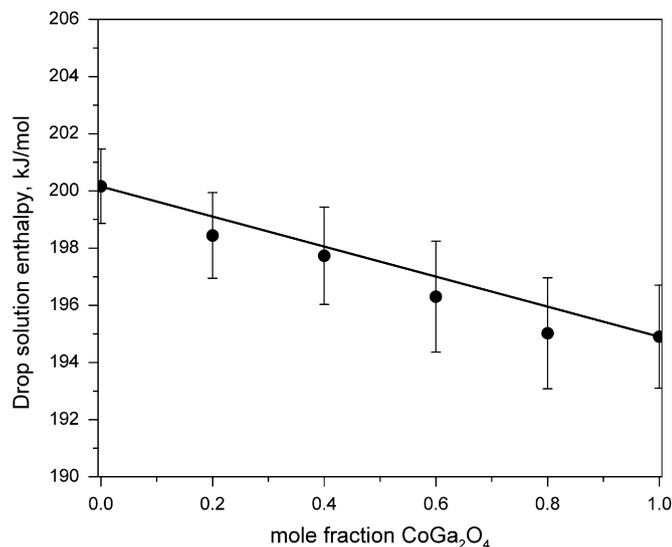
The average enthalpies of drop solution are given in Table 1.

The enthalpies of formation of end-members  $CoAl_2O_4$  and  $CoGa_2O_4$  and  $Co(Ga_zAl_{1-z})_2O_4$  solid solutions from the oxides (CoO,  $Al_2O_3$ , and  $Ga_2O_3$ ) were determined from the measured enthalpies of drop solution according to the thermodynamic cycle shown in Table 2.

**Table 2**

Thermodynamic cycles used to determine the enthalpies of formation from oxides.  $\Delta H_1$  is the drop solution enthalpy of end-members and solid solution, where  $2z$  is between 0 and 2.

$\text{Co}(\text{Ga}_z\text{Al}_{1-z})_2\text{O}_4$ (s, 298 K) $\rightarrow$ CoO (dis, 973 K) + $(1-z)\text{Al}_2\text{O}_3$ (dis, 973 K) + $z\text{Ga}_2\text{O}_3$ (dis, 973 K)	$\Delta H_1$
CoO (s, 298 K) $\rightarrow$ CoO (dissolved, 973 K)	$\Delta H_2$
$\text{Al}_2\text{O}_3$ (s, 298 K) $\rightarrow$ $\text{Al}_2\text{O}_3$ (dissolved, 973 K)	$\Delta H_3$
$\text{Ga}_2\text{O}_3$ (s, 298 K) $\rightarrow$ $\text{Ga}_2\text{O}_3$ (dissolved, 973 K)	$\Delta H_4$
CoO (s, 298 K) + $(1-z)\text{Al}_2\text{O}_3$ (s, 298 K) + $z\text{Ga}_2\text{O}_3$ (s, 298 K) $\rightarrow$ $\text{Co}(\text{Ga}_z\text{Al}_{1-z})_2\text{O}_4$ (s, 298 K)	$\Delta H_5$
$\Delta H_5 - \Delta H_1 + \Delta H_2 + z\Delta H_3 + (1-z)\Delta H_4$	



**Fig. 2.** Average drop solution enthalpy with error bars vs. mole fraction of  $\text{CoGa}_2\text{O}_4$ . The solid line connects the end-members.

There are approximately linear correlations of the enthalpy of drop solution (Fig. 2) and the enthalpy of formation from oxides of the solid solution with Ga content.

The enthalpy of formation from the constituent oxides is most negative for  $\text{CoAl}_2\text{O}_4$  and becomes less negative with increasing Ga content.  $\text{CoGa}_2\text{O}_4$  is thus significantly less stable than its aluminum analog. The molar enthalpies of formation at 970 K of  $\text{CoAl}_2\text{O}_4$  and  $\text{CoGa}_2\text{O}_4$  were measured by solution calorimetry in molten  $9\text{PbO} \cdot 3\text{CdO} \cdot 4\text{B}_2\text{O}_3$  by Navrotsky and Kleppa [27] as  $-37.24 \pm 0.96$  and  $-31.51 \pm 1.05$  kJ/mol, respectively. Their data are in a good agreement with our values:  $-35.35 \pm 1.68$  and  $-28.58 \pm 2.07$  kJ/mol (Table 1), especially since they are obtained by solution calorimetry at 973 K and ours, obtained by drop solution calorimetry, refer to 298 K, so there may be small correction terms arising from differences in heat capacity of products as well as differences in cation distribution.

The individual data points of all measured drop solution enthalpies were fitted, using linear and quadratic equations. The quadratic fit leads to  $\Delta H_{\text{mix}} = 2.57 \pm 3.04z(1-z)$  kJ/mol, where  $z$  is the mole fraction of  $\text{CoGa}_2\text{O}_4$ . The heat of mixing may be slightly positive, but it is zero within experimental error, and a quadratic fit is not warranted.

### 3.2. Volume of mixing

Melot et al. [26] found that the cell parameter increases with increasing Ga content. Vegard's law is not strictly followed, and for all intermediate  $x$  values, the cell parameter is slightly reduced from the values suggested by a weighted average of the

end-members. The data, already presented by Melot et al. [26], show small negative volumes of mixing ( $-0.2 \text{ cm}^3/\text{mol}$ ) for mole fraction  $z(\text{CoGa}_2\text{O}_4) \leq 0.6$  and small positive ( $0.01 \text{ cm}^3/\text{mol}$ ) for  $z(\text{CoGa}_2\text{O}_4) = 0.8$ .

## 4. Discussion

### 4.1. Cation distribution parameters for the $\text{CoAl}_2\text{O}_4$ – $\text{CoGa}_2\text{O}_4$ system

The cation distributions and free energies of mixing in spinel solid solutions can be calculated using the O'Neill and Navrotsky thermodynamic model [30]. It has been developed to evaluate mixing behavior and thermodynamic data of binary solid solution in 2–3 and 2–4 oxide spinels and widely used. The most important contributions of the model are related to the explanation of observed variations in stoichiometry and thermodynamic parameters, and extrapolation of the experimental data to different conditions and multicomponent systems as well as prediction of properties of unknown systems. Three factors are considered in this model—cation distribution, size mismatch, and electron exchange reactions. Since there is no change in the oxidation state, only the first two factors are significant for the cobalt aluminate–cobalt gallate solid solutions.

The model was formulated by minimizing the free energy of disorder, in which disordering enthalpy varies linearly with inversion parameter ( $x$ ) and disordering entropy is related to configurational entropy ( $S_c$ ). According to the model, both the composition and the cation arrangement of a solid solution can be described using a set of parameters [30]. As the substitution occurs on both cation sites, the distribution parameters can be defined as follows:

Ion	Tet.	Oct.	Sum
Co	$1-x$	$x$	1
Al	$x-y$	$2-2z-x+y$	$2-2z$
Ga	$y$	$2z-y$	$2z$
Sum	1	2	3

The inversion parameter is given by  $x$ . Using these parameters, the solid solution can be written in the form  $(\text{Co}_{1-x}\text{Ga}_y\text{Al}_{x-y})[\text{Co}_x\text{Ga}_{2z-y}\text{Al}_{2-2z-x+y}]\text{O}_4$ . The cation distribution equations are

$$-RT \ln \left[ \frac{(x-y)x}{(1-x)(2-2z-x+y)} \right] = \alpha_{\text{Co-Al}} + 2\beta x \quad (2)$$

$$-RT \ln \left[ \frac{xy}{(1-x)(2-y)} \right] = \alpha_{\text{Co-Ga}} + 2\beta x \quad (3)$$

Subtracting (3) from (2) gives

$$-RT \ln \left[ \frac{(x-y)(2z-y)}{y(2-2z-x+y)} \right] = \alpha_{\text{Ga-Al}} \quad (4)$$

The  $\alpha$  and  $\beta$  interchange enthalpy parameters are expected to be comparable in magnitude but opposite in sign.  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  terms may be defined as the difference between site preference energies of  $A^{2+}$  ( $\alpha_{\text{Co}}$ ) and  $B^{3+}$  cations ( $\alpha_{\text{Al}}/\alpha_{\text{Ga}}$ ). They are determined from experimentally measured equilibrium cation distributions [30]. It was found that for 2–3 spinels the  $\beta$  term takes values between  $-15$  and  $-25$  kJ/mol and an average value of  $-20$  kJ/mol can be adopted [31].

The cation distribution in synthetic  $\text{CoAl}_2\text{O}_4$  has been determined for samples quenched from 1023 to 1473 K by O'Neill [23]. The distribution parameters  $\alpha_{\text{Co-Al}} = 45.4 \pm 0.5$  and  $\beta = -18.3 \pm 1.2$  are obtained for inversion parameters between 0.11 and 0.25.

In the present study  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  are determined with  $\beta$  fixed at the average  $-20$  kJ/mol value and using site occupancies obtained by Melot et al. [26] and by Porta and Anichini [25]. The

**Table 3**

$\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  interchange enthalpy parameters calculated for  $\beta = -20$  kJ/mol. The samples from Melot et al. [26] (S1) are slowly cooled and the equilibration temperature is unknown; hence three temperatures are used for the calculations: 673, 773, and 873 K. The samples from Porta and Anichini [25] are quenched from 873 K (S2), 1073 K (S3), and 1473 K (S4) and calculated at five temperature, see the discussion below.

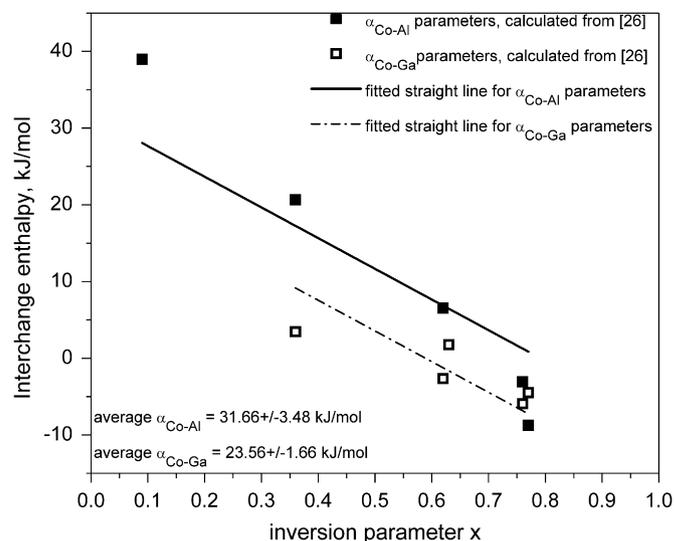
T (K)	$\alpha_{\text{Co-Al}}$	$\alpha_{\text{Co-Ga}}$	Sample
673	$29.17 \pm 1.57$	$23.91 \pm 1.88$	S1 [26]
	$35.89 \pm 3.35$	$26.27 \pm 2.20$	S2 [25]
	$38.02 \pm 2.83$	$25.38 \pm 2.26$	S3 [25]
	$34.62 \pm 2.89$	$24.74 \pm 2.70$	S4 [25]
773	$30.41 \pm 2.51$	$23.73 \pm 1.76$	S1 [26]
	$38.62 \pm 3.37$	$26.83 \pm 2.30$	S2 [25]
	$41.08 \pm 2.72$	$25.81 \pm 2.05$	S3 [25]
	$37.17 \pm 2.76$	$25.08 \pm 2.50$	S4 [25]
873	$31.66 \pm 3.48$	$23.56 \pm 1.66$	S1 [26]
	$41.36 \pm 3.53$	$27.39 \pm 2.52$	S2 [25]
	$44.13 \pm 2.66$	$26.24 \pm 1.91$	S3 [25]
	$39.71 \pm 2.67$	$25.41 \pm 2.32$	S4 [25]
1073	$50.23 \pm 2.68$	$27.09 \pm 1.83$	S3 [25]
1473	$54.98 \pm 2.94$	$27.41 \pm 1.85$	S4 [25]

main difference between samples in these two studies is their thermal treatment. The Melot et al. [26] samples (S1) are not quenched after annealing, but slowly cooled to room temperature. As a result, the cation distribution ceases to equilibrate at some temperature during cooling, but it is not clear what the effective quench temperature is and it may vary with Ga content. Experience with a large number of spinels suggests that the temperature at which the cation distribution is “frozen” during slow cooling lies between 673 and 873 K. To find the best values of the  $\alpha$  parameters and test the sensitivity to the assumed equilibrium temperature, three temperatures are chosen for the calculation: 673, 773, and 873 K (Table 3).

The parameters for each composition are calculated using Eqs. (2) and (3). For  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  the inversion parameter  $x$  is plotted vs. the left side of the equation, as calculated from the observed site occupancies; the slope ( $2\beta$ ) is fixed at  $-40$  kJ/mol and a straight line is fitted. An example of the fitted lines, calculated at 873 K, is shown in Fig. 3.

The Porta and Anichini [25] samples are quenched from three different temperatures: 873, 1073, and 1473 K and are designated as S2, S3, and S4, respectively (Table 3). The distribution parameter  $\alpha_{\text{Co-Al}} = 44.80 \pm 2.80$  for S3, quenched from 1473 K, is comparable to that obtained by O'Neill [23]. In general,  $\alpha$  parameters calculated for slowly cooled samples S1 have lower and more consistent values than the  $\alpha$  parameters calculated for S2–S4 samples. The  $\alpha_{\text{Co-Al}}$  calculated from [25] increases with quench temperature, but all  $\alpha_{\text{Co-Ga}}$  values are consistent. The results suggest that the cation distributions are not completely quenched for higher temperatures (particularly 1473 K) and probably the obtained cation distributions correspond to lower equilibrium temperature, perhaps near 873 K. In order to test this hypothesis, the same site occupancies are used to calculate the distribution parameters at lower temperatures: 673, 773, and 873 K. These values show better agreement between the two studies [25,26].

The calculated distribution parameters can be compared to those of other solid solutions, calculated using the same model. Nell et al. [32] and Ziemniak and Castelli [33] investigated the solid solution of magnetite and four spinels— $\text{MgAl}_2\text{O}_4$ ,  $\text{FeAl}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ , and  $\text{FeCr}_2\text{O}_4$ ;  $\alpha_{\text{Fe}^{2+}-\text{Fe}^{3+}} = 33.75$  kJ/mol and  $\alpha_{\text{Mg-Al}} = 38.19$  kJ/mol ( $T = 1573$  K) are found to be similar to our  $\alpha_{\text{Co-Al}}$  value, calculated from S1 [26] at 773 and 873 K and with the



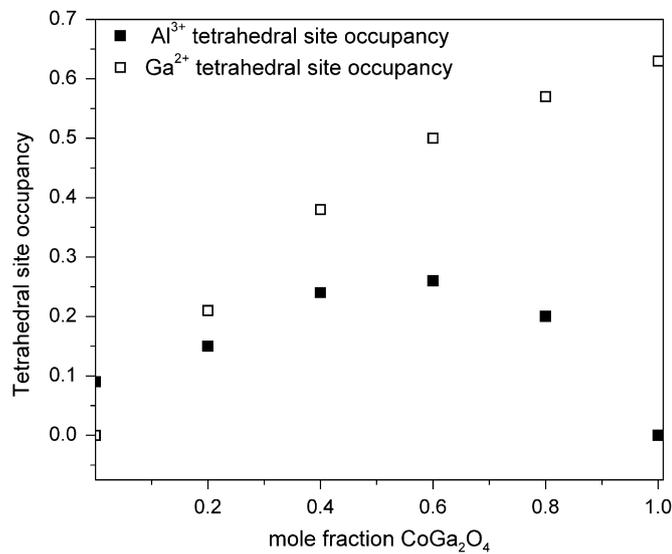
**Fig. 3.** Fitted distribution parameters  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  calculated for  $\beta = -20$  kJ/mol at 873 K vs. inversion parameter; data from Melot et al. [26]. Full squares represent calculated  $\alpha_{\text{Co-Al}}$  and the empty squares— $\alpha_{\text{Co-Ga}}$  parameters.

parameter for S2 [25], quenched at 873 K;  $\alpha_{\text{Mg-Fe}^{3+}} = 20.96$  kJ/mol ( $T = 1573$  K) and  $\alpha_{\text{Fe}^{2+}-\text{Cr}} = 23.52 \pm 3.85$  kJ/mol ( $T = 1273$  K) are close to calculated for S1 [26]  $\alpha_{\text{Co-Ga}}$ . In all cases,  $\beta$  is between  $-19$  and  $-26$  kJ/mol. In  $\text{Co}_2\text{TiO}_4\text{-Zn}_2\text{TiO}_4$   $\alpha_{\text{Co-Zn}}$  is calculated as 32.8 kJ/mol with  $\beta = -20$  kJ/mol ( $T = 1473$  K) [30];  $\alpha_{\text{Ga-Ge}}$  from  $\text{MgGa}_2\text{O}_4\text{-Mg}_2\text{GeO}_4$  is found to be 22 kJ/mol and  $\beta = -21$  kJ/mol ( $T = 1673$  K) [34].

#### 4.2. Contributions to the enthalpy of mixing

In general two factors contribute to the enthalpies of mixing—the enthalpy associated with change in cation distribution and the generally destabilizing effect of size mismatch. The cation distribution in the solid solution depends on the composition and preparation conditions, as shown by Porta and Anichini [25] and Melot et al. [26]. According to them, for the solid solution series,  $\text{Co}^{2+}$  octahedral occupancy first slightly decreases and then continuously increases with Ga content.  $\text{Ga}^{3+}$  may be expected to occupy octahedral sites because of its larger radius, but the amount of  $\text{Ga}^{3+}$  found on smaller tetrahedral sites is relatively high. In contrast  $\text{Al}^{3+}$  is found to remain mostly on octahedral sites. Nakatsuka et al. [24] found that replacing the relatively large  $\text{Co}^{2+}$  ( $r_{\text{tet}} = 0.58 \text{ \AA}$ ) on tetrahedral sites with  $\text{Al}^{3+}$  ( $r_{\text{tet}} = 0.39 \text{ \AA}$ ) results in abnormally long bond lengths, which are not favored. This effect is not as pronounced when  $\text{Ga}^{3+}$  moves to tetrahedral sites, given the larger radius ( $r_{\text{tet}} = 0.47 \text{ \AA}$ ) and the greater disorder in end-member  $\text{CoGa}_2\text{O}_4$  [26]. The tetrahedral site occupancies of  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  ions, plotted vs. mole fraction of  $\text{CoGa}_2\text{O}_4$ , are shown in Fig. 4. Increasing gallium content increases tetrahedral  $\text{Ga}^{3+}$ , while tetrahedral  $\text{Al}^{3+}$  increases to mole fraction of  $\text{CoGa}_2\text{O}_4$  around 0.6 and then decreases. According to Porta and Anichini [25], tetrahedral  $\text{Al}^{3+}$  decreases with Ga content (mole fraction of  $\text{CoGa}_2\text{O}_4$  up to 0.375), is zero between 0.375 and 0.5, and increases again above 0.5.

One can calculate the contribution to the heat of mixing arising from changes in cation distribution along the solid solution using the parameters derived for the O'Neill and Navrotsky model [30] for observed site occupancies (Table 4). The enthalpy of mixing is the difference between the disordering enthalpy of a mechanical mixture of end-members  $\text{CoAl}_2\text{O}_4$  and  $\text{CoGa}_2\text{O}_4$  and the disordering enthalpy of the solid solution. We use  $\alpha_{\text{Co-Al}} = 31.66 \pm 3.48$  kJ/mol and  $\alpha_{\text{Co-Ga}} = 23.56 \pm 1.66$  kJ/mol, as obtained



**Fig. 4.** Tetrahedral site occupancies of Al<sup>3+</sup> and Ga<sup>2+</sup> obtained by Melot et al. [26] plotted vs. mole fraction of CoGa<sub>2</sub>O<sub>4</sub>. Full squares represent Al<sup>3+</sup> and the empty squares—Ga<sup>2+</sup> tetrahedral occupancies.

**Table 4**

Disordering enthalpies of a mechanical mixture of end-members CoAl<sub>2</sub>O<sub>4</sub> and CoGa<sub>2</sub>O<sub>4</sub>: ( $\Delta H_{\text{dis,mm}}$ ); disordering enthalpies of the solid solution Co(Ga<sub>z</sub>Al<sub>1-z</sub>)<sub>2</sub>O<sub>4</sub> ( $\Delta H_{\text{dis,ss}}$ ); enthalpies of mixing ( $\Delta H_{\text{mix}}$ ) of the solid solution Co(Ga<sub>z</sub>Al<sub>1-z</sub>)<sub>2</sub>O<sub>4</sub>;  $x$  is the inversion parameter,  $y$  the tetrahedral occupancy of Ga<sup>3+</sup>,  $x-y$  the tetrahedral occupancy of Al<sup>3+</sup>, and  $z$  the mole fraction of CoGa<sub>2</sub>O<sub>4</sub>.

$z$	$x$	$y$	$x-y$	$\Delta H_{\text{dis,ss}}$ (kJ/mol)	$\Delta H_{\text{dis,mm}}$ (kJ/mol)	$\Delta H_{\text{mix}}$ (kJ/mol)
0	0.09	0	0.09	2.69	2.69	0
0.2	0.36	0.21	0.15	3.62	3.53	0.09
0.4	0.62	0.38	0.24	4.47	4.37	0.10
0.6	0.76	0.5	0.26	4.22	5.22	-0.99
0.8	0.77	0.57	0.2	4.37	6.06	-1.69
1	0.63	0.63	0	6.90	6.90	0

for sample S1, assuming an equilibrium temperature of 873 K, as discussed above. The uncertainties in the parameters lead to an uncertainty of about  $\pm 4$  kJ/mol in the calculated enthalpy of mixing. If the disordering enthalpy depends linearly on total degree of inversion  $x$

$$\Delta H_{\text{dis,ss}} = z(\alpha_{\text{Co-Ga}}y - 20xy) + (1-z)[\alpha_{\text{Co-Al}}(x-y) - 20x(x-y)] \quad (5)$$

where  $z$  is the mole fraction of CoGa<sub>2</sub>O<sub>4</sub>. Then for the mechanical mixture of the end-members

$$\Delta H_{\text{dis,mm}} = z(\Delta H_{\text{dis,CoGa}_2\text{O}_4}) + (1-z)(\Delta H_{\text{dis,CoAl}_2\text{O}_4}) \quad (6)$$

The calculation obtains small positive heats of mixing at CoAl<sub>2</sub>O<sub>4</sub>-rich compositions and small negative values at CoGa<sub>2</sub>O<sub>4</sub>-rich compositions. The observation by Melot et al. [26] that lattice parameters deviate negatively from Vegard's law at CoAl<sub>2</sub>O<sub>4</sub>-rich compositions and positively at CoGa<sub>2</sub>O<sub>4</sub>-rich ones may suggest, together with the argument on size mismatch above, that the strain effects of size mismatch may be greatest at CoGa<sub>2</sub>O<sub>4</sub>-rich compositions. Thus cation distributions and size mismatch may counterbalance each other, explaining the observed essentially zero heats of mixing. In any case, the heats of mixing are small in magnitude and mostly zero within the uncertainties, both as calculated from the observed cation distributions and as measured by calorimetry.

The calculations use the observed cation distributions of the Melot et al. [26] samples to compute the enthalpies of mixing

based on Eqs. (5) and (6). Since the same samples are used for calorimetry, the measured and calculated enthalpies of mixing can be compared directly without further consideration of the effective equilibrium temperature, though uncertainties in the latter lead to uncertainties in the values of  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$ , as discussed above.

### 4.3. Entropy of mixing

Nevertheless, despite a zero heat of mixing, the CoAl<sub>2</sub>O<sub>4</sub>-CoGa<sub>2</sub>O<sub>4</sub> system is not thermodynamically ideal in the sense of Raoult's law. The activity of CoGa<sub>2</sub>O<sub>4</sub> is not equal to its mole fraction, because both the number of sites and their occupancies are much more complex than simply 1 mol of ions mixing over 1 mol of sites.

If the non-configurational entropy changes associated with disordering are neglected, the entropy of mixing is configurational only. For random mixing of 1 mol of ions over 1 mol of sites, the configurational entropy will be

$$S_c = -R[z \ln z + (1-z) \ln(1-z)] \quad (7)$$

where  $z$  is the mole fraction. For random mixing of 2 mol of ions, it will be twice as large:

$$S_c = -2R[z \ln z + (1-z) \ln(1-z)] \quad (8)$$

Eq. (8) would hold if Al and Ga mixing occurred only on octahedral sites, that is, between two normal spinels. The activity of CoGa<sub>2</sub>O<sub>4</sub> would equal the square of its mole fraction because there are two octahedral sites per formula unit. The real case is more complicated, see below.

For a spinel AB<sub>2</sub>O<sub>4</sub> or A<sub>1-x</sub>B<sub>x</sub>(A<sub>x</sub>B<sub>2-x</sub>)O<sub>4</sub> with the number of octahedral sites twice that of tetrahedral sites and inversion parameter  $x$ , the configurational entropy can be written in the following form, assuming that the substitution of two ions on each sublattice is random:

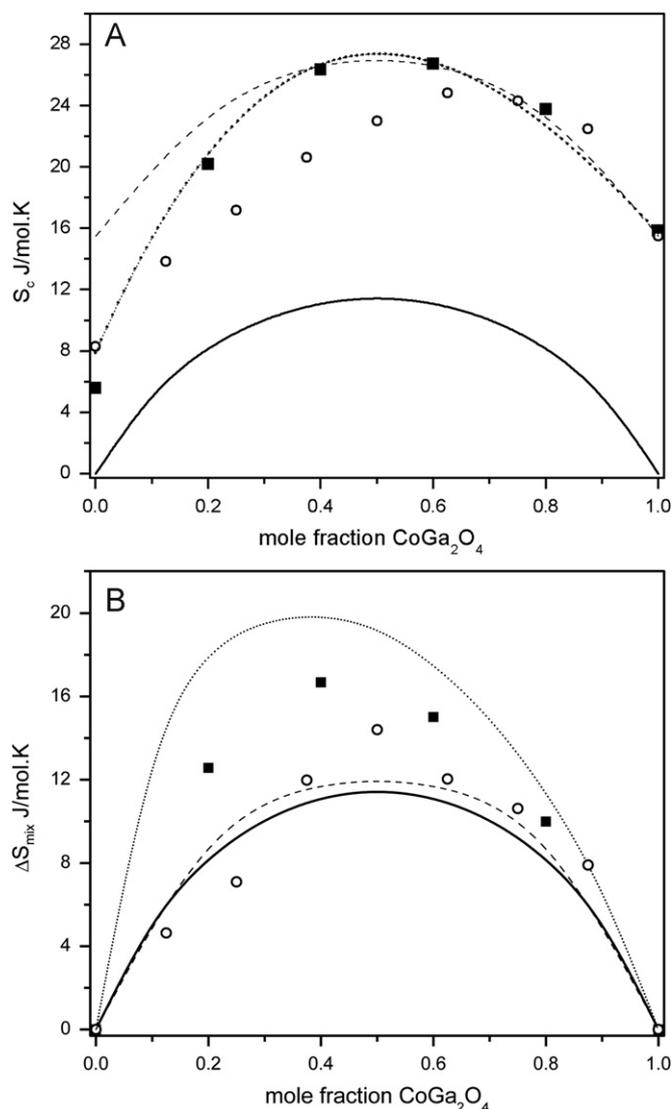
$$S_c = -R \left\{ x \ln x + (1-x) \ln(1-x) + 2 \left[ \frac{x}{2} \ln \frac{x}{2} + \left(1 - \frac{x}{2}\right) \ln \left(1 - \frac{x}{2}\right) \right] \right\} \quad (9)$$

The entropy value starts from 0 for a completely normal spinel, rises to a maximum of 15.48 J/molK for a random cation distribution, and has the value  $2R \ln 2$  or 11.53 J/molK for a totally inverse spinel [14].

For CoAl<sub>2</sub>O<sub>4</sub>-CoGa<sub>2</sub>O<sub>4</sub> solid solution with Co<sup>2+</sup>, Ga<sup>3+</sup>, and Al<sup>3+</sup> ions on both tetrahedral and octahedral sites, the configurational entropy can be expressed using the nomenclature of the O'Neill and Navrotsky model [30] (Eq. (1)):

$$S_c = -R \left\{ (1-x) \ln(1-x) + y \ln y + (x-y) \ln(x-y) + 2 \left[ \frac{x}{2} \ln \frac{x}{2} + \left(\frac{2z-y}{2}\right) \ln \left(\frac{2z-y}{2}\right) + \left(\frac{2-2z-x+y}{2}\right) \ln \left(\frac{2-2z-x+y}{2}\right) \right] \right\} \quad (10)$$

Fig. 5A shows the configurational entropy and Fig. 5B shows the change in configurational entropy on mixing. The O'Neill and Navrotsky thermodynamic model [30] is used, assuming a quench temperature of 873 K, and site occupancies are calculated from  $\alpha_{\text{Co-Al}}$  and  $\alpha_{\text{Co-Ga}}$  parameters (Table 3). It fits the Melot et al. [26] cation distribution data very well except for CoAl<sub>2</sub>O<sub>4</sub>, which was observed to be less disordered than predicted. The configurational entropy calculated from the O'Neill and Navrotsky model [30] is less than that of two completely random spinels below  $z=0.4$  and similar for  $z$  between 0.4 and 1. The entropy of mixing obtained using O'Neill and Navrotsky [30] parameters is more positive compared with values calculated from the observed cation distributions of Melot et al. [26] and Porta and Anichini [25].



**Fig. 5.** Configurational entropies (A) and entropies of mixing (B) of the CoAl<sub>2</sub>O<sub>4</sub>-CoGa<sub>2</sub>O<sub>4</sub> system. The solid curves represent the configurational entropy of a solid solution of two normal spinels. The dashed curve is the entropy of a solid solution of two completely random spinels. The dotted (A) and light dotted curves (B) represent configurational entropy calculated using the O'Neill and Navrotsky thermodynamic model [30], parameters  $\alpha_{Co-Al} = 31.66 \pm 3.48$  kJ/mol and  $\alpha_{Co-Ga} = 23.56 \pm 1.66$  kJ/mol, and a temperature of 873 K. The squares and open circles indicate values obtained from the observed cation distributions of Melot et al. [26] and Porta and Anichini [25], respectively. A. Configurational entropy; (B) entropy of mixing.

The change in configurational entropy calculated on the basis of observed cation distributions is greater than that for mixing two normal spinels or two completely random spinels but less than that calculated from O'Neill and Navrotsky model [30]. Part of this discrepancy may be attributed to the high sensitivity of entropy to the degree of disorder when the degree of inversion is small or near that of the normal spinel CoAl<sub>2</sub>O<sub>4</sub>. The configurational entropy of completely random end-members is greater than the

values obtained from the values, experimentally obtained or calculated using the model cation distributions.

## 5. Conclusion

The enthalpies of mixing in Co(Ga<sub>2</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>4</sub> are close to zero. Nevertheless, the solid solution is not ideal and the entropy of mixing, calculated from configurational entropies of end-members and solid solution, is different from and more positive than that of mixing normal spinels with substitution on octahedral sites only.

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