

Effect of Thermal History on the Antiferromagnetic Transition in Zinc Ferrite*

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Quenched zinc ferrite is ferrimagnetic, annealed ferrite paramagnetic at 300°K. Although annealed zinc ferrite has a lambda-type heat capacity transition at about 9.5°K, quenched zinc ferrite retains only elementary vestigia of this transition. A similar effect exists in $\text{Li}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$ in which the transition temperature is slightly lowered relative to that of zinc ferrite. This temperature shift does not appear to exist for $\text{Ni}_{0.9}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$. The magnetic entropy at 300°K is essentially unaltered by lithium substitution or thermal history.

ANNEALED zinc ferrite possesses the normal spinel structure. The movement of the zinc from the *A* to *B* sublattices can be described in terms of a small, positive energy increment ω .^{1,2} When kT is considerably larger than ω , the zinc can be considered to be uniformly distributed among the various possible sites on both sublattices and the resulting spinel is partially inverted. As the thermal agitation is decreased, the zinc cations tend to migrate preferentially towards the *A* sublattice.

The heat capacity of zinc ferrite shows a marked lambda-type anomaly at about 9.5°K.³ This anomaly is due to a type of antiferromagnetic ordering of *B* sublattice iron moments.⁴⁻⁶ The heat capacity of a sample of zinc ferrite made partially inverted by quenching from 1100°C was measured in the region of the thermal anomaly to determine if the anomaly would disappear in a quenched sample. Such indeed was the case. Comparable quenched and annealed samples of zinc ferrite plus 10% lithium ferrite (i.e., $\text{Li}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$) were also prepared and measured. Lithium zinc ferrite was considered particularly interesting because of the possibility of ordering of the Li ions on the *B* sublattice. The heat capacity results are shown in Fig. 1. It is apparent that quenching eliminated all except elemental vestigia of the antiferromagnetic type ordering below 9.5°. This is in agreement with the interpretation of the sublattice population and spinel inversion as discussed by Néel¹ and as evidenced by magnetic moment measurements of Brockman.² The annealed zinc ferrite had a sharp peak of magnitude greater than $2.3k$ per iron atom. Although we were unable to establish a strict upper limit to the magnitude of the peak, it is probable that it is less than the $3.37k$ predicted by Tachiki and Yosida.⁶ It is expected to be larger than the $2.36k$ given by their molecular field approximation. The measured value here is probably

low because (a) averages over finite temperature increments had to be measured and thus the numerical result must always be equal or less than the maximum, (b) the experimental procedure was difficult because of the large time lag in establishing thermal equilibrium, and (c) because our annealed sample was probably partially inverted. The reason for the latter is that the so-called Tammann temperature of zinc ferrite, the temperature for which body diffusion becomes negligible, is about 700°C. Although this is not a strict lower limit to the temperature at which the zinc population can be in equilibrium between the two sublattices, it is improbable that the equilibrium would persist to a very much lower temperature. Thus the conditions at about 700°C would be frozen into the annealed specimen.

Figure 1 also illustrates the difference in heat capacity at low temperature of annealed and quenched mixed 10% lithium and 90% zinc ferrite. The same general differences occur, but the height, shape, and temperature

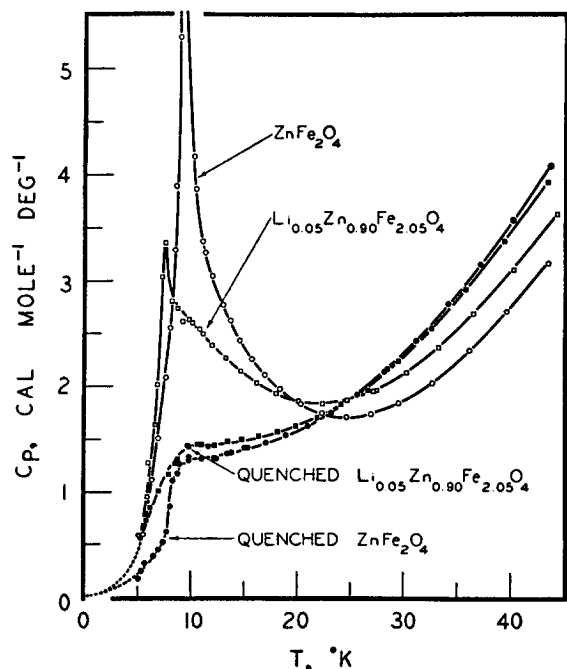


FIG. 1. Effect of thermal history on the antiferromagnetic transition in zinc ferrite.

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¹ L. Néel, *Compt. rend.* **230**, 375 (1950).

² F. G. Brockman, *Phys. Rev.* **77**, 841 (1950).

³ E. F. Westrum, Jr., and D. M. Grimes, *J. Phys. Chem. Solids* **3**, 44 (1957).

⁴ J. M. Hastings and L. M. Corliss, *Phys. Rev.* **102**, 1460 (1956).

⁵ A. Arrott and J. E. Goldman, *Phys. Rev.* **98**, 1201 (1955).

⁶ M. Tachiki and K. Yosida, *Progr. Theor. Phys.* **17**, 223 (1957).

of the transition in the annealed specimen is different from either that of zinc ferrite or of a mixed 10% nickel and 90% zinc ferrite.⁷

Of particular interest is the fact that the transition temperature of lithium zinc ferrite is about 0.8 of the corresponding zinc ferrite temperature. The corresponding temperature of nickel zinc ferrite is essentially unaltered, even though twice as much *B*-site iron has been substituted.

Although the interpretation remains obscure, there are two major differences. The nickel ion carries a magnetic moment while the lithium does not; it is possible that the lithium ions form an ordered sub-

⁷ E. F. Westrum, Jr., and D. M. Grimes, *J. Phys. Chem.* **61**, 761 (1957).

structure, as has been demonstrated for annealed $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$.⁸

The hypothesis that lithium ordering is the source of the temperature shift is substantiated by the fact that the residual maximum in the quenched sample is at essentially the same temperature as in zinc ferrite.

The heat capacity of both quenched samples from 50 to 300°K are from 4 to 10% greater than that of the corresponding annealed materials. The entropy increments ($S_T - S_0$) are 36.21 eu for ZnFe_2O_4 , 36.24 for $\text{Li}_{0.05}\text{Zn}_{0.90}\text{Fe}_{2.05}\text{O}_4$, but 36.46 and 36.47 for the corresponding quenched materials. Thus at 300°K and higher, neither a 10% lithium ferrite substitution, nor thermal history significantly alters the total magnetic entropy.

⁸ P. B. Braun, *Nature* **170**, 1123 (1952).

Magnetic Germanates Isostructural with Garnet

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In order to study the magnetic interaction between the eightfold and the combined six- and fourfold sites in the garnet structure, several germanate garnets have been synthesized. If no magnetic cation is present in the fourfold site no spontaneous magnetization has been found in the temperature range 90° to 500°K. A partial substitution of the nonmagnetic cation in the fourfold site by magnetic cations, however, leads to a spontaneous magnetization.

INTRODUCTION

THE discovery of magnetic rare earth garnets, $\text{A}_3^{+3}\text{B}_5^{+3}\text{O}_{12}$ has stimulated a keen interest in both the crystal chemistry and the origin of the magnetic properties of these substances. It has been observed^{1,2} that the spontaneous magnetization which is found in such compounds as gadolinium iron garnet ($\text{Gd}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$) arises from a weak negative interaction between (a) the spins of magnetic cations on eightfold sites and (b) the resultant of a strong negative interaction between spins on fourfold and sixfold sites. Because this type of magnetic coupling is new, its nature is of fundamental interest.

In order to study the coupling between the spins on the eightfold and the sixfold sites, it is desirable to have cations with no unpaired electrons on the fourfold sites. The silicate garnets offer just such a distribution of cations. However, silicate garnets exist in nature only as solid solutions of end members; for example, one finds as the mineral $(\text{Mn,Ca})_3(\text{Al,Fe})_2\text{Si}_3\text{O}_{12}$ but not

$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ or $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$. The synthesis of silicate garnets has generally proved difficult, since glassy phases are usually formed; furthermore, special conditions such as high pressures and mineralizers are required. Reactions with GeO_2 on the other hand, have the advantage of taking place at lower temperatures than similar SiO_2 reactions. Durif and Bertaut³ and Romeijn⁴ have demonstrated this in the preparation of ferrites. Consequently, germanium has been substituted for silicon in the present investigation of garnet type compounds.

SAMPLE PREPARATION AND EVALUATION TECHNIQUES

Two methods of sample preparation were used: (a) Disks $\frac{1}{4}$ in. in diameter were pressed at 25 000 lb/sq in. from intimate mixtures of oxides, cp or better. (b) Mixtures of the metallic oxides were dissolved in concentrated nitric acid; the solutions were evaporated to dryness. GeO_2 was intimately mixed with

¹ M. A. Gilleo and S. Geller, *Bull. Am. Phys. Soc. Ser. II*, **2**, 238 (1957).

² R. Pauthenet, *Comp. rend.* **243**, 1499-1502 (1956).

³ Durif, Bertaut, and Pauthenet, *Ann. chim. phys. (Paris)* **1**, 525-545 (1956).

⁴ F. C. Romeijn, *Philips Research Repts.* **8**, 321-342 (1953).