

## Microwave Resonance Absorption in Nickel Ferrite-Aluminate\*

THOMAS R. MCGUIRE

United States Naval Ordnance Laboratory, White Oak, Maryland

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Magnetic resonance measurements on  $\text{NiOAl}_t\text{Fe}_{2-t}\text{O}_3$  gave  $g$  values which shifted from  $g > 2$  to  $g < 2$  at approximately  $t = 0.7$ . At this composition the dominant magnetic moment changes from the  $B$  to the  $A$  sites and the shift in  $g$  values is believed to be correlated with the vanishing of the magnetic moment and angular momentum at different points close to  $t = 0.7$ . The  $g$  values have the general characteristic of decreasing in magnitude as the temperature is raised. At  $t = 1.75$  and  $-196^\circ\text{C}$  two resonant peaks were observed, one with  $g = 1.4$  and a new peak with  $g = 4.0$ , while for  $t = 2$  (nickel aluminate) no resonance absorption was observed. The half-widths of the resonance curves increased to a maximum value at  $t = 0.5$  and went through a minimum in the region of  $t = 1.25$ .

### INTRODUCTION

**E**LECTRONIC magnetic resonance absorption at microwave frequencies in nickel ferrite where a magnetic atom is partially replaced by a nonmagnetic one has been investigated<sup>1,2</sup> only for the case of  $\text{Ni}^{++}$  replaced by  $\text{Zn}^{++}$ . For this substitution the saturation magnetization<sup>3</sup> increases in a regular manner when zinc is first added, while the  $g$  values obtained from microwave resonance measurements of corresponding zinc content samples decrease slightly below the value found for pure nickel ferrite. At first glance this is not an unexpected behavior since the  $g$  values are all close to two.

Recently Maxwell and Pickart<sup>4</sup> and also Gorter<sup>5</sup> have found that when  $\text{Al}^{+++}$  is substituted for  $\text{Fe}^{+++}$  in nickel ferrite the magnetization decreases rapidly and exhibits the unusual effect of going through a zero magnetization point at a small percentage of aluminum. These nickel ferrite-aluminate compounds are identified as  $\text{NiOAl}_t\text{Fe}_{2-t}\text{O}_3$  where  $t$  takes on values from 0 to 2. Zero magnetization is approached at  $t = 0.7$  and for greater values of  $t$  the magnetization again increases. In the present paper the experimental results of magnetic resonance in nickel ferrite-aluminates are presented with particular attention given to the region of aluminum content where the magnetic moment approaches zero.

### EXPERIMENTAL

The resonance measurements were made on spherical specimens made from the same batches used by Maxwell and Pickart<sup>4</sup> in their work. Spheres, ranging in diameter from 0.020 in. to 0.065 in. were ground to size by allowing sintered pieces to tumble in an air stream with abrasive powder, a method used by Bond<sup>6</sup> and

Healy.<sup>7</sup> Two sets of measurements were made, the first after the samples were annealed and the second set following quenching. The annealed heat treatment consisted of heating the spheres to  $1050^\circ\text{C}$  and then allowing them to cool slowly over a 24-hour period, while quenching was done from  $1400^\circ\text{C}$  by plunging the specimens, enclosed in quartz tubes, into cold water.

The resonance apparatus has been described in some detail in a previous paper.<sup>8</sup> It is a microwave bridge that operates at a frequency of approximately 9300 Mc/sec, arranged so that a full-resonance curve is traced out as the dc magnetic field sweeps from 50 to 10 000 gauss. This arrangement facilitates the measurement of line shapes. A specimen of diphenyl trinitro-

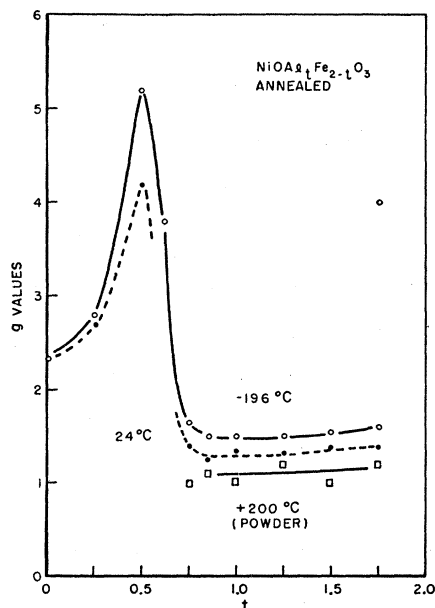


FIG. 1.  $g$  values as a function of aluminum content shown for  $200^\circ\text{C}$ ,  $24^\circ\text{C}$ , and  $-196^\circ\text{C}$ .

\* A preliminary report of this work was given at the North Carolina meeting of the American Physical Society [Phys. Rev. **91**, 206 (1953)].

<sup>1</sup> H. G. Beljers and D. Polder, Nature **165**, 800 (1950).

<sup>2</sup> T. Okamura (private communication to R. K. Wangsness).

<sup>3</sup> E. W. Gorter, Nature **165**, 798 (1950).

<sup>4</sup> L. R. Maxwell and S. J. Pickart, Phys. Rev. **92**, 1120 (1953).

<sup>5</sup> E. W. Gorter, private communication to L. R. Maxwell (to be published).

<sup>6</sup> W. L. Bond, Rev. Sci. Instr. **22**, 344 (1951).

<sup>7</sup> D. W. Healy, Jr., Harvard University Technical Report No. 135, Aug. 15, 1951 (unpublished); Phys. Rev. **86**, 1009 (1952).

<sup>8</sup> L. R. Maxwell and T. R. McGuire, Revs. Modern Phys. **25**, 279 (1953).

phenyl hydrazyl, with the known  $g$  value<sup>9</sup> of 2.004, was usually added to the cavity for calibration purposes.

The resonance frequency of the cavity containing the specimen will vary appreciably, as a function of the intensity of the dc magnetic field, because of magnetic dispersion. In order to obtain the absorption at the true resonance frequency, the reflector potential of the klystron (Varian V50) was modulated (6 cps) by a small alternating potential. In this way it is possible to pass through the resonance frequency of the cavity a hundred times or more in the course of one sweep. The specimens were mounted with Duco cement on the surface of a rotating platform about 0.070 in. in diameter which formed a part of the terminating end of the resonant cavity. The Duco cement provided an insulating layer between the specimen and the wave

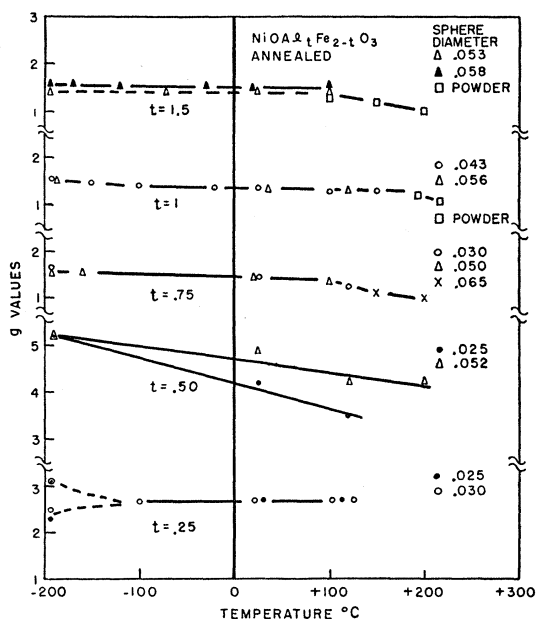


FIG. 2.  $g$  values as a function of temperature for specimens of different composition and sphere diameter.

guide while the platform allowed the specimen to be rotated in order to detect demagnetization effects due to departures from spherical shapes. Measurements were made on samples of two or three different diameters to see if there was any change in the resonance magnetic field value as a function of sphere size. Size effects were first observed in nickel ferrite and nickel zinc ferrite by Beljers and Polder,<sup>1</sup> who found that the  $g$  factors increased as sphere size became smaller although this is not necessarily a general behavior.

In addition to the size effect, the resonance behavior may be affected by the chemical composition and also the heat treatment. When measurements are repeated on a new group of samples variation is found in the experimental data probably because of the above fac-

<sup>9</sup> C. H. Townes and J. Turkevich, Phys. Rev. **77**, 148 (1950).

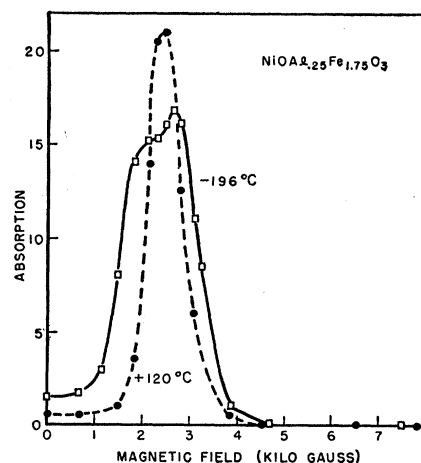


FIG. 3. Resonance curves for  $t=0.25$  at  $120^{\circ}\text{C}$  and  $-196^{\circ}\text{C}$ .

tors. It is estimated that the accuracy of both the  $g$  values and the half-widths is within  $\pm 3$  percent.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The  $g$  values, shown in Figs. 1-9, are calculated using Kittel's<sup>10</sup> resonance condition for a ferromagnetic sphere:

$$\omega = \gamma H, \quad (1)$$

where  $\gamma = ge/2mc$ . The  $g$  value for a free electron spin is 2, while values larger than 2 are attributed to the nonquenched magnetic moment of orbital electron motion.

Figures 1 and 2 show  $g$  as a function of composition and temperature. For  $t=0.25$  a slight splitting which has been plotted as a single mean value in Fig. 1 but as two different values in Fig. 2 was observed at  $-196^{\circ}\text{C}$ . The shape of the corresponding resonance curve ( $t=0.25$ ) is illustrated in Fig. 3.

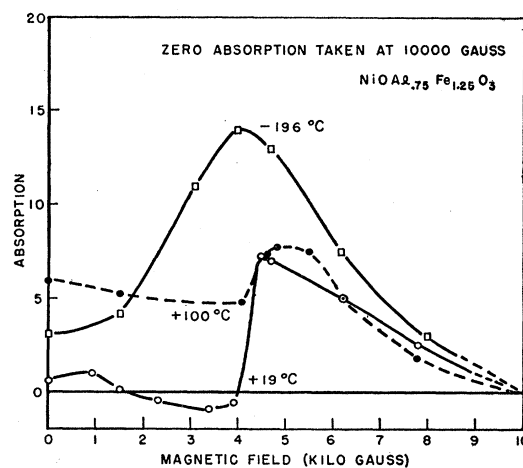


FIG. 4. Resonance curves for  $t=0.75$  at  $19^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$ , and  $-196^{\circ}\text{C}$ .

<sup>10</sup> C. Kittel, Phys. Rev. **73**, 155 (1948).

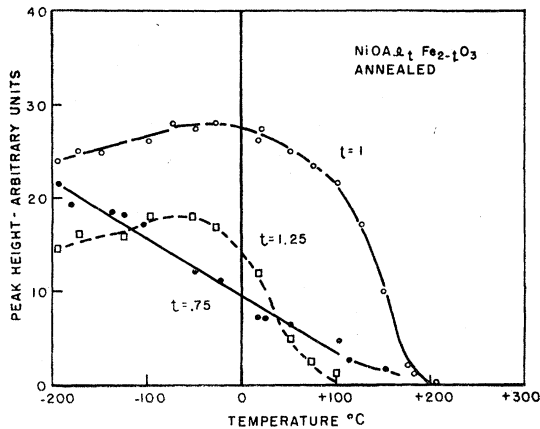


FIG. 5. Variation of the height of the resonance absorption with temperature for three different compositions.

The specimens of composition  $t=0.5$  were the only ones that showed a  $g$  value dependent upon the sphere size. This dependence (Fig. 2) was most pronounced at room temperature but it disappeared at  $-196^\circ\text{C}$ . From Figs. 1 and 7 it is seen that this composition had the greatest  $g$  value and half-width of the annealed group. It is possible, however, that the accuracy of these values is somewhat less than the measurements on other compositions because, at the low applied fields (1000 gauss) at which resonance took place, the specimen might not be magnetically saturated.

Samples of composition  $t=0.75$  through 1.50 all had similar behavior with the exception of the absorption curve of  $t=0.75$  (Fig. 4) which showed a lack of symmetry at the higher temperatures and seemed to indicate a second resonance peak at low fields. For this same range of compositions, Curie temperatures are well defined by the gradual disappearance of the absorption in the spherical specimens as a function of

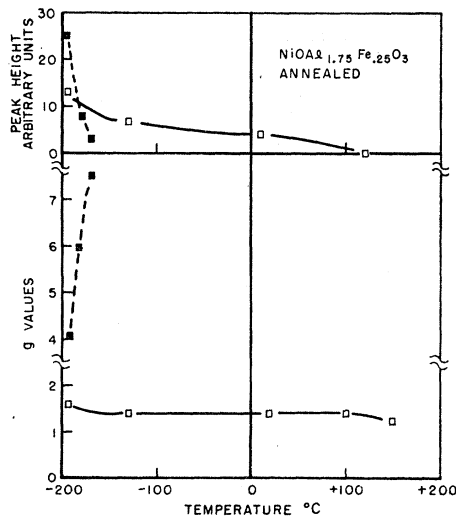


FIG. 6.  $g$  values and height of the resonance absorption curve for sample  $t=1.75$  showing two resonant peaks at low temperatures.

the temperature (see Fig. 5). In general they follow the shape of the magnetization curves given by Maxwell and Pickart.<sup>4</sup> Above the Curie temperatures measurements made on powder samples gave  $g$  values of approximately unity. This unexpected low value of  $g$  bears further investigation.

Nickel aluminate ( $t=2$ ) exhibited no resonance absorption at any temperature from  $-196^\circ\text{C}$  to  $+250^\circ\text{C}$ . This result might be expected since the half-width curve (Fig. 7) is increasing rapidly as  $t$  approaches 2.

When the samples are quenched from  $1400^\circ\text{C}$  an entirely new ionic distribution occurs which gives rise to the  $g$  values and half-widths shown in Figs. 8 and 9. Both  $g$  and the half-width remain large in the region of  $t=0.5$  to 0.85. Thus we see that the shift in  $g$  from above 2 to less than 2 that was present in the annealed

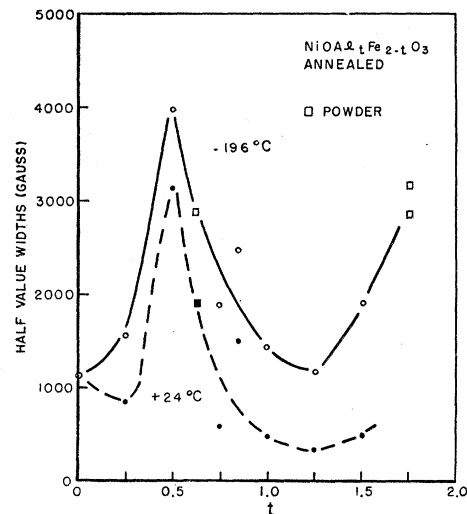


FIG. 7. Variation of half-widths with composition at  $24^\circ\text{C}$  and  $-196^\circ\text{C}$ .

material does not occur when the specimens are quenched. For higher aluminum content than  $t=1$ , resonance absorption was very weak and it was not possible to estimate half-widths with any reasonable degree of accuracy.

The unusual behavior of the  $g$  values as a function of composition in the annealed condition can best be understood by considering the nature of the saturation magnetization of this group of compounds. The Néel theory<sup>11</sup> considers two types of interstices or magnetic sites in the spinel structure. These sites are designated Type *A* (tetrahedral holes) and Type *B* (octahedral holes) in which the magnetic atoms are surrounded by 4 and 6 oxygen ions, respectively. As aluminum atoms are added in the nickel ferrite aluminates, the resultant magnetic moment of the ions on the *B* sites decrease until a composition is reached ( $t=0.7$ ) where the

<sup>11</sup> L. Néel, Ann. phys. 3, 137 (1948).

moments on the  $A$  and  $B$  sites are approximately equal and opposite. For aluminum content greater than  $t=0.7$  there is evidence that the magnetic moment of the ions on the  $A$  sites becomes greater than those on the  $B$ . We see that the shift in  $g$  values and half-widths occurs at the particular composition where the dominant magnetic moment shifts from the ions on the  $B$  sites to those on the  $A$  sites.

Wangsness<sup>12</sup> and Tsuya<sup>13</sup> have both examined sublattice effects in magnetic resonance, and their work shows that the effective  $g$  is given simply by the algebraic sum of the ion-magnetic moments divided by the algebraic sum of the spin angular momentum of the system. This can be written for a single molecule as

$$g_{\text{eff}} = \frac{\sum_n \sum_i g_{ni} f_{ni} S_n}{\sum_n \sum_i f_{ni} S_n}, \quad (2)$$

$$\mu = \sum_n \sum_i g_{ni} f_{ni} S_n, \quad (3)$$

where  $S_n$  is the spin value of the  $n$ th type ion and  $f_{ni}$  and  $g_{ni}$  are the fraction and  $g$  value of this ion on the  $i$ th lattice, while  $\mu$  is the magnetic moment of the molecule in Bohr magnetons.

Smart<sup>14</sup> has made the proposal that for ferrites such as the nickel ferrite-aluminate system Eqs. (2) and (3) can be solved for the  $f$ 's thus obtaining the distribution of ions. He has made calculations which show reasonable results for the ion locations using  $g_i$  values obtained from other sources.

Without considering the distribution of ions in detail, it is possible to make two observations concerning the data with the use of Eq. (2). If we assume that the nickel ferrite ( $t=0$ ) is not completely inverted, then on an average a small fraction  $x$  of an  $\text{Ni}^{++}$  ion will be on an  $A$  site while the remainder  $1-x$  is on a  $B$  site. In the case of nickel ferrite the fractions of  $\text{Fe}^{+++}$  ions on the  $A$  sites and  $B$  sites are  $1-x$  and  $1+x$ , respectively. Using 1 for the spin value of  $\text{Ni}^{++}$  and  $5/2$  for the spin of  $\text{Fe}^{+++}$  Eq. (2) may be written

$$x = \frac{1}{3} \left[ \left( \frac{\mu}{g_{\text{eff}}} \right) - 1 \right]. \quad (4)$$

The measured values for nickel ferrite are  $\mu = 2.2$  Bohr magnetons and  $g_{\text{eff}} = 2.35$  which when substituted in (4) lead to a negative value of  $x$ . We see that for any positive value of  $x$ ,  $g_{\text{eff}}$  must be less than  $\mu$ .

A possible solution to the difficulty outlined above, that  $g_{\text{eff}}$  must be no greater than  $\mu$  in nickel ferrite, has been given by Okamura<sup>15</sup> and his colleagues who have found that  $g_{\text{eff}}$  as given by Eq. (1) is frequency dependent. At low frequencies (9000 Mc/sec)  $g_{\text{eff}}$  is much larger than it should be because there is an internal field ( $H_i$ ) present which aids the applied field  $H$ , and

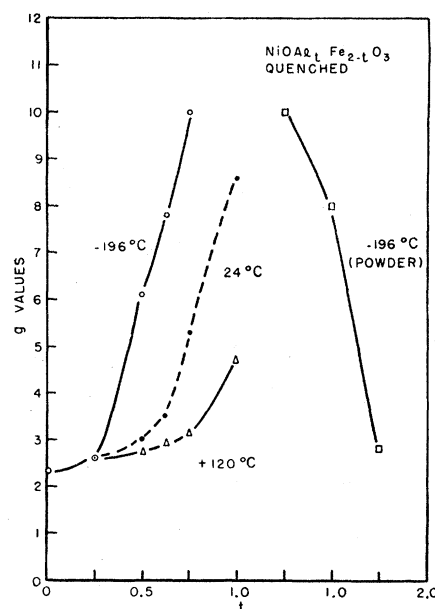


FIG. 8.  $g$  values for quenched samples as a function of composition at 120°C, 24°C, and -196°C.

Eq. (1) should be written as

$$\omega = \gamma(H + H_i). \quad (5)$$

Okamura has made measurements at four different frequencies from 9400 to 47 000 Mc/sec and solved Eq. (5) to find a value of  $H_i = 510$  gauss and  $g_{\text{eff}} = 2.05$  for nickel ferrite at room temperature. This new  $g_{\text{eff}}$  calculated from Eq. (5) is less than  $\mu$  in agreement

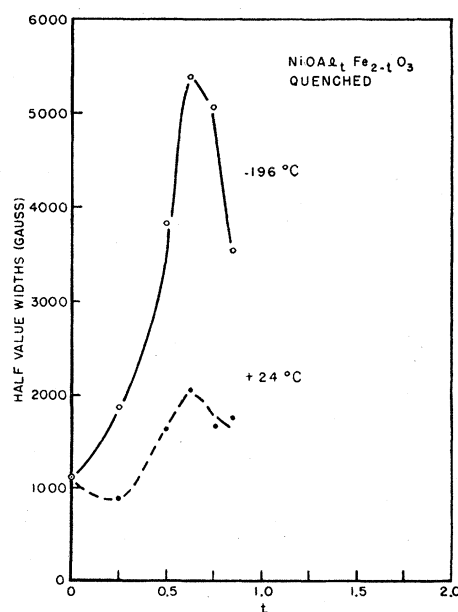


FIG. 9. Variation of half-widths for quenched samples at 24°C and -196°C as a function of composition.

<sup>12</sup> R. K. Wangsness, Phys. Rev. **91**, 1085 (1953).

<sup>13</sup> N. Tsuya, Progr. Theoret. Phys. Japan **7**, 263 (1952).

<sup>14</sup> J. Samuel Smart, private communication (to be published).

<sup>15</sup> Okamura, Torizuka, and Kojima, Phys. Rev. **88**, 1425 (1952).

with Eq. (4). Using  $g_{\text{eff}} = 2.05$  and  $\mu = 2.2$  Eq. (4) gives a value of  $x = 0.24$  which is quite reasonable. It is important that further measurements be made at higher frequencies on the nickel ferrite aluminates to obtain data on the frequency dependence of  $g_{\text{eff}}$ .

At the composition near  $t = 0.7$  the shift in  $g_{\text{eff}}$  from high to low values is tentatively identified with the assumption that the magnetic moment on the  $A$  sites becomes greater than the contribution of the  $B$  sites. The interpretation given by Eq. (2) is that the change in  $g_{\text{eff}}$  is a consequence of the algebraic sum of the spins and magnetic moments going through zero at slightly different compositions. This simple picture lends validity to the foregoing assumption that the magnetic moment on the  $A$  sites is the dominant one for  $t > 0.7$ . When the samples are quenched, the rearrangement of the ions in a more random condition shifts the moment back to the  $B$  sites with a corresponding large change in  $g$  values. It is of course necessary that the  $g$  values be different for the two ions, in this case  $\text{Ni}^{++}$  and  $\text{Fe}^{+++}$ , or for the same ion in different sites, otherwise the change in distribution of the various magnetic atoms

either due to heat treatment or chemical composition would not alter the ratio which gives  $g_{\text{eff}}$ .

### CONCLUSIONS

It is seen from this work that there can be large variations in the resonance behavior of a substitutional ferrite and that for any particular composition further changes can be effected depending on the particular heat treatment the specimen has undergone. With the aid of Eq. (2) a simple interpretation of both very large and small  $g$  values is possible, and this in turn bears on the broader question of the exact distribution of ions for the specimen.

### ACKNOWLEDGMENTS

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## Effect of a Two-Dimensional Pressure on the Curie Point of Barium Titanate\*

P. W. FORSBERGH, JR.

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts

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By hydraulic means, a single crystal of barium titanate in the shape of a flat circular disk was subjected to a pressure exerted on its edges and not on its faces. A very slight pressure removed all domains that were not normal to the disk. The stress system then consisted of equal pressures on the two  $a$  axes, and no pressure on the  $c$  axis. The transition temperature increased with the square of the two-dimensional pressure, while, according to Merz, a hydrostatic pressure produces a linear drop. Using Devonshire's expansion for the free energy and the appropriate Legendre transformation, the free energy, depending on polarization and pressure, was obtained for both two-dimensional and hydrostatic stress systems. This yielded a purely linear-pressure dependence, and it was, therefore, necessary to supplement Devonshire's expansion with higher terms in order to obtain a quadratic effect.

Although it was too difficult to evaluate the effect of pressure

on the transition temperature itself when higher terms were included, it was easy to determine the effect on the Curie-Weiss temperature  $T_0$ . This is the temperature at which the inverse susceptibility of the cubic phase extrapolates to zero, and its pressure dependence will be the subject of a future paper. For both two-dimensional and hydrostatic pressures, the linear part of the shift of the Curie-Weiss temperature was found to depend only on the lower terms in the free energy, and provide two independent relations for determining the two  $g$  coefficients. The quadratic shift of the Curie-Weiss temperature depends on the higher terms with which Devonshire's expansion was supplemented, and a reasonable interpretation of these higher terms gave an upward direction to the quadratic shift of the Curie-Weiss temperature.

### INTRODUCTION

IT has long been known that substitution of strontium for barium in barium titanate<sup>1,2</sup> causes a drop in the Curie temperature that depends linearly on the strontium concentration. This has been explained as the

result of an effective decrease of the unit-cell size caused by the smaller strontium ions. If, instead, the unit-cell size is reduced by application of hydrostatic pressure, the transition temperature decreases with decreasing unit-cell size at about the same rate.<sup>3</sup> The substitution of lead for barium, on the other hand, raises the transition temperature at a rate depending linearly on the lead concentration.<sup>2</sup> Lead titanate itself has a much higher Curie temperature (490°C) and is much more

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<sup>1</sup> A. von Hippel *et al.*, National Defense Research Council Reports 14-300, 1944 and 14-540, 1945 (unpublished); von Hippel, Breckenridge, Chesley, and Tisza, *Ind. Eng. Chem.* **38**, 1097 (1946).

<sup>2</sup> D. F. Rushman and M. A. Strivens, *Trans. Faraday Soc.* **A42**, 231 (1946).

<sup>3</sup> W. J. Merz, *Phys. Rev.* **78**, 52 (1950).