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1965-01-01

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Daniel L. Decker  
dldecker@broadweave.net

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### Original Publication Citation

Decker, Daniel L. "Equation of State of NaCl and Its Use as a Pressure Gauge in High-Pressure Research." *Journal of Applied Physics* 36 (1965): 157-161.

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## Equation of State of NaCl and Its Use as a Pressure Gauge in High-Pressure Research\*

DANIEL L. DECKER

*Brigham Young University, Provo, Utah*

(Received 28 April 1964; in final form 1 July 1964)

The pressure as a function of lattice parameter and temperature has been calculated for NaCl over a pressure range of 0 to 500 kbar for temperatures between 0° and 1500°C. The calculation used the Mie-Grüneisen equation of state with Born-Mayer type repulsion terms between first and second nearest neighbors. The Grüneisen constant was expanded about its value at room temperature and atmospheric pressure; the first coefficient in the expansion being evaluated by forcing the calculated thermal expansion at atmospheric pressure to fit the experimental results of Enck. The two empirical parameters in the repulsion terms were evaluated using the experimental lattice parameter and isothermal compressibility at atmospheric pressure. The calculated pressure vs volume agrees with Bridgman's room-temperature measurements on NaCl below 100 kbar to within 3% and with high-pressure high-temperature shock data to better than 2%. It is proposed to use the numerical results to calibrate the pressure in high-pressure high-temperature apparatus.

### I. INTRODUCTION

IN recent years many laboratories have been pursuing high-pressure research at pressures above 30 kbar. In this pressure range the pressure transmitting medium must of necessity be a solid rather than a liquid or gas. Since solids are not perfectly hydrostatic, it becomes difficult to determine the pressure at points within the solid material. This difficulty is particularly troublesome in devices where part of the load is used in maintaining the gaskets as well as internal friction of the pressure transmitting material. To determine the pressure at the sample under investigation one usually "calibrates" his press by noting the ram loading at which certain isomorphous transitions occur in such materials as bismuth, thallium, barium, etc. The pressure corresponding to these transitions must previously have been measured in some high-pressure apparatus where corrections could be estimated for mechanical and internal friction.

When using a solid pressure-transmitting medium, the above calibration will yield somewhat different results for different samples and sample shapes. Further, the calibration is valid only for runs of continuously increasing load. If the loading is reduced or cycled, one loses all knowledge of the pressure at points internal to the solid medium. Another difficulty with the calibration is encountered if one wishes to make high-pressure measurements at high temperatures. A pressure calibration at room temperature cannot be employed in high-temperature experiments because of thermal expansion and changes in compressibility of the sample and the pressure transmitting material.<sup>1</sup>

The ideal situation would be to have a pressure gauge which would sample the pressure directly at the specimen under investigation. Such a gauge is realizable

\* Work partially supported by the U. S. Air Force Office of Scientific Research.

<sup>1</sup> Dr. H. B. Vanfleet and the author have made measurements of the melting curve of gold under pressure. The analysis of our data indicates that the pressure calibration at room temperature gives results which may be several percent low at 1300°C. We hope to solve the calibration problem in order to publish these data.

using the x-ray press designed by Barnett and Hall.<sup>2</sup> In order to determine the pressure at a point within the pressure cell, one can place at that point a substance whose equation of state is known. The pressure is then calculated from the equation of state after measuring the temperature of this substance and its lattice parameter; the lattice parameter being determined by x-ray methods.

The purpose of this paper is to calculate the equation of state of NaCl and indicate its possible use as a high-pressure gauge. Following papers will discuss experiments demonstrating the usefulness of this approach. An ionic crystal was chosen for this purpose because the principal terms in the lattice energy are well known and a rather simple physical model proposed for these crystals will give results that agree closely with experiments. Of the ionic crystals, NaCl was chosen for this study because there is a wealth of experimental data to evaluate the parameters in the calculations and check against the results and because it has no isomorphous transition under pressure.<sup>3</sup> Previous calculations of the equation of state of alkali halide crystals are available, but they do not cover the range of pressure and temperature of interest in this application.<sup>4</sup>

### II. METHOD OF CALCULATION

The theory of atomic forces and lattice vibrations in ionic crystals is summarized by Born and Huang.<sup>5</sup>

<sup>2</sup> J. D. Barnett and H. T. Hall, *Rev. Sci. Instr.* **35**, 175 (1964).

<sup>3</sup> V. V. Evdokimova and L. F. Vereshchagin, *Fiz. Tverd. Tela* **4**, 1965 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 1438 (1963)] and *Zh. Eksperim. i Teor. Fiz.* **43**, 1208 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 855 (1963)] claim to have found a transition in NaCl at about 18 kbar, but this transition has not been verified by other experimenters even at pressures up to 100 kbar. In this connection it is interesting to note that Jansen and Lombardi calculate that increased pressure should increase the stability of the sodium chloride lattice for NaCl. L. Jansen and E. Lombardi, *Phys. Rev. Letters* **12**, 11 (1964).

<sup>4</sup> M. Arenstein, R. D. Hatcher, and J. Neuberger, *Phys. Rev.* **132**, 73 (1963).

<sup>5</sup> Max Born and Kun Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), Chaps. 1-3.

Lattice vibrations are handled by assuming the ionic crystal to be composed of a set of harmonic oscillators. A parameter  $\gamma_i = -d(\ln\omega_i)/d(\ln V)$  is introduced into the theory where  $\omega_i$  is the frequency of the  $i$ th mode of vibration and  $V$  is the volume. If one now assumes that  $\gamma_i = \gamma$  (the Grüneisen parameter) for all  $i$ , one arrives at the Mie-Grüneisen equation of state,<sup>6</sup> i.e.,

$$P = - (d\Phi(V)/dV) + (\gamma/V)E_v(V, T), \quad (1)$$

where  $P$  is the pressure,  $\Phi(V)$  the lattice potential energy,  $E_v$  the vibrational contribution to the energy, and  $T$  the absolute temperature. If the Debye characteristic temperature is represented by  $\theta$ , then

$$E_v = 2.25R\theta + 6RTD(\theta/T), \quad (2)$$

in which  $R$  is the molar gas constant and  $D(\theta/T)$  is the Debye function. The assumptions leading to the Mie-Grüneisen equation of state are good approximations for  $T \gtrsim \theta$ .<sup>7</sup>

The Grüneisen parameter may be a function of volume, but there seems to be no accurate determination of its volume dependence. Therefore we have expanded  $\gamma$  about the value  $\gamma_0(r_0)$ , where  $r_0$  is the nearest-neighbor distance at temperature  $T_0$  and atmospheric pressure. With  $\Delta r = r - r_0$ ,

$$\gamma = \gamma_0 + \lambda(\Delta r/r_0) + \dots \quad (3)$$

The parameter  $\lambda$  is determined empirically as discussed below. The Debye temperature in Eq. (2) is also dependent upon volume. It can be found by integrating the following equation:

$$-\frac{1}{3}d(\ln \theta)/d(\ln r) = \gamma_0 + \lambda(\Delta r/r_0). \quad (4)$$

In integrating Eq. (4) the constant of integration  $\theta_0(r_0)$  was set equal to the experimental value of the Debye temperature at  $T_0$  and atmospheric pressure.

It now remains to specify a form for the potential energy  $\Phi(V)$ . This energy includes attractive Madalung and van der Waals terms and repulsion terms due to overlap of the ion core wavefunctions. Using a Born-Mayer type repulsion term with 6 nearest and 12 next-nearest neighbors,  $\Phi$  can be expressed in terms of the nearest-neighbor distance  $r$  as

$$\Phi = N_0(-Aq^2/r - C/r^6 - D/r^8 + 6be^{-r/\rho} + 6b_-e^{-\sqrt{2}r/\rho_-} + 6b_+e^{-\sqrt{2}r/\rho_+}). \quad (5)$$

This gives the lattice potential energy per mole with  $N_0$  being Avagadro's number.

The first term in Eq. (5) is the Madalung energy where  $q$  stands for the charge on the electron and  $A$  is the appropriate Madalung constant. The second and

third terms are the van der Waals potentials for dipole-dipole and dipole-quadrupole interactions, respectively. Values for the coefficients were taken from the calculations of Mayer.<sup>8</sup> The exponential form for the repulsion terms is commonly used because it gives rather accurate results and yet is much easier to manipulate than a precise quantum-mechanical calculation. The constants  $b$  and  $\rho$  must be determined empirically.

To keep the number of arbitrary parameters as small as possible, the constants  $b_+$ ,  $b_-$ ,  $\rho_+$ , and  $\rho_-$  in the second nearest-neighbor repulsion terms were related to  $b$  and  $\rho$ . It is possible to make somewhat arbitrary assumptions here because the like-ion repulsion terms represent a small part of the total repulsion and the calculated values of  $\rho$  and  $b$  tend to compensate for different choices of  $b_+/b$ ,  $b_-/b$ ,  $\rho_+/\rho$ , and  $\rho_-/\rho$  as noted in Sec. III. The + and - indices correspond to repulsion between pairs of positive ions and pairs of negative ions, respectively. Since the parameters  $\rho$ ,  $\rho_+$ , and  $\rho_-$  represent a characteristic distance for the respective interactions, they can be related to the physical size of the ion core pairs. The simplest assumption is that these parameters are proportional to the sum of the radii of the two ions in the respective repulsion terms. Thus  $\rho_+/\rho = 2r_+/(r_+ + r_-)$  and  $\rho_-/\rho = 2r_-/(r_+ + r_-)$ , where  $r_+$  and  $r_-$  are the appropriate ionic radii according to Pauling.<sup>9</sup> This method of choosing the exponent in the second nearest-neighbor terms is somewhat simpler to handle mathematically and yet is as meaningful as methods previously suggested.<sup>10</sup> The parameters  $b$ ,  $b_+$ , and  $b_-$  correspond to the relative strengths of the interactions compared at their characteristic distances. In this paper these factors were assumed to be inversely proportional to the sum of the polarizabilities of the respective ions. This assumption treats the more polarizable ions as more compressible.<sup>11</sup> Letting  $\alpha_+$  and  $\alpha_-$  represent the polarizabilities, we arrive at the relations  $b_+/b = (\alpha_+ + \alpha_-)/2\alpha_+$  and  $b_-/b = (\alpha_+ + \alpha_-)/2\alpha_-$ . The polarizabilities were taken from the calculations of Tressman, Kahn, and Shockley.<sup>12</sup>

The remaining parameters  $\rho$ ,  $b$ , and  $\lambda$  were determined as follows: Equation (1) is evaluated at zero pressure and temperature  $T_0$ , where the measured value of the lattice parameter is  $r_0$ . Thus

$$(d\Phi/dV)|_{V_0} = \gamma_0 E_v(V_0, T_0)/V_0, \quad (6)$$

where  $V_0$  is the volume for  $r = r_0$ . Equation (1) is then multiplied by  $V$  and differentiated with respect to  $V$ . The resulting expression is evaluated at zero pressure

<sup>8</sup> J. E. Mayer, *J. Chem. Phys.* **1**, 270 (1933).

<sup>9</sup> Linus Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 514.

<sup>10</sup> Reference 5, pp. 29-33.

<sup>11</sup> It is admitted that this choice is rather arbitrary and not necessary in this paper. It was originally used in an attempt to explain pressure induced phase transitions in NaCl type ionic crystals.

<sup>12</sup> J. R. Tressman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

<sup>6</sup> E. Grüneisen, *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer-Verlag, Berlin, 1926), Vol. 10, Chap. d.  
<sup>7</sup> F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids* **23**, 395 (1962).

TABLE I. Parameters used in the calculation.

$T_0 = 25^\circ\text{C}$									
$r_0^a$ (Å)	$K_0^b$	$\theta_0^c$ (°K)	$\gamma_0^e$	$b_+/b$	$b_-/b$	$r_+^d$ (Å)	$r_-^d$ (Å)	$C^e$	$D^f$
2.8205	$4.27 \pm 0.04$	$290 \pm 12$	$1.59 \pm 0.16$	6.331	0.543	$0.95 \pm 0.10$	$1.81 \pm 0.18$	$1.80 \pm 0.36$	$1.79 \pm 0.90$
$\rho = 0.3155 \text{ \AA} \quad b = 1.7267 \times 10^{-9} \text{ erg} \quad \lambda = 2.55$									

<sup>a</sup> M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Julius Springer-Verlag, Berlin, 1931).  
<sup>b</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. **64**, 33 (1929); David Lazarus, Phys. Rev. **76**, 545 (1949); and W. C. Overton, Jr., and R. T. Swim, Phys. Rev. **84**, 758 (1951). Units of  $10^{-12} \text{ cm}^2/\text{dyn}$ .  
<sup>c</sup> B. Yates and C. H. Panter, Proc. Phys. Soc. (London) **80**, 373 (1962).  
<sup>d</sup> Linus Pauling, Ref. 9.  
<sup>e</sup> In units of  $10^{-59} \text{ erg-cm}^6$ , J. E. Mayer, Ref. 8.  
<sup>f</sup> In units of  $10^{-74} \text{ erg-cm}^8$ , J. E. Mayer, Ref. 8.

as above to yield the equation

$$\frac{1}{K_0} \left. \frac{d\Phi}{dV} \right|_{V_0} + V_0 \left. \frac{d^2\Phi}{dV^2} \right|_{V_0} - \frac{\gamma_0^2 T_0}{V_0} \left. \frac{\partial E_v}{\partial T} \right|_{V_0, T_0} + \frac{E_v(V_0, T_0)}{V_0} (\gamma_0^2 - \frac{2}{3}\lambda). \quad (7)$$

$K_0$  is the experimental compressibility measured at atmospheric pressure and temperature  $T_0$ .

The calculations were performed by the IBM 7040 at Brigham Young University. An initial value was chosen for  $\lambda$ ; then  $\rho$  and  $b$  were determined by simultaneously solving (6) and (7) using an iterative process. A numerical equation of state was then calculated from which the lattice parameter at atmospheric pressure was determined for several temperatures between  $0^\circ$  and  $800^\circ\text{C}$  and compared with the data of Enck.<sup>13</sup> Another value of  $\lambda$  was tried and the process repeated until the calculated thermal expansion agreed with the experimental measurements to within one-half the experimental mean deviation. The resulting values of  $\lambda$ ,  $\rho$ , and  $b$  were then

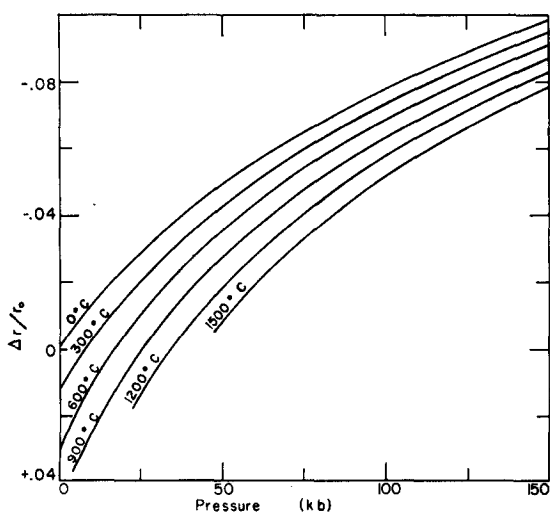


FIG. 1. Calculated change in the lattice parameter of NaCl as a function of pressure and temperature.  $r_0$  is the lattice parameter at atmospheric pressure and  $25^\circ\text{C}$ .

<sup>13</sup> F. D. Enck (private communication).

used to calculate the pressure as a function of the nearest-neighbor distance and temperature. Values chosen for the input parameters as well as the empirically determined parameters are tabulated in Table I.

### III. RESULTS

Once the optimum values for the parameters  $\rho$ ,  $b$ , and  $\lambda$  are known it is possible to calculate a numerical equation of state. The resulting calculation covered the range of temperature between  $0^\circ$  and  $1500^\circ\text{C}$  and the range of pressure between 0 and 500 kbars. The results for pressures up to 150 kbar are displayed in Fig. 1. In this graph the percentage change in lattice parameter is plotted vs pressure for constant temperature along several isotherms.

The coefficient of linear thermal expansion at constant pressure and the isothermal compressibility were calculated from the equation of state. These quantities are graphed in Figs. 2 and 3 as functions of temperature along several isobars. Hunter and Siegel<sup>14</sup> and Stepanov and Eidus<sup>15</sup> have measured the adiabatic compressibility

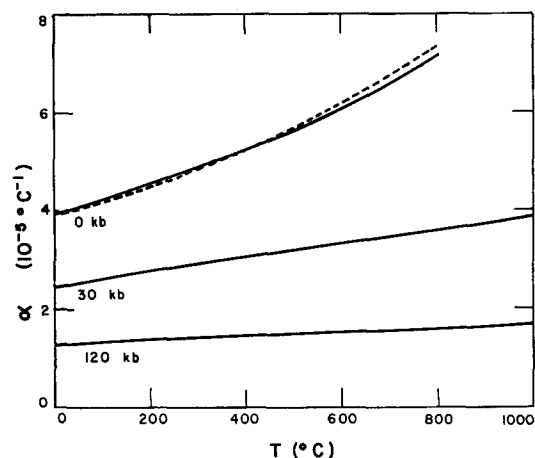


FIG. 2. Coefficient of linear thermal expansion of NaCl vs temperature along 3 isobars. The dashed line is taken from an equation which fits the experimental measurements of Enck at atmospheric pressure. See Ref. 13.

<sup>14</sup> L. Hunter and S. Siegel, Phys. Rev. **61**, 84 (1942).

<sup>15</sup> A. V. Stepanov and I. M. Eidus, Zh. Eksperim. i Teor. Fiz. **29**, 669 (1955) [English transl.: Soviet Phys.—JETP **2**, 377 (1956)].

of NaCl at high temperatures and atmospheric pressure. Their results, adjusted to give the isothermal compressibility, are shown in Fig. 3 for comparison with the theoretical zero pressure curve.

The volume compression, at room temperature, as a function of pressure is compared with the experimental measurements of Bridgman<sup>16</sup> in Fig. 4. The agreement in pressure is within 3% over the entire range and is well within the experimental scatter quoted by Bridgman. A further comparison at higher pressures was made against the dynamic shock measurements of Al'tshuler, Kuleshova, and Pavlovskii.<sup>17</sup> Again the agreement is

TABLE II. Calculated pressure compared with high-pressure shock measurements.

$V_0/V^a$	$T$ (°K)	$P_H$ (meas.) <sup>b</sup> (kbar)	$P$ (calc.) (kbar)
1.22	380	78	74.8
1.32	550	134	133.8
1.43	920	208	208.7
1.53	1500	311	308.6

<sup>a</sup>  $V_0$  is the volume at atmospheric pressure and 25°C.

<sup>b</sup> L. V. Al'tshuler, L. V. Kuleshova, and M. N. Pavlovskii, Ref. 17.

extremely good. This comparison is given in Table II in which the calculated and experimental values of

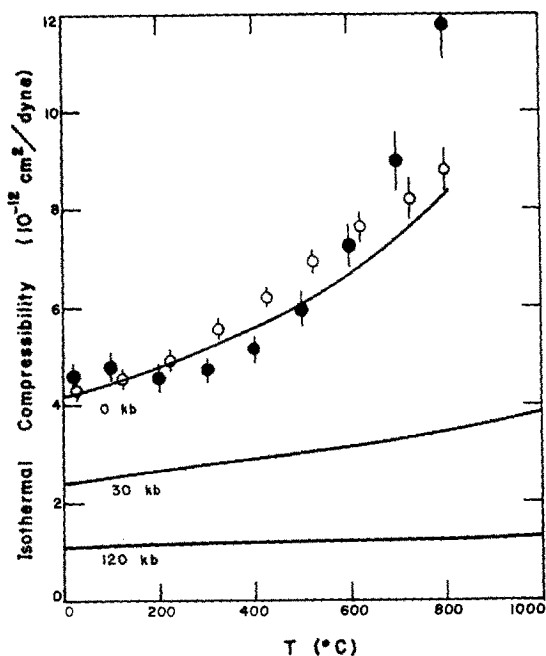


FIG. 3. Isothermal compressibility of NaCl vs temperature along 3 isobars. The open circles were taken from atmospheric pressure measurements of Hunter and Siegel. See Ref. 14. The solid circles were taken from atmospheric pressure measurements of Stepanov and Eidus. See Ref. 15.

<sup>16</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940) and 76, 1 (1945).

<sup>17</sup> L. V. Al'tshuler, L. V. Kuleshova, and M. N. Pavlovskii, Zh. Eksperim. i Teor. Fiz. 39, 16 (1960) [English transl.: Soviet Phys.—JETP 12, 10 (1961)].

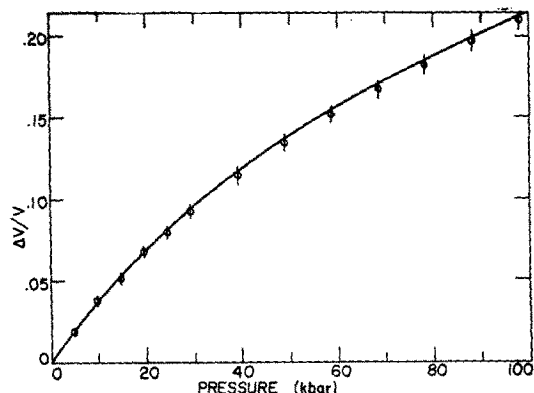


FIG. 4. Volume change as a function of pressure for NaCl at 25°C. Solid line is calculated and circles are from Bridgman's measurements. See Ref. 16.

the pressure are compared at the points given in Table II of the article by Al'tshuler, Kuleshova, and Pavlovskii.

Some of the parameters employed in this calculation are not well known. In order to determine the effect of this uncertainty on the equation of state, calculations were made in which each parameter was varied over the range shown in Table I. In this manner it was determined that the results are insensitive to uncertainties in  $r_+$ ,  $r_-$ ,  $C$ ,  $D$ , and  $\theta_0$ . The entire range of these parameters does not vary the value of  $P(r, T)$  more than  $\pm 0.30$  kbar over the range of  $P$  and  $T$  covered in Fig. 1. The effects of changing  $b_+/b$  and  $b_-/b$  were also determined by using 1.25 and 0.75, respectively, for these ratios rather than the values in Table I. The pressure at a given  $r$  and  $T$  was not altered by more than  $\pm 0.10$  kbar over the above range. The calculation is not sensitive to these parameters because the values of  $b$  and  $\rho$  vary in such a manner as to compensate for changes in these quantities. Variations in the parameter  $\gamma_0$  are also partially compensated by a change in the optimum value of  $\lambda$ . However, the fit to the experimental thermal expansion became quite poor for values of  $\gamma_0$  at the extreme ends of the range shown in Table I. Variations in the parameter  $K_0$  make the most noticeable differences in the results. However, a 1% change in this quantity causes at most a 1.5% change in the calculated pressures as high as 150 kbar.

#### IV. CONCLUSIONS

The numerical equation of state for NaCl presented in this paper is felt to be accurate to better than 2% for any pressure in the range 0 to 150 kbar for temperatures up to 1500°C. This conclusion is drawn from the following facts: (1)  $P(r, T)$  does not vary by more than 1.5% at any point in this range for any value of the experimental parameters, introduced into the calculation, within their range of experimental error. (2) The agreement between the calculated and measured pressure below 100 kbar is better than 3%. (3) The theoretical results are in very good agreement with the shock data

at pressures even far above 150 kbar and at elevated temperatures.

The isothermal compressibility at atmospheric pressure calculated in this paper agrees with the experimental results below 400°C but seems to be somewhat low at higher temperatures. The experimental results in the literature are quite contradictory and therefore do not give an unambiguous indication as to the accuracy of the theory.

The fact that one set of values for  $\rho$  and  $b$  fit all experimental data to pressures as high as 300 kbar indicates that the Born-Mayer repulsion term is indeed very close to the actual form of the repulsion. It is interesting to note that it is not possible to fit pressure data over such a large range using a repulsion term of the form  $1/r^n$  with a single value of  $n$ .<sup>18</sup> The calculated values of  $\gamma$  are not given because they probably are not valid over the large range of temperature and

<sup>18</sup> P. Negrete and F. E. Prieto, *J. Chem. Phys.* **40**, 255 (1964).

lattice parameter covered in the paper. The temperature dependence of  $\gamma$  should be very small above 300°C but for large changes in volume, the volume dependence given in Eq. (3) is less reliable.

The present accuracy at which lattice parameters can be determined by high-pressure x-ray techniques is about 0.1%. Thus, with a known equation of state, one could determine the pressure with an accuracy of better than  $\pm 3$  kbar for any pressure less than 150 kbar. Use of this equation of state for calibration of ultrahigh pressure apparatus should yield the most accurate pressure calibration to the present time. This approach is particularly useful for determining the pressure in an experiment at high temperatures.

#### ACKNOWLEDGMENTS

I wish to thank F. D. Enck for sending me an equation fitting his thermal expansion data on NaCl prior to publication. I am also grateful to Dr. J. Dean Barnett for many helpful discussions and much encouragement.

## Biquadratic Exchange and the Temperature Dependence of Sublattice Magnetization in Lithium Ferrite

E. PRINCE

*U. S. Naval Research Laboratory, Washington, D. C. 20390*

(Received 24 July 1964)

Neutron diffraction measurements have shown that the sublattice magnetizations in lithium ferrite are significantly higher, in the temperature range from  $0.4 T_c$  to  $0.9 T_c$ , where  $T_c$  is the Curie temperature, than predicted by molecular field calculations. An approximate analysis of the effect of adding a biquadratic term to the exchange interaction suggests that the principal effect is to distort the temperature scale in such a way as to make  $T/T_c = (T'/T_c)(1 + \beta \langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle)$ , where  $T'$  is the temperature calculated from a molecular field model and  $\beta$  is of the order of the ratio of the biquadratic to bilinear exchange coefficients. If the  $A-A$   $B-B$  interactions are neglected, but a biquadratic term is included in the  $A-B$  interaction with  $\beta = 0.04$ , the calculated curves are in good agreement with experiment.

#### INTRODUCTION

THE sublattice magnetizations<sup>1</sup> in the ferrimagnetic compound lithium ferrite,  $\text{LiFe}_5\text{O}_8$ , as determined by neutron diffraction measurements, are substantially higher at temperatures between  $0.4 T_c$  and  $0.9 T_c$  than those predicted by the molecular field calculations of Rado and Folen.<sup>2</sup> In order to account for similar behavior previously observed<sup>3,4</sup> in the anti-ferromagnetic oxides NiO and MnO, Rodbell, Jacobs, Owen, and Harris,<sup>5</sup> and Rodbell and Owen<sup>6</sup> have pro-

posed two mechanisms which predict similar departures from molecular field calculations. One of these mechanisms<sup>6</sup> takes account of a separation dependence of the exchange interactions, and requires that there be a distortion of the crystal lattice associated with the magnetic transition. The magnitude of the distortion in lithium ferrite, as determined from magnetostriction,<sup>7</sup> is a factor of a hundred too small to account for any significant portion of the observed effect. The other mechanism postulates a biquadratic term, in addition to the usual bilinear one, in the exchange energy. In this paper we shall consider the effect of this hypothesis in the case of a ferrimagnet, and derive an approximate formula which leads to a remarkably good agreement with the experimental data and needs only one adjustable parameter.

<sup>1</sup> E. Prince, *J. Phys.* **25**, 503 (1964).

<sup>2</sup> G. T. Rado and V. J. Folen, *J. Appl. Phys.* **31**, 62 (1960).

<sup>3</sup> C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.* **83**, 333 (1951).

<sup>4</sup> W. L. Roth, *Phys. Rev.* **111**, 772 (1958).

<sup>5</sup> D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, *Phys. Rev. Letters* **11**, 10 (1963).

<sup>6</sup> D. S. Rodbell and J. Owen, *J. Appl. Phys.* **35**, 1002 (1964).

<sup>7</sup> V. J. Folen (private communication).