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David H. Anderson

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Quadrupole Coupling in Lithium Nitrate†

DAVID H. ANDERSON
Sandia Laboratory, Albuquerque, New Mexico

(Received March 6, 1961)

The value of the Li^7 quadrupole coupling constant in a single crystal of $LiNO_3$ has been found to be 35.5 ± 0.2 kc. It is expected that a reliable estimate of the quadrupole moment of Li^7 may be made with the observed coupling constant and the point-charge field gradient, because of the good agreement for Na^{23} in the case of the isomorphous crystal $NaNO_3$. The value found in this manner is ±0.069 b. The $LiNO_3$ crystal was γ irradiated to facilitate the measurements, and a γ-irradiated crystal of $NaNO_3$ was studied for comparison. It appears that the broadening of the Na^{23} satellite lines in the irradiated $NaNO_3$ results from a relaxation process and not from a wide distribution of static field gradients, and it is concluded that γ irradiation has little or no effect on the Li^7 coupling constant in $LiNO_3$. A precise knowledge of the Li^7 quadrupole moment would provide a test of the ionic model in $LiNO_3$.

INTRODUCTION

THE main objective of this paper is to attempt to estimate the nuclear electric quadrupole moment of Li^7 by a solid-state technique. The crystal studied was $LiNO_3$, which was chosen because of Bersohn's[1] apparent success in calculating the electric field gradient at the Na position in the isomorphous crystal $NaNO_3$. This calculation was based on an ionic model, which we will apply to $LiNO_3$. Similar ionic models have also been used by Bernheim and Gutowsky[2] to account for the pressure dependence of the Na^{23} quadrupole coupling in $NaNO_3$, and by Hewitt[3] who applied an extended ionic model to the magnitude and temperature dependence of the Nb^{93} quadrupole coupling in $KNbO_3$.

Previous attempts to arrive at the quadrupole moment of Li^7 using the known coupling constant of Li_2 and calculating the field gradient have been unsuccessful. The main reason is that the contribution of the nuclear charge to the field gradient is almost exactly canceled by the electron contribution. Thus, the magnitude and even the sign of the field gradient are uncertain.[4,5] It is hoped that this work will lead to a more reliable value of the quadrupole moment of Li^7, and, in addition, add information which will be of assistance in furthering our understanding of field gradients in ionic crystals.

THEORY

The crystal structure of $LiNO_3$ is isomorphous with that of $NaNO_3$,[6] and since the spin of Li^7 is $\frac{3}{2}$ we expect the quadrupole interaction to be completely analogous to the case of Na^{23} in $NaNO_3$, which was first studied by Pound.[7] (This assumes that the energy of the quadrupole interaction is much less than the Zeeman energy which proves to be the case.) In this case, with the symmetry axis of the crystal oriented at an angle θ to the magnetic field H_0 we therefore expect a three-line pattern consisting of a main center line at the normal frequency $\mu H_0/Ih$ plus two satellites given by

$$\nu_{\pm}=(\mu H_0/Ih)\pm(1/4h)e^2qQ(3\cos^2\theta-1). \qquad (1)$$

In Eq. (1), μ, I, and Q are, respectively, the magnetic dipole moment, spin and electric quadrupole moment of the nucleus in question. Consequently, to obtain the coupling constant (e^2qQ/h) we merely measure the maximum separation between the satellites when H_0 is in the plane of the symmetry axis.

Having the coupling constant we then calculate the field gradient q which is, by convention, the zz component. To do this we use a point-charge model of the crystalline lattice and calculate the field gradient by direct summation.[1] Evaluation of the series was carried out on the Sandia Laboratory IBM 704 computer.[8]

Thus far we have not considered the effect of forces which polarize the electron charge cloud surrounding the nucleus, first discussed by Sternheimer and coworkers.[9] In the free ion the nucleus is usually "antishielded" due to the polarizing forces of the ionic charge and the nuclear quadrupole moment. In a solid the amount of "antishielding" may differ from the free-ion value due to the polarizing effects of external charges. Therefore to relate the experimental coupling constant $(\Delta\nu_{zz})$ to the field gradient we write

$$(e^2q/h)(1-\gamma_\infty)Q=\Delta\nu_{zz}. \qquad (2)$$

Numerous papers have shown the importance of the antishielding factor $(1-\gamma_\infty)$ in quadrupole coupling. Although, at this time, it does not seem to be *generally*

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† Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

[2] R. A. Bernheim and H. S. Gutowsky, J. Chem. Phys. **32**, 1072 (1960).

[3] R. R. Hewitt, Phys. Rev. **121**, 45 (1961).

[4] E. G. Harris and M. A. Melkanoff, Phys. Rev. **90**, 585 (1953).

[5] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

[6] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1957).

[7] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[8] We are indebted to R. Bersohn for providing the IBM 704 program.

[9] See for example, R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956), and references cited therein.

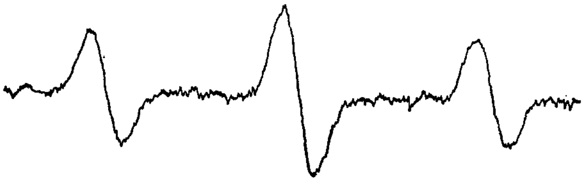

FIG. 1. The first derivative of the Li^7 resonance absorption in γ-irradiated $LiNO_3$ with H_0 approximately parallel to the hexagonal crystal axis. The lines are shown as a function of field with high field to the right and are slightly saturated.

valid to apply antishielding values, which are calculated from free-atom wave functions, to the consideration of quadrupole coupling in solids, it does seem apparent from recent work involving ultrasonic techniques[10,11] as well as the results of field gradient calculations,[3,12,13] that one can expect fairly good agreement between calculated and observed antishielding factors for positive ions. (For the smaller positive ions one might expect even better agreement because of low polarizabilities and the availability of more accurate wave functions.) For our specific application, if the calculated and observed $(1-\gamma_\infty)$ factors agree for Na^{23} in the case of $NaNO_3$, then we would expect similar agreement in the isomorphous $LiNO_3$ for Li^7. We actually obtain better agreement than Bersohn[1] due to a newer value[14] ($Q=+0.087\pm0.010$ b) of the quadrupole moment of Na^{23}. If we assume with Bersohn that the effective charge on the nitrogen atom is zero (this will be discussed later), use the calculated field gradient,[1] and the above value of the quadrupole moment, we find $(1-\gamma_\infty)_{\text{exp}}=5.52$ for Na^+ in $NaNO_3$. The agreement between this value and the calculated values of Das and Bersohn[15] (5.53), Sternheimer[16] (5.56), and Burns[17] (5.65) is very good. If this agreement is other than fortuitous, then we would expect the theoretical value of $(1-\gamma_\infty)$ for Li^+ to be applicable to Li^7 in $LiNO_3$.

EXPERIMENTAL PROCEDURE AND RESULTS

Our attempts at growing a single crystal of $LiNO_3$ from aqueous solution[7] at 65° were unsuccessful largely because of the difficulty of controlling the degree of supersaturation. Since $LiNO_3$ forms no methyl alcoholate[18] we tried growing the crystal from CH_3OH at room temperature but again failed. However, using reagent-grade $LiNO_3$ and absolute C_2H_5OH we isolated a single crystal about $1\times1\times0.5$ cm in size. This crystal was used for the coupling constant determination. (X-ray analysis gave the expected cell constants of $LiNO_3$.[19]) The $NaNO_3$ crystal used in the radiation studies, which will be discussed below, was grown from the melt and obtained from the Harshaw Chemical Company.

The nuclear magnetic resonance apparatus consisted of a Varian Associates wide-line rf unit (operated at about 16 Mc for the Li^7 spectra and about 11 Mc for Na^{23}), 12-in. electromagnet, and regulated power supply. Frequency measurements were made with a Hewlett-Packard 524-C frequency counter, having a stated accuracy of 5 parts in 10^8. To make the angular measurements the crystal was fastened to a rod which was concentric with an angular scale. The scale was attached to the top of the cross-coil probe and an indicator fixed to the rod. Thus, after aligning the crystal with respect to the indicator, angle readings could be made directly from the indicator and scale.

Our first measurements on the $LiNO_3$ crystal showed the long relaxation time observed previously.[7] This factor and the rather small size of the crystal prevented us from getting sufficiently good signal to noise ratios for accurate measurements. Irradiation had been used previously to reduce spin lattice relaxation times,[20,21] and therefore we exposed the $LiNO_3$ to approximately 5×10^8 rad of 1-Mev gamma rays. Figure 1 shows an example of a spectrum taken shortly after irradiation. (The signal was more and more easily saturated as the period from its irradiation time increased.) The peak-to-peak linewidth of the satellites and central line was about 3 kc ($\sim$1.8 gauss). Figure 2 shows the angular dependence of the satellite-satellite separation. Alignment was achieved by using the fact that the maximum separation was obtained when H_0 was parallel to the symmetry axis. From these measurements we found[22] $\Delta\nu_{zz}=35.5\pm0.2$ kc and $\Delta\nu_{xx}=\Delta\nu_{yy}=\Delta\nu_{zz}/2$.

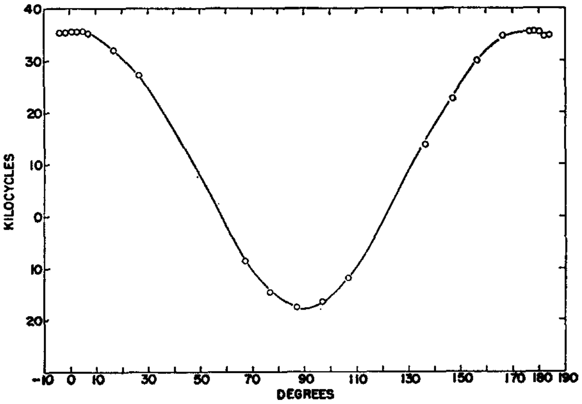

FIG. 2. The dependence of the Li^7 satellite-satellite separation in γ-irradiated $LiNO_3$ as a function of the angle (θ) between the crystal symmetry (Z) axis and the applied magnetic field (H_0).

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[10] D. A. Jennings, W. H. Tantilla, and O. Kraus, Phys. Rev. **109**, 1059 (1958).

[11] D. S. Bolef and M. Menes, Phys. Rev. **114**, 1441 (1959).

[12] G. Burns, Phys. Rev. **115**, 357 (1959).

[13] E. G. Wilkner and T. P. Das, Phys. Rev. **109**, 360 (1958).

[14] See the discussion in reference 2.

[15] T. P. Das and R. Bersohn, Phys. Rev. **104**, 733 (1956).

[16] R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

[17] G. Burns, J. Chem. Phys. **31**, 1253 (1959).

[18] M. M. Markowitz and R. Harris, J. Phys. Chem. **64**, 670 (1960).

[19] *Standard X-Ray Diffraction Powder Patterns*, National Bureau of Standards Circ. No. 539 (U. S. Dept. of Commerce, National Bureau of Standards, Washington, D. C.), Vol. 7.

[20] R. V. Pound, Phys. Rev. **81**, 156 (1951).

[21] J. F. Hon and P. J. Bray, Phys. Rev. **110**, 624 (1958).

[22] The coupling constant is about 10% smaller than that inferred from a powder pattern in reference 21.

Since the $LiNO_3$ crystal was irradiated prior to observation, we were interested in the specific effect that the radiation would produce on the observed spectra and in particular whether there would be any change of the quadrupole coupling constant. Not having a good nonirradiated crystal of $LiNO_3$ for comparison, we felt the next best substance would be $NaNO_3$. Before irradiation, we obtained the same results as Pound[7] and Eades *et al.*[23]; we found $\Delta\nu_{zz}=334.3\pm0.7$ kc, and the peak-to-peak linewidth of the components about 1.6 kc. By considerations similar to those of Andrew and Swanson[24] we found the Na^{23} relaxation in the $NaNO_3$ crystal to be quadrupolar (as expected), and the Li^7 relaxation in the γ-irradiated $LiNO_3$ crystal to be magnetic dipolar in origin. After irradiation to 5×10^8 rad (approximately 1-Mev γ rays) we obtained the spectrum shown in Fig. 3. (Only one satellite and the central component are shown; the other satellite was symmetrically placed.) The central line as shown is modulation broadened, but was observed to have approximately the same width as before irradiation. The satellites were much broader and weaker, the peak-to-peak linewidth being about 23 kc ($\sim$20 gauss), although broadened somewhat by the large modulation amplitudes utilized for observation. Using the crossover point of the derivative curves of the satellites for the measurement of the maximum separation we found $\Delta\nu_{zz}=339\pm2$ kc. In general, the line shapes of the satellites seemed to be rather asymmetric.

DISCUSSION AND CONCLUSIONS

First let us consider why the Na^{23} satellites are so broad in the γ-irradiated $NaNO_3$ crystal. Since the important defects are apparently NO_2 or NO_3 molecules and possibly F centers,[25] the breadth of the irradiated satellites might be ascribed to a wide distribution of static field gradients arising through both the charge and size effect.[26] Assuming that essentially the same defects are produced in γ-irradiated $LiNO_3$, this seems unlikely because then the irradiated $LiNO_3$ satellites would be expected to have a corresponding breadth. (The observed 3-kc width is about that expected from dipole-dipole interactions, but it is possible that radiation annealing is more important in $LiNO_3$ than $NaNO_3$.[27]) Since the $NaNO_3$ crystal has a quadrupolar relaxation mechanism and $LiNO_3$, magnetic dipolar, it seems probable that the Na^{23} satellite broadening is caused by the quadrupolar relaxation mechanism rather than the static field gradient distribution. Here, it may be the case that the diffusion of defects, which are introduced by the γ irradiation, may cause lifetime broadening of the satellites through the quadrupolar interaction.[28] The effect of the diffusion of defects should become small relative to the static field gradient effects at low temperatures, and the two effects could probably be separated by a study of the satellite width as a function of temperature.[28] The slight asymmetry in the satellite shape might be due to second-order quadrupole effects or, possibly, to a small static field gradient asymmetry.[28] This asymmetry could be studied by field- and angular-dependence measurements. However, the detailed consideration of the shape of the Na^{23} satellite in γ-irradiated $NaNO_3$ is not our main concern in this report.

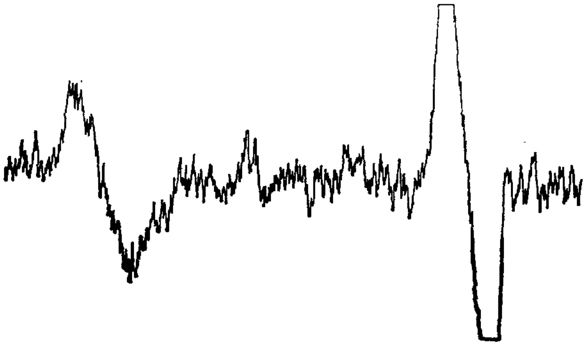

FIG. 3. The first derivative of the central line and one satellite from the Na^{23} resonance absorption in γ-irradiated $NaNO_3$. The lines, shown as a function of field with high field to the right, are modulation broadened and obtained at the position of maximum separation.

From our results and the above considerations we also conclude that there is little, if any, change in the quadrupole coupling constant of Li^7 in $LiNO_3$ produced by the γ irradiation. It is true that a small change (1.5%) is noted in the Na^{23} coupling in $NaNO_3$. Here, however, the satellites were probably broadened by the quadrupolar relaxation mechanism, and were apparently somewhat asymmetric. The change in coupling is interpreted as arising from the change in crossover point of the derivative curve which results from the asymmetry. In the case of $LiNO_3$ the Li^7 relaxation is magnetic dipolar and no broadening of the satellites is observed. The decrease in spin lattice relaxation time of Li^7 in the irradiated $LiNO_3$ is attributed to the large dipole-dipole coupling between the paramagnetic centers and the Li^7 nuclei.

Let us now turn to an evaluation of the quadrupole moment of Li^7 through Eq. (2). From our experiment $\Delta\nu_{zz}=35.5\pm0.2$ kc, and we choose $(1-\gamma_\infty)=0.744$ based upon good wave functions for Li^+.[15,29] Using recently determined rhombohedral cell constants for $LiNO_3$[19] ($a=5.638$, $\alpha=48$ deg 7.8 min) the field gradient at the Li position was calculated with the IBM 704

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[23] R. G. Eades, D. G. Hughes, and E. R. Andrew, Proc. Phys. Soc. (London) **71**, 1019 (1958).

[24] E. R. Andrew and K. M. Swanson, Proc. Phys. Soc. (London) **70**, 436 (1957).

[25] W. B. Ard, Jr., J. Chem. Phys. **23**, 1967 (1955).

[26] See for example T. P. Das and E. L. Hahn, Solid State Phys. Suppl. **1**, 205 (1958).

[27] J. F. Hon and P. J. Bray, J. Phys. Chem. Solids **11**, 144 (1959).

[28] M. H. Cohen and F. Reif, Solid State Phys. **5**, 321 (1957).

[29] A. Dalgarno, W. D. Davison, and A. L. Stewart, Proc. Roy. Soc. (London) **A257**, 115 (1960).

program developed by Bersohn.[1] We find that

$$q = \frac{3.5497 - 7.3697 Z_{\mathrm{N}}}{a^3}.$$

If, as in the case of $NaNO_3$, we let the effective charge (Z_{N}) on the nitrogen be zero, we arrive at the following equation:

$$e^2/h \frac{(3.5497)}{(5.638\times10^{-8})^3}(0.744)Q(\mathrm{Li}^7) = \pm 35.5\times10^3$$

and $Q(\mathrm{Li}^7) = \pm 0.069$ b.

From this determination we, of course, get no information regarding the sign of Q. (In principle one might be able to determine the sign by working at very low temperatures.) Unfortunately, as is well known, the field gradient is quite sensitive to the x-ray-determined structural parameters. (In the case of $LiNO_3$, the unit cell coordinates were determined in 1928, when the determinations were considerably less accurate than today.) To show this, the field gradient was calculated for $u = 0.262 \pm 0.01$, where u is the parameter which represents the various positions of the oxygen atoms in the unit cell. (The structure[6] of $LiNO_3$ is such that only the oxygen position is uncertain from the recent cell constant determination.[19]) Allowing the old value of $u = 0.262$ to vary by ± 0.01 (about ± 0.06 A) is a reasonable method, therefore, to estimate the range of $Q(L_1{}^7)$ due to structural uncertainty. We find

$$Q(\mathrm{Li}^7) = \pm 0.093 \text{ b } (u = 0.272),$$
$$Q(\mathrm{Li}^7) = \pm 0.056 \text{ b } (u = 0.252).$$

Thus, a 4% change in the oxygen position can lead to a 30% change in the value of the calculated quadrupole moment.

Some comment is warranted on the assignment of zero charge to the nitrogen atoms in both the nitrate crystals. As noted by Bersohn[1] there is some theoretical justification for this (Pauling's hypothesis of neutrality), but the state of affairs is still rather unsatisfactory. For example, in $NaNO_3$, knowing the coupling constant and quadrupole moment one would like to be able to determine *both* Z_{N} and $(1-\gamma_\infty)$ uniquely. As pointed out by Bersohn[1] and Bernheim and Gutowsky,[2] this is not possible here because the data are insufficient. But if more information were available for a given crystal, e.g., if $\eta \neq 0$, or if two coupling constants were known, then one could possibly make such a unique assignment. For the application to $LiNO_3$ we observe that agreement is obtained in the case of $NaNO_3$ if $Z_{\mathrm{N}} = 0$ and therefore similar results may be expected for $LiNO_3$.

Some recent work[3,12] has included the contribution of induced ionic dipole moments to the electric field gradient. In the former study[3] supplemental information was utilized; the latter study[12] involved the diatomic alkali halide gases, intrinsically a simpler system than a crystalline solid. In our case, the calculation would be more difficult. However, unless the agreement in the case of $NaNO_3$ is coincidental, the induced dipole effect should be small. Qualitatively, this may be expected for the following reasons: The largest contribution to the electric field gradient at the Na^+ (or Li^+) ion from induced moments would probably be expected from the induced dipoles of the nearby nitrate ions which lie on the symmetry (Z) axis with the Na^+ (or Li^+) ions. However, the Z components of these dipoles which would be induced by the alkali ions exactly cancel each other because of the crystalline symmetry. Therefore, any large effect upon the field gradient by induced dipoles seems unlikely.

Let us now compare our value (± 0.069 b) of the quadrupole moment of Li^7 with other recent evaluations. Harris and Melkanoff[4] used an 18-term James function for the field gradient calculation in Li_2 and arrived at $Q = -0.042$ b. They noted the extreme sensitivity of the field gradient to the wave function, however, and concluded that the magnitude was still in doubt but that the sign was probably negative. A wave function, which predicts a dissociation energy quite close to the experimental value, has been used by Mannari and Arai[30] to calculate the field gradient in Li_2. Neglecting shielding effects (which would increase the field gradient by about 15%) they find $Q = -0.025$ b. Both of the above determinations use the value of $+0.060$ Mc[31] for the quadrupole coupling in Li_2. Since this value was obtained from the half-width of an unresolved line, the quadrupole coupling in Li_2 is rather uncertain. By considering induced dipole effects in the lithium halide gases, Burns[12] arrived at $Q = -0.016$ b. This value is in agreement with various estimates of about -0.02 b from nuclear-shell theory.[32]

Thus, our value for Q seems somewhat high in comparison to the most recent determinations. In terms of the theoretical model used here, we observe that allowing the nitrogen atom to have an effective positive charge would *lower* the field gradient and raise the calculated quadrupole moment. (Allowing the nitrogen atom to have an effective negative charge is physically unreasonable.) It is possible that a detailed treatment of induced dipoles will increase the field gradient, thereby lowering the calculated quadrupole moment. However, we see that in order for our calculated value to be about 0.02 b, the field gradient would have to increase by almost a factor of four. Such a relatively large effect from induced dipoles (or higher moments) would not be expected.

Finally, the possibility exists that the ionic model, even including the contributions of higher induced moments, is not adequate for the calculation of field gradients in ionic crystals. At present, there is not

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[30] I. Mannari and T. Arai, J. Chem. Phys. **28**, 28 (1958).

[31] R. A. Logan, R. E. Coté, and P. Kusch, Phys. Rev. **86**, 280 (1952).

[32] See for example R. J. Blin-Stoyle, Revs. Modern Phys. **28**, 75 (1956).

enough information to allow a general statement to be made. To test the ionic model in the special case of $LiNO_3$ a precise determination of the quadrupole moment of Li^7 would be desirable. Because of the sensitivity of the field gradient to the wave function, as well as the question of the accuracy of the experimental coupling constant, the determination of Q from Li_2 is unsatisfactory. In the lithium halide gases, the internuclear distances are relatively small and ionic distortions can be expected. These distortions are not taken into account in an ionic model and may have a significant effect on the field gradient. A determination based upon the molecular-beam measurement of the coupling constant in LiH, which is not planned in this laboratory, appears to be promising.[33] Here, the charge asymmetry would probably lead to a resolvable coupling and, the fact that the molecule has only four electrons should allow an accurate wave function to be obtained. Also, if LiD were studied with a molecular-beam technique, a check on the accuracy of the wave function would be available since the quadrupole moment of D^2 is quite accurately known.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. R. Bersohn and Dr. R. A. Berheim for discussions which led to this work. We would also like to thank A. Brouillard for experimental assistance, Mrs. D. Martin for helping with the computations, and E. Graeber for performing the x-ray analysis.

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[33] *Note added in proof*: A recent communication [S. L. Kahalas and R. K. Nesbet, Phys. Rev. Letters **6**, 549 (1961)] describes the determination of $Q(Li^7)$ from the Li^7 quadrupole coupling in LiH and the calculated field gradient. The value obtained was -0.0356 b with an estimated error of less than 10%. Although our estimate (0.069 b) is within a factor of 2 of this value, the agreement is not as good as in the case of $NaNO_3$. (This result is still dependent, of course, on an accurate knowledge of the crystal structure; a more accurate determination is desirable for $LiNO_3$.) In order to improve the calculation of the field gradient in $LiNO_3$, the distribution of charge in the NO_3^- ion should be examined more critically. Probably the weakest point in our procedure is the idealization of NO_3^- ion by simple point charges. A more realistic model would consider the moments of the charge distribution of the ion, which, however, would involve considerably more complex calculations.

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Tetrafluoromethane: *P–V–T* and Intermolecular Potential Energy Relations*

D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough

Thermodynamics Laboratory, Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Oklahoma

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Measurements of the gas compressibility of tetrafluoromethane were made in the region, 0–350°, 15–394 atm. From these results, values of the compressibility factor $Z=PV/RT$, the second, third, and fourth virial coefficients, and the parameters of the Beattie-Bridgeman and Benedict-Webb-Rubin equations of state were derived. The virial coefficients were correlated by the Lennard-Jones (12, 6), Lennard-Jones (28, 7), Stockmayer, and Kihara intermolecular potential energy functions, and numerical values for the molecular parameters were obtained. One of the first tests of the theoretical fourth virial coefficient of the Lennard-Jones (12, 6) potential was made using the experimental fourth virial coefficients of tetrafluoromethane.

THE pressure-volume-temperature properties of hydrocarbons, fluorocarbons, and mixtures of hydrocarbons and fluorocarbons are determined by the Bureau of Mines as part of an extensive program for evaluating the chemical thermodynamic properties of these and other materials over a wide range of temperatures and pressures. Because of its structural simplicity and high thermal stability, tetrafluoromethane is a compound of exceptional interest in the theoretical and correlational phases of these studies.

The most extensive previous experimental work on the gas compressibility of tetrafluoromethane was reported, for pressures below 50 atm, by MacCormack and Schneider.[1] Experimental values for the second virial coefficient, obtained from unpublished measurements by W. J. McManamey (University of Sydney), were given by Hamann and Lambert[2] in a theoretical treatment of tetrafluoromethane as a quasi-spherical molecule. Cawood and Patterson[3] reported a value for the second virial coefficient of tetrafluoromethane at 21°.

The present measurements covered a temperature range from 0 to 350° at pressures up to 394 atm. These data were used to derive the parameters of two closed

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* Contribution No. 102.

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[3] W. Cawood and H. S. Patterson, Phil. Trans. Roy. Soc. London **A236**, 77 (1937).