

Thermodynamic Relations among Olivine, Spinel, and Phenacite Structures in Silicates and Germanates. V. The System MgO-"FeO"-GeO₂

A. NAVROTSKY* AND L. HUGHES, JR.†

Department of Chemistry, Arizona State University, Tempe, Arizona 85821

Received March 10, 1975

Subsolidus phase relations in the system MgO-"FeO"-GeO₂ at 1035°C were determined. From the data, the free energy of the transformation of Fe₂GeO₄ (spinel) to Fe₂GeO₄ (olivine) is estimated to be $7.1 \pm \sim 1.5$ kcal/mole. This value is consistent with the trends shown by other germanates and silicates.

Introduction

In previous communications (1-4), we reported phase relations and thermodynamic properties of ternary germanate systems containing MgO, CoO, NiO, ZnO, and CuO. With regard to the olivine-spinel transition, the geologically significant system is, of course, MgO-FeO-SiO₂, and a large number of phase equilibrium studies, both at atmospheric pressure and under high pressure, have been performed; see, for example, (5-7). The present work, the last in this series of papers, reports a study of the phase equilibria in the analogous germanate system, FeO-MgO-GeO₂ at 1035°C. This system differs from the silicate system in two important respects: (a) Fe₂GeO₄ is a spinel at atmospheric pressure, rather than an olivine, and (b) the pyroxene solid solution series is complete from MgGeO₃ to FeGeO₃. Since both these features are found in the silicate system at high pressure, the germanate system can be considered an easily accessible model for natural systems. In addition, study of this system is another step in determining the

systematics of stability of olivine, spinel, and phenacite structures in silicates and germanates containing various divalent ions.

Experimental

The silicate system usually has been studied under atmospheres of known low oxygen fugacity produced by flowing gaseous mixtures of CO and CO₂ or CO and H₂O (5). This method proved unsatisfactory for the germanate system because of substantial loss of germanium as Ge vapor and/or GeO vapor at oxygen fugacities within the wüstite field. Instead, we performed the experiments in evacuated sealed silica glass tubes. The starting materials were Fe powder, magnetite, and GeO₂, ground together under acetone and pressed into ¼-in. diameter pellets. At 1035°C, the samples reacted fully in 48 hr and attack on the silica ampoules was minimal. The latter point was confirmed by X-ray fluorescence analysis of several reacted samples, which showed no increase in silica content (~0.01% or less SiO₂) compared to the starting materials. Identification of products and determination of lattice parameters were done on an X-ray diffractometer using CuKα radiation as before (1-4).

* To whom all correspondence should be addressed.

† Research done in partial fulfillment of the requirements for degree of Master of Science.

In all cases, samples were synthesized from compositions corresponding to the true ternary system FeO–MgO–GeO₂. “FeO” itself is, of course, nonstoichiometric (oxygen rich), as are iron-rich members of the FeO–MgO solid solution series (8–10). We did not investigate deviations from stoichiometry in the Fe–Mg–Ge–O system and we shall treat our results as though each join, (Mg,Fe)O, (Mg,Fe)₂GeO₄, and (Mg,Fe)GeO₃ can be regarded as a line on a ternary FeO–MgO–GeO₂ phase diagram. For the immediate purposes of this work, this is probably a sufficiently good approximation.

Results

The subsolidus phase relations are shown in Fig. 1. The lattice parameters of (Fe,Mg)O rocksalt and (Fe,Mg)₂GeO₄ spinel solid solutions are shown in Figs. 2 and 3. The rocksalt solid solution shows positive deviations from Vegard's Law, in agreement with the data of Hahn and Muan (10). The agreement in lattice parameters is excellent, despite differences in preparation conditions and therefore, possibly, in metal/oxygen ratio between our and Hahn and Muan's samples. The spinel solid solutions follow Vegard's Law and the lattice parameters extrapolate to that of Mg₂GeO₄ spinel synthesized hydrothermally below 810°C (1). The extensive solubility of Mg₂GeO₄ in the spinel phase at 1035°C (~ 67 mole %) is noteworthy.

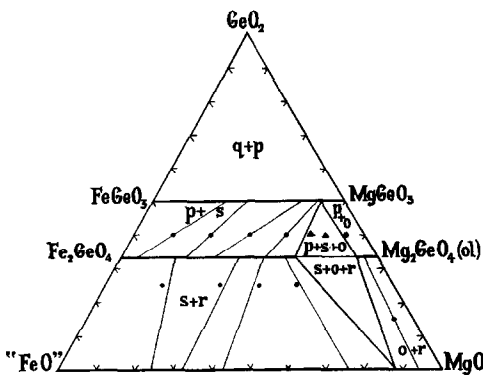


Fig. 1. Subsolidus phase relations in the system MgO–FeO–GeO₂ at 1035°C.

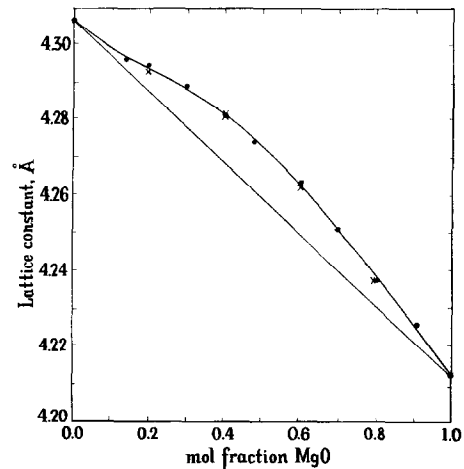


Fig. 2. Lattice parameters of (Mg,Fe)O rocksalt solid solutions. Filled circles, our results, open circles, Hahn and Muan (10).

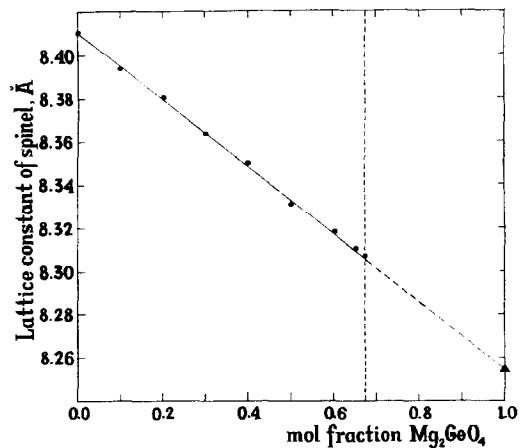


Fig. 3. Lattice parameters of (MgFe)₂GeO₄ spinel solid solutions. Solid circles, our results on samples quenched from 1035°C; open circle, Mg₂GeO₄ spinel synthesized hydrothermally below 810°C (1).

The tie lines between rocksalt and spinel phases were obtained by measuring the lattice parameters of both phases in mixtures corresponding to the bulk compositions shown by open circles. The curves in Figs. 2 and 3 were then used to calculate the compositions. The tie lines so computed do not pass exactly through the bulk compositions in all cases, but the deviations do not appear systematic in

direction and magnitude. We believe these deviations to be caused by the cumulative effects of experimental errors and we estimate an uncertainty of ± 3 mole % in the composition of each phase. Tie lines between spinel and pyroxene phases were determined from the bulk composition and the lattice parameter of the spinel phase only.

No difficulty was observed in obtaining equilibrium in samples with compositions richer in GeO₂ than the orthogermanate. The orthogermanate plus rocksalt phase assemblages sometimes showed anomalous lattice parameters, irreproducible colors, and the occasional presence of magnetite. The results shown for these runs are those of later experiments, in which sample pellets were prereacted, ground, reformed, and finally equilibrated for 48 hr. The difficulties may have arisen for two reasons. First, these samples initially contained a larger amount of magnetite and metallic iron than the more GeO₂-rich ones, and therefore, they required longer equilibration times and showed greater problems of inhomogeneity and capsule attack. In that context, early attempts to prepare Fe₂GeO₄ from GeO₂, Fe₂O₃, and a correspondingly larger amount of Fe proved fruitless because of much more severe attack on the silica tube. The second source of difficulty may have been the nonstoichiometry of the (Fe,Mg)O phase. The system may have retained a small amount of metallic iron so that the oxide phase could be correspondingly oxygen rich. This may have led to sample inhomogeneity and capsule attack.

The Olivine-Spinel Transition in Fe₂GeO₄ and Comparison with Data for Other Silicates and Germanates

In principle, the location of the lines between orthogermanate and rocksalt phases and the known activity-composition relations in the FeO-MgO system permit the calculation of activity-composition relations along the orthogermanate join. However, the accuracy of such calculations is limited in this instance by two factors. First, the experimental difficulties encountered in this study, as

discussed above, suggest that the accuracy with which coexisting spinel and rocksalt compositions are known is of the order of $\pm 3\%$, and perhaps even poorer on the iron-rich end. Second, the activity-composition relations in "FeO"-MgO, complicated by the fact that this is not a binary system because of nonstoichiometry, are not agreed upon by various investigators. In particular, the data of Engell (19), Hahn and Muan (10), Maja and Abbattista (11), and Bogdanovich (12) are in considerable disagreement.

Accordingly, we shall estimate the free energy of the olivine-spinel transition in Fe₂GeO₄ using the simplest possible assumption, namely, that if one chooses components having the same structure, then both the olivine and the spinel solid solutions behave ideally. This corresponds to a redefinition of standard states, and, under those assumptions, for the transition:

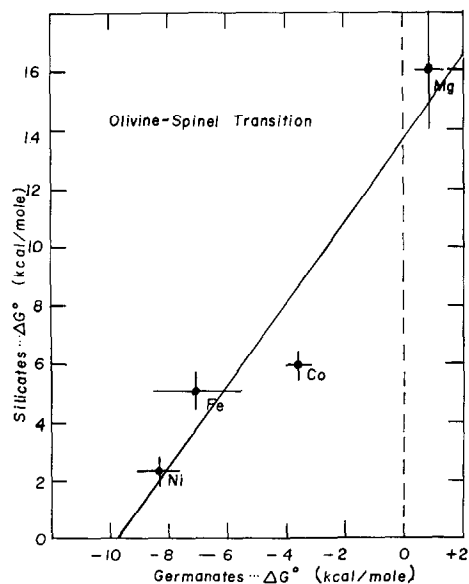
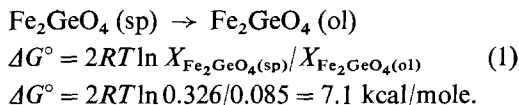


FIG. 4. Standard free energy of the olivine-spinel transition for a given silicate M_2SiO_4 versus the same quantity for the corresponding germanate, M_2GeO_4 . Data from this work and Refs. (1-4, 13).

The factor of 2 arises because 2 moles of divalent cations are mixed per mole of M_2GeO_4 .

The uncertainty in this value is probably of the order of ± 1.5 kcal/mole.

In Fig. 4, we plot the free energy of the olivine-spinel transition for a number of silicates and germanates. The data for the germanates is taken from our previous work at 1 atm (1-4), while for the silicates, ΔG° is estimated as $-P\Delta V$ for the transition, from high pressure phase equilibrium studies, as tabulated in (13). The data refer to various temperatures, as shown, in the range 1000-1200°C. The relation between $\Delta G_{\text{silicate}}^\circ$ and $\Delta G_{\text{germanate}}^\circ$ is approximately linear, a least-squares fit gives, for the olivine-spinel transition

$$\Delta G_{\text{silicate}}^\circ = 13.6 + 1.4\Delta G_{\text{germanate}}^\circ \quad (2)$$

Because one is comparing free energies at different temperatures and because the uncertainties in each value are quite large, we do not wish to attach too much quantitative significance to this equation. For the same reasons, although the point for cobalt appears to lie somewhat below the line, we doubt that difference is significant. However, it should be noted that the $\partial P/\partial T$ for the olivine-spinel transition in Co_2SiO_4 appears to show substantial curvature (14), which may be related to cation disorder in the spinel (15) and may lead to some extra stabilization of the spinel phase.

Our data do show that there is a very regular trend in the stability of spinel versus olivine phases in both the silicates and germanates, with the stability of the spinel increasing in the order Mg, Co, Fe, Ni. In all cases, the spinel is more stable relative to the olivine for the corresponding germanate than from the

silicate. One also should note that the enthalpy of formation from the oxides is substantially more negative for the germanate of a given metal than for the silicate (16).

Acknowledgments

This work was supported by the National Science Foundation (Grants GP 20402 and GH 39767) and the Alfred P. Sloan Foundation. The germanium dioxide was donated by the Sylvania Corporation.

References

1. A. NAVROTSKY, *J. Solid State Chem.* **6**, 21 (1973).
2. A. NAVROTSKY, *J. Solid State Chem.* **6**, 42 (1973).
3. A. NAVROTSKY, *J. Solid State Chem.* **11**, 10 (1974).
4. A. NAVROTSKY, *J. Solid State Chem.* **12**, 12 (1975).
5. R. H. NAFZIGER AND A. MUAN, *Amer. Mineral.* **52**, 1364 (1967).
6. S. AKIMOTO AND H. FUJISAWA, *J. Geophys. Res.* **73**, 1467 (1968).
7. A. E. RINGWOOD AND A. MAJOR, *Phys. Earth Planet. Interiors* **3**, 89 (1970).
8. L. S. DARKEN AND R. W. GURRY, *J. Amer. Chem. Soc.* **67**, 1398 (1945).
9. H. J. ENGELL, *Z. Physik. Chem.* **35**, 192 (1962).
10. W. J. HAHN, JR. AND A. MUAN, *Trans. Met. Soc. A.I.M.E.* **224**, 416 (1962).
11. M. MAJA AND F. ABBATTISTA, *Metal. Ital.* **70**, 565 (1973).
12. M. P. BOGDANOVICH *et al.*, *Zh. Fiz. Khim.* **43**, 142 (1969).
13. A. NAVROTSKY, in "Phase Transitions—1973, Proceedings of the Conference on Phase Transitions and their Applications in Materials Science" (L. E. Cross, Ed.), p. 393, Pergamon Press, New York, 1974.
14. S. AKIMOTO AND Y. SATO, Tech. Rept. of I.S.S.P., Univ. Tokyo, A 328 (1968).
15. T. YAGI, F. MARUMO, AND S. AKIMOTO, *Amer. Mineral.* **59**, 486 (1974).
16. A. NAVROTSKY, *J. Inorg. Nucl. Chem.* **33**, 4035 (1971).