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Nuclear Quadrupole Coupling Constants of Li^7 in Lithium Compounds*

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Quadrupolar splittings of the Li^7 nuclear magnetic resonance have been detected and measured in powders of LiOH, $LiOH\cdot H_2O$, $LiNO_3$, $LiNO_3\cdot 3H_2O$, $LiIO_3$, Li_3PO_4, Li_2TiO_3, and Li_2ZrO_3. The theoretical powder pattern for a nonvanishing asymmetry parameter, η, has been checked by observations in spodumene, $LiAl(SiO_3)_2$, and applied in the analysis of several of the observed spectra. It was found necessary to shorten the Li^7 spin-lattice relaxation time, T_1, in most of the compounds before successful measurements could be made.

I. INTRODUCTION

The splitting of nuclear magnetic dipole resonances by quadrupole interactions has been studied in many compounds[1,2] since the investigations by Pound.[3] Little work has been done on lithium resonances, however, other than the investigations of $Li_2SO_4\cdot H_2O$ and Li_2CO_3 by Pound,[3] a study of spodumene,[4] and recent work[5] on the still unsettled[1] structure of lithium sulfate. The studies have been made unattractive by the long relaxation time exhibited[3] by the Li^7 nuclear spin system in many compounds and by the lack of single crystals (e.g., $LiNO_3$; see reference 3).

The present work is an investigation of lithium-containing powders in which the spin-lattice relaxation time has been lowered by gamma irradiation[6] where necessary. A successful check of the theory for first-order quadrupolar splittings when the asymmetry parameter is not zero is reported, and the theory and experimental results are used to deduce probable local configurations around the lithium atoms in unknown crystal structures.

II. THEORY

A. Line Shape in Powders

The general theory of quadrupole effects in nuclear magnetic resonance is readily available[1–4] in the literature. Hence, we confine ourselves to remarks which are of special pertinence to the study reported in this paper.

The quadrupole coupling constant of Li^7 in solids would be predicted as small because (a) the quadrupole moment of the Li^7 nucleus is relatively small ($|Q|=0.10$ barn[7]); (b) the Sternheimer[1,8] factor γ_∞ is negative[9] for Li^7, leading to a small shielding of the field gradient from charges external to the lithium ion; and (c) the bonding is normally ionic. If the coupling constant is sufficiently small, quadrupolar splittings of the Li^7 nuclear magnetic-dipole resonance should be observable in powders and an analysis involving first-order effects of the coupling constant should be sufficient.

The line shape for the nuclear magnetic resonance with first-order quadrupole splitting and vanishing asymmetry parameter in a powder sample has been developed by Pound.[3] The characteristic shape for spin $I=\frac{3}{2}$ without dipolar broadening is displayed in Fig. 1. (The large $m=\frac{1}{2}\rightarrow m=-\frac{1}{2}$ response at ν_0 is omitted in Figs. 1 and 2.) The coupling constant is given by

$$e^2qQ/h=4\Delta\nu_1. \quad (1)$$

It is theoretically possible to obtain measurements of

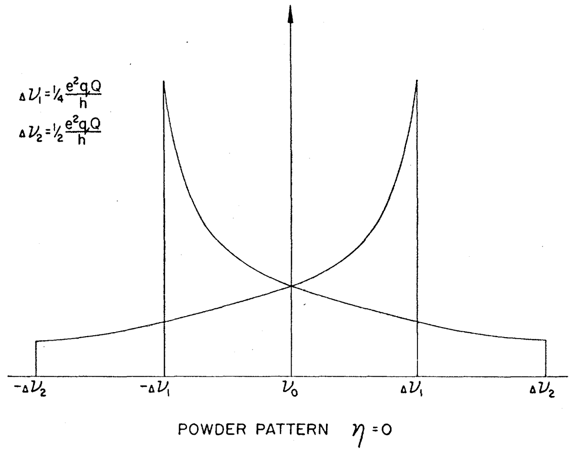

FIG. 1. The theoretical powder line shape for a nuclear spin of $\frac{3}{2}$ and a vanishing asymmetry parameter η. Dipolar broadening effects are not shown and the large $m=\frac{1}{2}\rightarrow m=-\frac{1}{2}$ response (unaffected in first order by quadrupolar effects) is omitted.

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*This work was supported by the U. S. Atomic Energy Commission.

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[1] M. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), supplement to Vol. 5.

[2] T. P. Das and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

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

[4] Volkoff, Petch, and Smellie, Can. J. Phys. **30**, 270 (1952).

[5] E. Hirahara and M. Murakami, J. Phys. Soc. (Japan) **11**, 608 (1956).

[6] R. V. Pound, Phys. Rev. **81**, 1956 (1951).

[7] This value is based on a calculation by Dr. Richard Bersohn of the electric field gradient at the lithium position in $LiNO_3$ and the value of 39.2 kc/sec reported in this paper for the Li^7 coupling constant in that compound. We wish to thank Dr. Bersohn for this communication.

[8] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

[9] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

two frequency increments, $\Delta\nu_1$ and $\Delta\nu_2$, but $\Delta\nu_2$ has never been observed. Fortunately, a measurement of $\Delta\nu_1$ is sufficient to determine the coupling constant.

The powder line shape for a nonvanishing asymmetry parameter is given by Cohen and Reif[1] and is displayed in Fig. 2 for $I=\frac{3}{2}$. It is based on the solution of Bloembergen and Rowland[10] for the theoretical line shape due to anisotropy of the Knight shift in a polycrystalline powder of a conductor with less than axial symmetry. The coupling constant e^2qQ/h and asymmetry parameter η are given by

$$e^2qQ/h=2(\Delta\nu_1+\Delta\nu_2), \qquad (2)$$

$$\eta=(\Delta\nu_2-\Delta\nu_1)/(\Delta\nu_2+\Delta\nu_1). \qquad (3)$$

The number of experimentally observable responses when $\eta\neq 0$ depends on the size of η. It is convenient to consider three ranges of η:

(a) $\eta\ll 1$. The pattern is that of Fig. 1 for $\eta=0$ except for some splitting of $\Delta\nu_1$ (Fig. 1) into $\Delta\nu_1$ and $\Delta\nu_2$ (Fig. 2) and consequent probable broadening of the peak in this region. The responses at $\nu_0\pm\Delta\nu_3$ will be unobservable.

(b) η almost unity. The divergence at $\nu_0\pm\Delta\nu_1$ of Fig. 2 moves to ν_0 and $\Delta\nu_2\simeq\Delta\nu_3$. A three-response pattern similar to the $\eta=0$ case is observed but the satellite intensity is considerably reduced.

(c) η has an intermediate value. η and e^2qQ/h can be evaluated from Eqs. (2) and (3). The responses at $\nu_0\pm\Delta\nu_3$ are probably not observable (Fig. 2).

B. Spin-Lattice Relaxation Time

It has been shown by Pound[3] that the spin-lattice relaxation time is determined by electrical quadrupole interaction in cases of nuclei displaying sufficiently large coupling constants. The expected and measured coupling constants for Li^7 are small, however, and the relaxation times may be long. Pound[3] found this to be the case in LiNO$_3$, where only a transient response was observed during a traversal of the resonance frequency region. The same saturation condition was found in several of the compounds reported in this paper. In cases such as this, the introduction of paramagnetic impurities can reduce T_1 sufficiently to render the resonance observable.

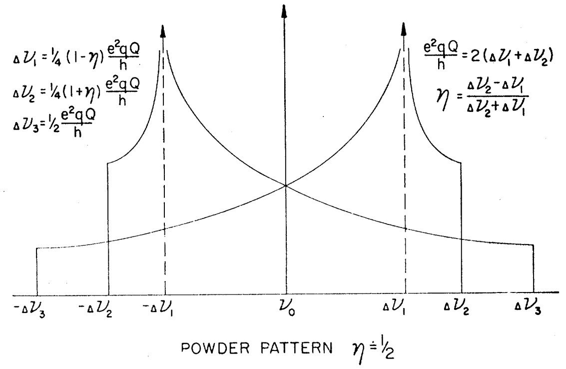

FIG. 2. The theoretical powder line shape for a nuclear spin of $\frac{3}{2}$ and $\eta\neq 0$. Dipolar broadening effects are not shown and the large $m=\frac{1}{2}\rightarrow m=-\frac{1}{2}$ response (unaffected in first order by quadrupolar effects) is omitted.

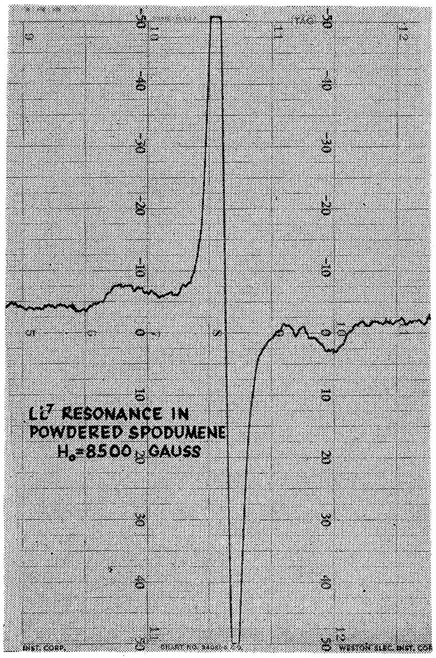

FIG. 3. The Li^7 resonance in powdered spodumene, LiAl(SiO$_3$)$_2$, in a magnetic field of 8500 gauss. The recorded signal in this and all subsequent figures is the derivative of the absorption line.

III. EXPERIMENTAL METHOD

A. Equipment

The radio-frequency spectrometer employed was a Pound-Watkins recording type purchased from the Nuclear Magnetics Corporation and modified to yield greatly increased signal-to-noise ratios. Two magnets were used: a permanent magnet with six-inch diameter pole faces, a gap of one and a half inches, and a nominal field of 5250 gauss from the Indiana Steel Products Company; and a Varian Model V-4007 six-inch electromagnet and V-2200 power supply.

The quadrupolar splittings were measured by superposing 10-kc/sec markers from a General Radio Unit Crystal Oscillator (Type No. 1213 AB) on the recording of the resonance.

B. Procedure

In order to check the validity and applicability of the powder pattern theory for $\eta\neq 0$, a natural crystal of spodumene, LiAl(SiO$_3$)$_2$, was ground into a fine powder. The recorded resonance[11] is shown in Fig. 3. The

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[10] N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[11] A previous effort to find the Li^7 quadrupolar splittings in polycrystalline spodumene was not successful. See the communication from R. M. Cotts and W. D. Knight quoted in reference 1.

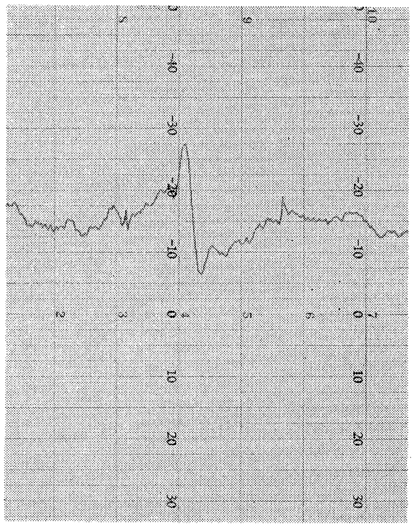

FIG. 4. The Li^7 resonance in LiOH powder in a magnetic field of 5250 gauss. The sample was not γ irradiated and the lowest available radio-frequency power was employed.

satellite responses are much smaller in intensity relative to the central line than the splittings in LiOH (Fig. 5) which is known to be a case of $\eta=0$. Hence, η is nonvanishing and the fact that a three-response pattern is observed indicates η to be large, causing the divergences at $\nu_0\pm\Delta\nu_1$ to be in the central line and the outer peaks ($\nu_0\pm\Delta\nu_2$ and $\nu_0\pm\Delta\nu_3$) to coincide. Upon using the data of Volkoff, Petch, and Smellie[4] for Li^7 in spodumene, $e^2qQ/h=75.7\pm0.5$ kc/sec and $\eta=0.79\pm0.01$, the $\Delta\nu$ values should be

$$\Delta\nu_1=(e^2qQ/h)\tfrac{1}{4}(1-\eta)=3.97\pm0.22 \text{ kc/sec}, \qquad (4)$$

$$\Delta\nu_2=(e^2qQ/h)\tfrac{1}{4}(1+\eta)=33.8\pm0.4 \text{ kc/sec}, \qquad (5)$$

and

$$\Delta\nu_3=\tfrac{1}{2}(e^2qQ/h)=37.85\pm0.25 \text{ kc/sec}. \qquad (6)$$

The small difference of 4 kc/sec between $\Delta\nu_2$ and $\Delta\nu_3$ is insufficient to resolve the outer peaks when the effects of dipolar broadening are considered. Experimentally, the maximum derivative in the unresolved peak occurs at $\Delta\nu=34.9\pm2$ kc/sec. This value lies between the calculated values of $\Delta\nu_2$ and $\Delta\nu_3$ [Eqs. (5) and (6)] as expected.

The central line in Fig. 3 has been broadened by the modulation necessary to reveal the satellites. Smaller modulation yields a maximum positive derivative to maximum negative derivative separation of 3.8 ± 0.4 kc/sec for this central response. Thus the divergences at $\nu_0\pm\Delta\nu_1$ lie within the central line and are unobservable because of dipolar broadening and their relatively small intensity in comparison to the response at ν_0.

Most of the compounds studied exhibited a long T_1 which causes saturation of the resonance as in the case[3] of $LiNO_3$. In order to decrease T_1, the samples were irradiated with gamma rays from the Co^{60} source at Rensselaer Polytechnic Institute,[12] the dosage being 6×10^7 roentgens. The effectiveness in decreasing T_1 and hence the saturation can be seen by comparing the Li^7 resonance in LiOH before irradiation (Fig. 4) with the resonance in the irradiated sample (Fig. 5). In the case of $LiNO_3$, the resonance still saturates in the irradiated sample (as can be seen from the recorder trace in Fig. 7). The line is in the process of saturating as the resonance is being recorded so that the central line appears quite asymmetric. However, the reduction in saturation was sufficient to permit determination of the quadrupolar splittings.

IV. RESULTS AND DISCUSSION

A summary of data for the compounds which have been studied is given in Table I. A possible error of ±10% should be ascribed to each coupling constant in those cases where the asymmetry parameter is known to vanish. This is larger than the measurement error and takes into consideration the fact that the frequency at maximum slope in the experimental absorption curve does not occur at exactly the edge or divergence frequency because of the dipolar effects. Larger uncertainties are inherent in those cases for which η is not known to vanish.

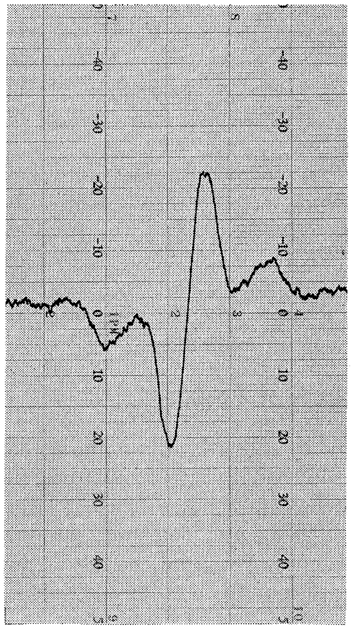

FIG. 5. The Li^7 resonance in LiOH powder in a magnetic field of 5250 gauss. This and all subsequent figures (except Figs. 11 and 12) are for samples which have received 60 megaroentgens of Co^{60} gamma irradiation.

LiOH

The structure of LiOH is tetragonal.[13] The principal axes of the electric field-gradient tensor coincide with the crystal axes since there are two perpendicular planes

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[12] We are indebted to Dr. Dwight Wilson of Rensselaer Polytechnic Institute for the use of their facility.

[13] Th. Ernst, Z. physik. Chem. (Leipzig) **20B**, 65 (1933).

of symmetry defined by the c and b axes and the c and a axes. It is not apparent that the asymmetry parameter vanishes since the local environment of the lithium atoms displays only twofold rotational symmetry. However, a 90° rotation about the c axis plus a reflection through the $a-b$ plane leaves the crystal unchanged, so that $\eta=0$. The coupling constant is given by Eq. (1) and the measured splitting.

$LiOH\cdot H_2O$

The structure of $LiOH\cdot H_2O$ is monoclinic.[14] The local environment of the lithium atoms is an irregular tetrahedron formed by two water molecules and two hydroxyl groups. A nonvanishing asymmetry parameter would be expected. If the observed line (Fig. 6) is compared with the line for LiOH (Fig. 5) run under identical conditions, there are indications of an additional response between each outermost satellite and the central peak. This cannot be explained by dipolar effects since the central line is more narrow in the hydrated compound. It appears reasonable to identify the outer satellite frequencies with $\nu_0\pm\Delta\nu_2$ and the inner satellites with $\nu_0\pm\Delta\nu_1$. The estimated values (Table I) of e^2qQ/h and η are obtained with the very approximate relation $\Delta\nu_1=\frac{1}{2}\Delta\nu_2$ obtained from inspection of Fig. 6.

TABLE I. Summary of data.

Compound	Measured splitting (kc/sec)	Coupling constant e^2qQ/h (kc/sec)	Asymmetry parameter η
LiOH	27.5	110	0
$LiOH\cdot H_2O$	28	~84	~0.3
	~14		
$LiNO_3$	9.80	39.2	0
$LiNO_3\cdot 3H_2O$	9.85	~39.4	~0
$LiIO_3$	11.3	45.2	0
Li_2PO_3	32.4	~91.6	~0.42
	13.4		
Li_2TiO_3	22.9	~70.4	~0.29
	12.3		
Li_2ZrO_3	27.0	108	0
	16.4	65.6	0
$Li_2C_2O_4$	None		
Li_2SiO_3	None		
$LiBH_4$	None		

$LiNO_3$

The hexagonal crystal structure[15] of $LiNO_3$ is isomorphic with that of $NaNO_3$, the metal ions residing on an axis of threefold rotational symmetry. Pound[3] has confirmed that $\eta=0$ from a study of the quadrupolar splitting of the Na^{23} resonance in a single crystal of $NaNO_3$. Equation (1) and the observed splitting (Fig. 7) yield the coupling constant in $LiNO_3$.

The quadrupolar splitting for $LiNO_3\cdot 3H_2O$, discussed in the next section, is practically the same as in $LiNO_3$.

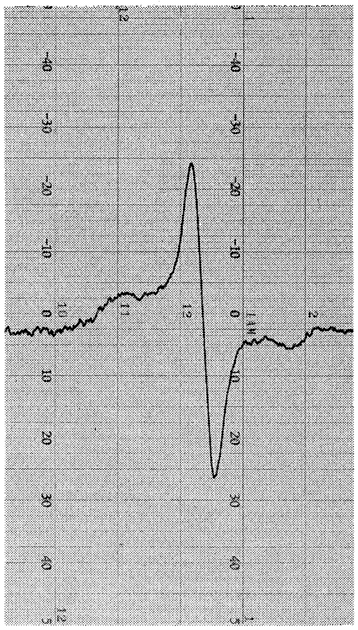

FIG. 6. The Li^7 resonance in $LiOH\cdot H_2O$ powder.

Since the latter compound is quite deliquescent and could take up enough water to form $LiNO_3\cdot 3H_2O$, the purported $LiNO_3$ sample was baked at 90°C for three days. This treatment should have removed any water originally present. Subsequent investigations of the baked sample showed no change from the line shape first observed (Fig. 7).

$LiNO_3\cdot 3H_2O$

The splittings (Fig. 8) in this compound are, within the limits of experimental error, equal to the splittings in $LiNO_3$. Precautions undertaken to insure that the

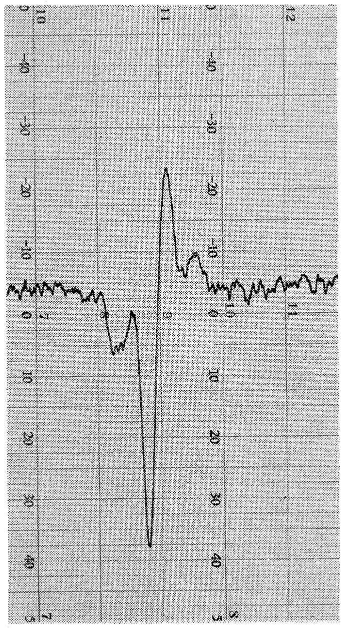

FIG. 7. The Li^7 resonance in $LiNO_3$ powder.

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[14] R. Pepinsky, Z. Krist. **102**, 119 (1939).

[15] R. W. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948).

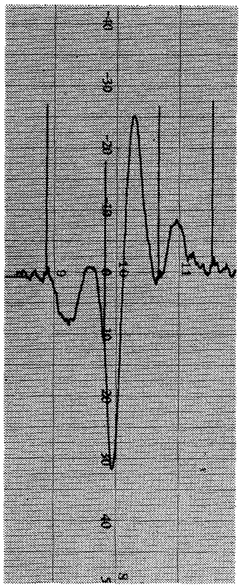

FIG. 8. The Li^7 resonance in $LiNO_3\cdot 3H_2O$ powder.

$LiNO_3$ sample was not in fact $LiNO_3\cdot 3H_2O$ were given in the previous section. There remains the possibility that the $LiNO_3\cdot 3H_2O$ sample was actually $LiNO_3$. Saturation behavior was quite different in the two samples, however, the hydrated material displaying a shorter spin-lattice relaxation time T_1. This is consistent with the expected influence of the large proton magnetic moments. However, the comparison of saturation behavior was made *after* irradiation. The possibility exists that the different T_1 values arise from a difference of radiation damage in the two compounds. It is also possible that inclusion of water of hydration in the structure opens up the lattice, allowing more impurities to be present.

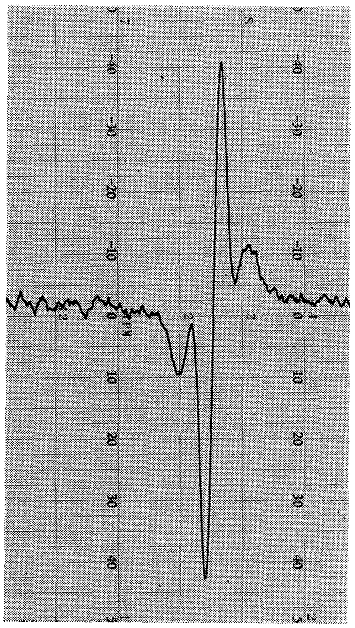

FIG. 9. The Li^7 resonance in $LiIO_3$ powder.

The structure of $LiNO_3\cdot 3H_2O$ is apparently not known. From comparison of the observed line shape (Fig. 8) for the compound, with the lines in LiOH (Fig. 5), $LiNO_3$ (Fig. 7), and $LiIO_3$ (Fig. 9), all of which have $\eta = 0$, it is probable that η is zero or very small in $LiNO_3\cdot 3H_2O$. Perhaps the three waters of hydration arrange themselves in threefold symmetry with respect to the lithium sites.

$LiIO_3$

The structure[16] of $LiIO_3$ displays threefold rotational symmetry about an axis through the lithium site. Hence $\eta = 0$ and the observed splitting (Fig. 9) yields the coupling constant directly [Eq. (1)].

Though the $LiIO_3$ and $LiNO_3$ structures are similar, the spin-lattice relaxation time is so much shorter in the former than in the latter that the Li^7 line can be observed without benefit of gamma irradiation. The signal-to-noise ratio is increased by a factor of 3 or 4, however, if the sample is irradiated. The response shown in Fig. 9 is from a specimen which received the same gamma dosage as the $LiNO_3$ sample of Fig. 7. It is clear that $LiIO_3$ again shows much smaller saturation effects.

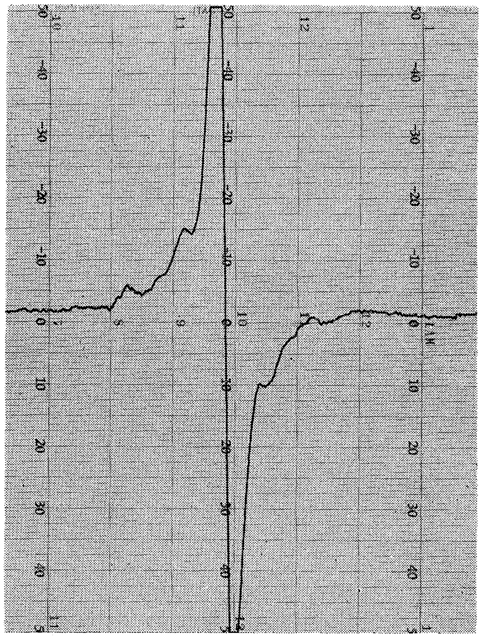

FIG. 10. The Li^7 resonance in Li_3PO_4 powder.

At least two explanations can be advanced for the shorter Li^7 spin-lattice relaxation time in the iodate. The magnetic moment of I^{127} is almost seven times as large as that of N^{14}. This should greatly increase the influence of spin-spin interactions[17] on T_1. It is also the case that the quadrupole moment and antishielding factor[1,8,9] of

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[16] W. H. Zachariasen and F. A. Barta, Phys. Rev. **37**, 1626 (1931).

[17] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

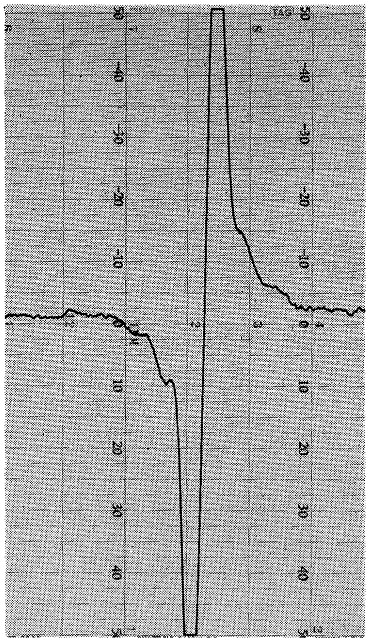

FIG. 11. The Li^7 resonance in Li_2TiO_3 powder. The sample was not γ irradiated.

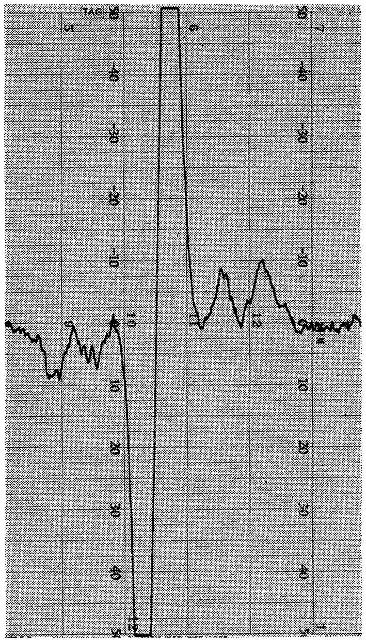

FIG. 12. The Li^7 resonance in Li_2ZrO_3 powder. The sample was not γ irradiated.

I^{127} are much larger than the corresponding values for N^{14}. The I^{127} spins are then coupled strongly to the lattice by quadrupolar interaction and can relax into the lattice energy transmitted from the Li^7 spins by spin-spin interaction.

Li_3PO_4

Two pairs of satellites are observed in the nuclear magnetic resonance of this compound (Fig. 10). Either there is one Li position with $\eta \neq 0$, or there are two inequivalent Li positions. The structure of the compound has not been determined. However, comparison of the intensity of the satellite responses with that of the central line indicates that this is a case of $\eta \neq 0$. The values of e^2qQ/h and η given in Table I are calculated on this basis.

Li_2TiO_3

Both ordered and disordered structures have been reported[18] for this compound. The presence of observable satellites indicates that the sample is predominantly of the ordered form. This is in agreement with a powder-pattern x-ray picture[19] which indicates an ordered structure with perhaps a small amount of the disordered material as well.

As in the case of Li_3PO_4, consideration of the intensity ratios (Fig. 11) leads to a tentative conclusion that the effects of $\eta \neq 0$ are being observed. The values of e^2qQ/h and η given in Table I are obtained with this assumption.

Li_2ZrO_3

The structure of lithium zirconate is apparently undetermined. It would appear from the intensity of the satellites (Fig. 12) that there are two inequivalent Li lattice sites with a quite small or vanishing asymmetry parameter. The x-ray powder pattern[19] confirms this evidence that the structures of Li_2ZO_3 and Li_2TiO_3 are different.

$Li_2C_2O_4$, Li_2SiO_3, $LiBH_4$

Finally, we list three compounds whose over-all crystal symmetry is lower than cubic and which would, therefore, be expected to exhibit satellites—but did not. In view of the success in finding satellites in spodumene, we might conclude that though the over-all symmetry of the lattice is lower than cubic, the local environment of the Li site is cubic and the field gradient is zero at the Li nucleus.

In the case of $LiBH_4$, the line is extremely broad and small splittings would not be observable. The line breadth presumably arises from the large magnetic moments of the hydrogen nuclei.

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[18] F. Barblan, Schweiz. mineral. petrog. Mitt. **23**, 295 (1943); Barblan, Brandenberger, and Niggli, Helv. Chim. Acta **27**, 88 (1944).

[19] We are indebted to Dr. Virginia Ross for this information.

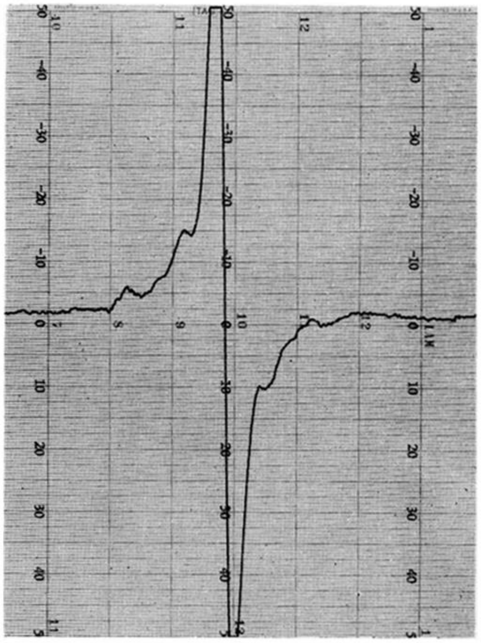


FIG. 10. The Li^7 resonance in Li_3PO_4 powder.

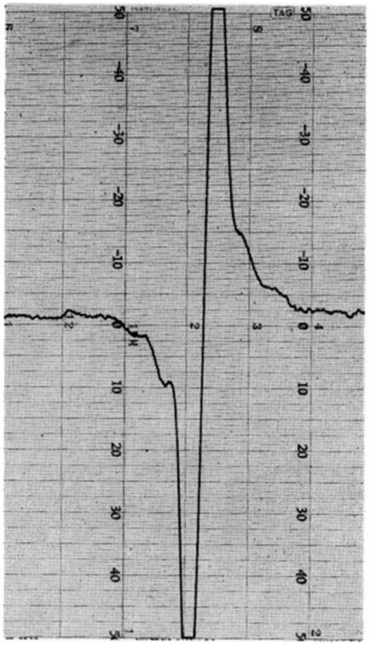


FIG. 11. The Li^7 resonance in Li_2TiO_3 powder. The sample was not γ irradiated.

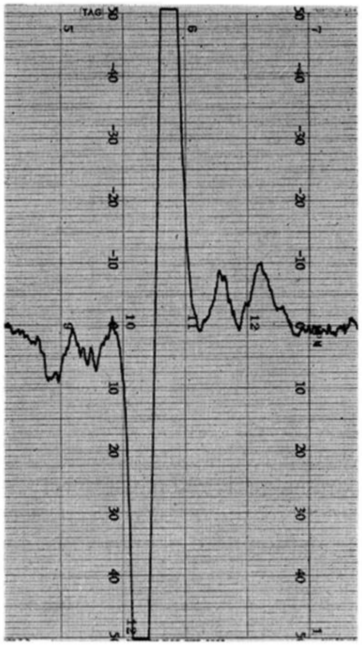


FIG. 12. The Li^7 resonance in Li_2ZrO_3 powder. The sample was not γ irradiated.

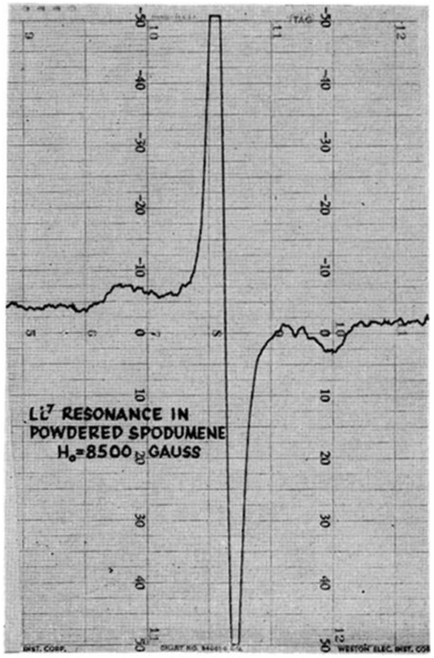


FIG. 3. The Li^7 resonance in powdered spodumene, LiAl(SiO$_3$)$_2$, in a magnetic field of 8500 gauss. The recorded signal in this and all subsequent figures is the derivative of the absorption line.

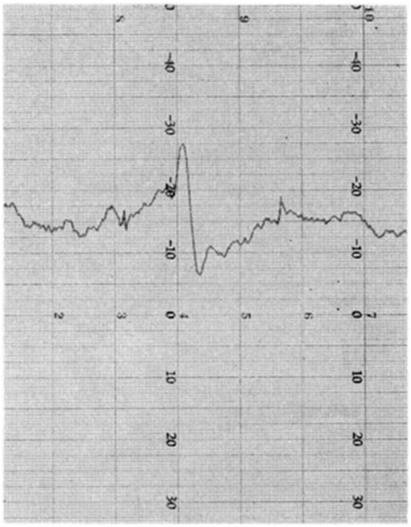


FIG. 4. The Li^7 resonance in LiOH powder in a magnetic field of 5250 gauss. The sample was not γ irradiated and the lowest available radio-frequency power was employed.

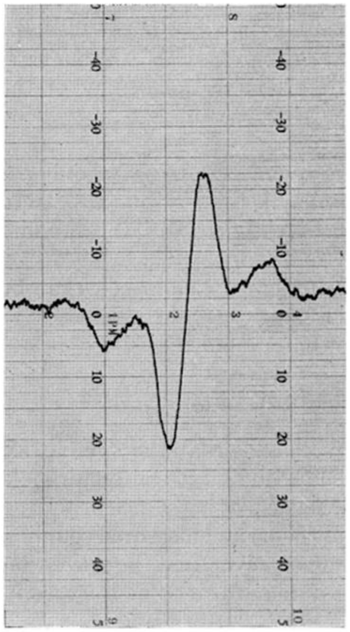
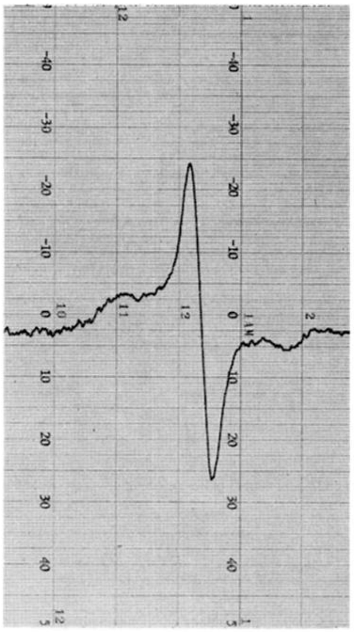


FIG. 5. The Li^7 resonance in LiOH powder in a magnetic field of 5250 gauss. This and all subsequent figures (except Figs. 11 and 12) are for samples which have received 60 megaroentgens of Co^{60} gamma irradiation.

FIG. 6. The Li^7 resonance in $LiOH \cdot H_2O$ powder.



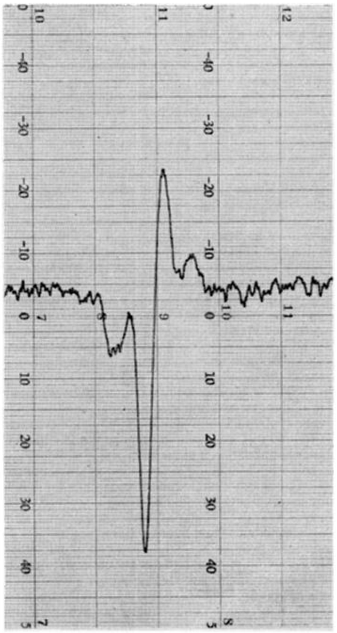


FIG. 7. The Li^7 resonance in $LiNO_3$ powder.

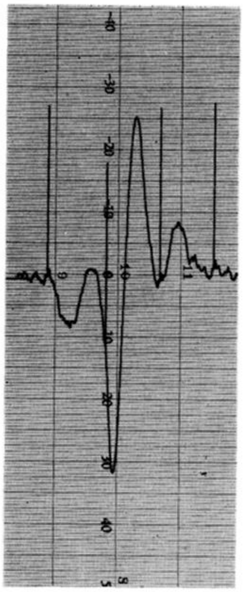


FIG. 8. The Li^7 resonance in $LiNO_3 \cdot 3H_2O$ powder.

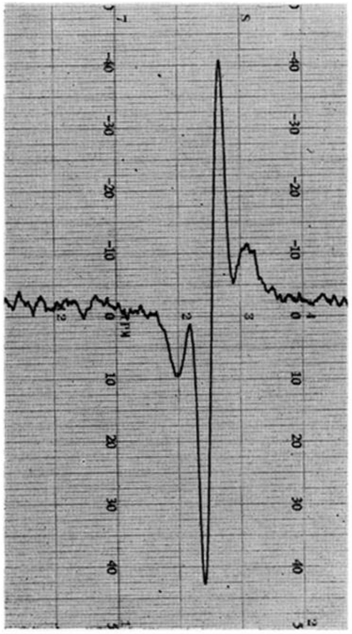


FIG. 9. The Li^7 resonance in $LiIO_3$ powder.