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# Nuclear Quadrupole Coupling Constant of $Be^9$ in BeO†

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From the splitting of the nuclear magnetic resonance line in polycrystalline BeO, the quadrupole coupling constant of $Be^9$ in BeO has been determined to be $41\pm4$ kc/sec with zero asymmetry parameter. The effects of anisotropic distribution of crystallites were observed and used in the analysis of the data.

## I. INTRODUCTION

THE splitting of nuclear magnetic dipole resonances by quadrupole interactions in solids was first investigated by Pound.[1] Since then, many solids have been studied in both single crystal and polycrystalline form. Results of these studies are reviewed by Cohen and Reif[2] and Das and Hahn.[3] Methods of determining quadrupole coupling constants $e^2qQ/h$ and asymmetry parameters $\eta$ from data obtained from single crystals are reviewed by Cohen and Reif.[2] The determination of $e^2qQ/h$ and $\eta$ from resonance patterns obtained from polycrystalline samples wherein there is an isotropic distribution of crystallite orientations with respect to the polarizing field is discussed by Cohen and Reif[2] and Hon and Bray.[4] Interpretation of resonance patterns obtained from samples in which the distribution of crystallite orientations is anisotropic with respect to the polarizing field has not previously been discussed.

There exist possibilities of ambiguities in the interpretation of resonance patterns obtained from polycrystalline samples having isotropic distributions of crystallite orientation. As an example, consider a case in which the crystal structure of the sample is not known and a complex resonance pattern is obtained. The complexities in the resonance pattern could arise because there are inequivalent sites, because the asymmetry parameter is nonzero, or a combination of both of these. For reasons such as these, data obtained from polycrystalline samples are not so definitive as data obtained from single-crystal samples.

This paper reports measurements made on the $Be^9$ resonance in polycrystalline beryllium oxide (BeO) in samples which displayed marked anisotropy in the distribution of crystallite orientation. The theoretical resonance pattern to be expected from the particular distribution displayed by the samples is derived. Comparison of the observed resonance patterns with the theoretical patterns reduces considerably the possibility of ambiguity and leads to values for the quadrupole coupling constant and the asymmetry parameter in which a fair degree of confidence is justified.

## II. THEORY

### A. Shape Functions for Resonance Patterns Obtained from Polycrystalline Samples

The theory of quadrupolar splitting of nuclear magnetic resonance lines is covered quite comprehensively in references 1, 2, and 3. Therefore, our attention will be confined to that part of the theory which is pertinent to the measurements reported here. $Be^9$ has a spin of $\frac{3}{2}$ and the quadrupolar coupling is small enough so that only first-order effects are important. Shape functions for the resonance absorption in polycrystalline samples are shown in Figs. 1 and 2 for the cases $\eta=0$ and $\eta\neq0$, respectively, when all crystallite orientations are equally probable (isotropic distribution of crystallite orientation). The resonance pattern is obtained by superimposing dipolar broadening on the shape function curves as displayed in Fig. 1, where the dotted lines represent the shape function for the $m=\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transition and the solid line, the resonance pattern. All subsequent figures display only the shape function curves for the $m=\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transition. The manner in which these shape functions are derived can be found in reference 2. In the case to be considered below, however, the distribution of crystallites (and therefore, electric field gradients) was anisotropic in a rather

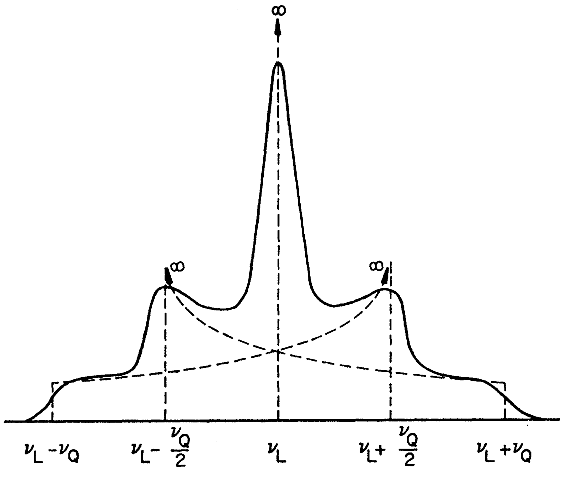

FIG. 1. First-order nuclear magnetic resonance powder pattern for $I=\frac{3}{2}$ and $\eta=0$ with $\nu_Q=e^2qQ/2h$. The dotted line represents the shape function, and the solid line gives the absorption pattern including dipolar broadening.

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

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

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

[3] T. P. Das and E. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Suppl. No. 1.

[4] J. F. Hon and P. J. Bray, Phys. Rev. **110**, 624 (1959).

special way. The shape functions corresponding to this particular distribution are derived below.

The distribution of crystallite orientation in the samples studied was such that the $c$ axes of the crystallites were preferentially confined to a plane. From the crystal symmetry of BeO, which, according to x-ray data,[5] has the wurtzite structure, we expect the electric field gradient tensor to be diagonal in a coordinate system which has one axis ($z'$ axis) normal to the hexagonal planes (parallel to the $c$ axis) and the other two axes in the hexagonal plane (perpendicular to the $c$ axis). With the polarizing field in the $z$ direction, we consider the case when the $z'$ axis of the principal axes coordinate system of the electric field gradient ($c$ axis in the crystallites) is confined to a plane. The particular geometry used in the experimental procedures is shown in Fig. 3. The sample is rotated in the polarizing field about the $x$ axis which lies in the plane containing the $z'$ axis. This plane is depicted in Fig. 3 by the solid and dotted ellipse. The solid portion represents that part of the plane above the $x$-$y$ plane (towards the reader) and the dotted portion represents that part of the plane below the $x$-$y$ plane. Rotating the sample about the $x$ axis places the $z''$ axis, which is the normal to the plane containing the $z'$ axis, at an angle $\psi$ with respect to the polarizing field. The angle $\phi$ is the angle between the $x$ axis and the $z'$ axis for a particular crystallite. These two angles, $\phi$ and $\psi$, determine two of the Eulerian angles,[6] $\alpha$ and $\beta$, which specify the transformation from the space coordinate system to the principal axis coordinate system of the electric field gradient. The $x''$ axis is the line of nodes for the Eulerian transformation from the space coordinate system to the principal axis system of electric field gradient.

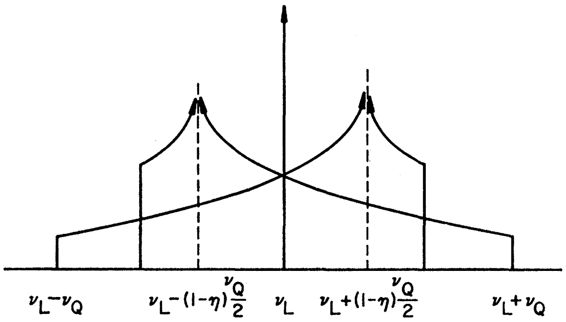

FIG. 2. Shape function of first-order powder pattern for $I=\frac{3}{2}$ and $\eta\neq 0\,(\eta\cong\frac{1}{3})$.

Using the notation of reference 2, the first-order quadrupolar splitting of the nuclear magnetic resonance is given by

$$\nu_m=\tfrac{1}{2}(m-\tfrac{1}{2})\nu_Q\{3\cos^2\beta-1-\eta\sin^2\beta\cos 2\alpha\},\qquad(1)$$

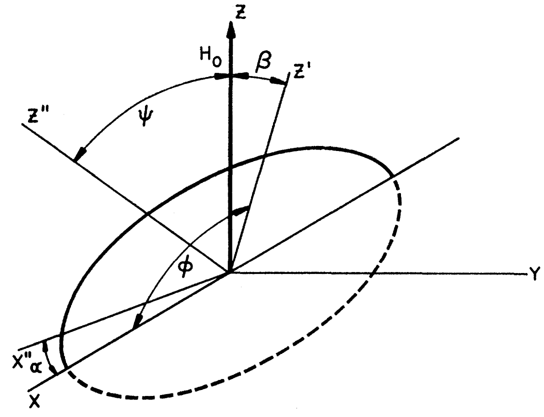

FIG. 3. Geometry for sample cut so that the axis of rotation ($x$) is in the plane containing the $c$ axes of the crystallites. The angle $\alpha$ is determined by the requirements that the $x''$ axis lie in the $x$-$y$ plane and be normal to the $z$-$z'$ plane.

where

$$\nu_Q=3e^2qQ/2I(2I-1)h.\qquad(2)$$

From Fig. 3, relationships for $\alpha$ and $\beta$ in terms of the angles $\phi$ and $\psi$ are found to be

$$\cos\beta=\sin\phi\,\sin\psi,\qquad(3)$$

and

$$\cos\alpha\,\sin\beta=\sin\phi\,\cos\psi.\qquad(4)$$

Substitution of Eqs. (3) and (4) into Eq. (1) gives the quadrupolar splitting as a function of the angles $\phi$ and $\psi$:

$$\nu_m=\tfrac{1}{2}(m-\tfrac{1}{2})\nu_Q\{3\sin^2\phi\,\sin^2\psi-1-\eta\times[\sin^2\phi(1+\cos^2\psi)-1]\}.\qquad(5)$$

Letting $\omega$ be defined by

$$\omega\equiv 2\nu_m/\nu_Q|m-\tfrac{1}{2}|,\qquad(6)$$

we can calculate the probability, $P(\omega)$, of splitting after the fashion shown in Reference 2. $P(\omega)$ is related to $P(\phi)$, the probability of occurrence of an angle $\phi$, by

$$P(\omega)=P(\phi)|d\phi/d\omega|.\qquad(7)$$

Assuming all angles $\phi$ are equally probable,

$$P(\phi)=1/2\pi.\qquad(8)$$

(Examination of the samples under a polariscope revealed that the $c$ axes of the crystallites were oriented at random in the plane containing them.) From Eq. (5),

$$d\phi/d\omega=\{2\sin\phi\,\cos\phi[3\sin^2\psi-\eta(1+\cos^2\psi)]\}^{-1},\qquad(9)$$

and

$$P(\omega)=|\{4\pi\sin\phi\,\cos\phi\times[3\sin^2\psi-\eta(1+\cos^2\psi)]\}^{-1}|.\qquad(10)$$

Using Eq. (5), Eq. (10) could be written in terms of $\omega$ giving the shape function for any angle $\psi$. However, for our purposes it will be sufficient to consider two

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[5] G. A. Jeffrey, G. S. Parry, and R. L. Mozzi, J. Chem. Phys. **25**, 1024 (1956).

[6] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1951), p. 107.

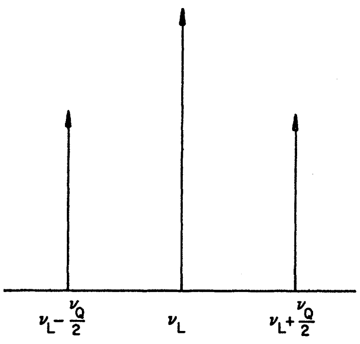

FIG. 4. Shape function of first-order powder pattern for $I=\frac{3}{2}$ and $\eta=0$ when polarizing field is normal to the plane containing the $c$ axes of the crystallites.

special cases: $\psi=0$ and $\psi=\pi/2$. When $\psi=0$, the polarizing field is normal to the plane containing the $c$ axes. For $\eta=0$ all splittings are the same so that if $\nu_L$ is the unsplit resonance (Larmor) frequency, $P(\omega)$ is infinite at the frequency $\nu_L\pm\nu_Q/2$ and zero elsewhere. This shape function is shown in Fig. 4. For $\eta$ not zero, $P(\omega)$ is given by

$$P(\omega)=|\{-8\pi\eta\sin\phi\cos\phi\}|^{-1}, \tag{11}$$

and $\omega$, by

$$\omega=-[1+\eta(2\sin^2\phi-1)]. \tag{12}$$

These two equations define the shape function which is shown in Fig. 5. When $\psi=\pi/2$, the polarizing field is in the plane containing the $c$ axes. For $\eta=0$, $P(\omega)$ is given by

$$P(\omega)=|\{12\pi\sin\phi\cos\phi\}|^{-1}, \tag{13}$$

and $\omega$, by

$$\omega=3\sin^2\phi-1. \tag{14}$$

These equations define the shape function drawn in Fig. 6. For $\eta$ not zero, $P(\omega)$ is given by

$$P(\omega)=|\{4\pi\sin\phi\cos\phi(3-\eta)\}|^{-1}, \tag{15}$$

and $\omega$, by

$$\omega=(3-\eta)\sin^2\phi-1+\eta. \tag{16}$$

The shape function for this case is shown in Fig. 7. The experimental results will be compared with these special cases.

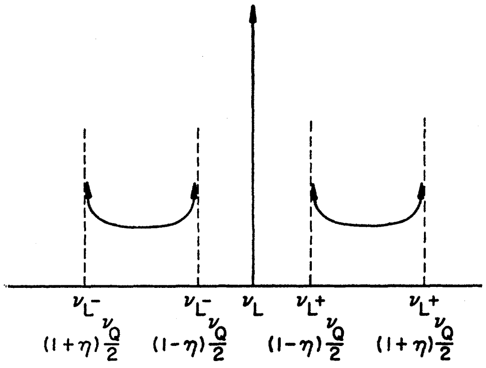

FIG. 5. Shape function of first-order powder pattern for $I=\frac{3}{2}$ and $\eta\neq0(\eta\cong\frac{1}{2})$ when polarizing field is normal to the plane containing the $c$ axes of the crystallites.

## B. Ionic Electric Field Gradient

The electric field gradient that would exist if the bonding were purely ionic can be calculated by summing over the lattice the field gradient from point charges.[7] This has been done by considering the lattice to be composed of four interpenetrating simple hexagonal lattices, two of which are composed of oxygen ions while the other two are composed of beryllium ions. The electric field gradient at the nucleus is different from the electric field gradient outside the ion core by a multiplicative factor, $1-\gamma_\infty$, which takes into account the antishielding properties of the ion core. This factor has been calculated for Be$^{++}$ by Das and Bersohn[8] for a free ion, with the result that $1-\gamma_\infty$ is 0.815. Structure parameters used in the computation are those given by Jeffrey *et al.*[5] The computed value of electric field gradient, $q$, for doubly charged ions including the factor $1-\gamma_\infty$ is $0.0023\times10^{24}$ v/cm$^2$. This computed value of $q$ involves the difference of nearly equal quantities so that small errors in lattice parameters would be reflected by appreciable differences in the computed value of $q$.

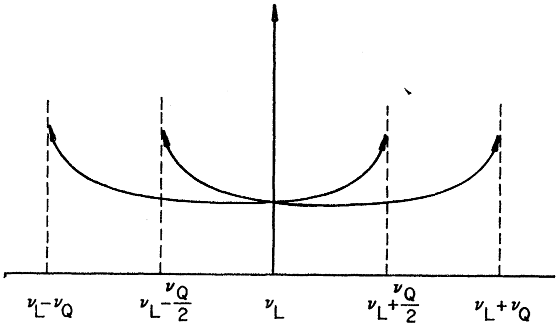

FIG. 6. Shape function of first-order powder pattern for $I=\frac{3}{2}$ and $\eta=0$ when polarizing field is in the plane containing the $c$ axes of the crystallites.

## III. EXPERIMENTAL PROCEDURES

### A. Apparatus

The resonance patterns were observed using a Pound-Watkins type spectrometer which records the first derivative of the absorption signal. The polarizing field was produced by a Varian 12-in. electromagnet system. Satellite frequency separations were determined by superimposing 10-kc/sec markers from a General Radio unit crystal oscillator (type 1213-C) on the recording trace. A simple goniometer to which the sample was glued allowed rotation of the sample in the rf coil about an axis normal to the polarizing field.

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

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

### B. Samples[9]

Samples were prepared by pressing powdered BeO in a hot die having the shape of a right-circular cylinder. A density of better than 99% of theoretical was obtained. This preparation procedure yielded polycrystalline samples with crystallization taking place preferentially in the *c* direction. Furthermore, most of the crystallites were aligned with the long dimension (*c* axis) perpendicular to the axis of the cylinder. This gives rise to samples having a distribution of crystallite orientations which is to a good approximation that described in the theory section. Samples were cut from the hot-pressed blank in such a way that the plane containing the *c* axes could be rotated with respect to the polarizing field in two ways. One sample was cut so that the axis of rotation was normal to the plane containing the *c* axes, and a second sample was cut so that the axis of rotation was in the plane containing the *c* axes.

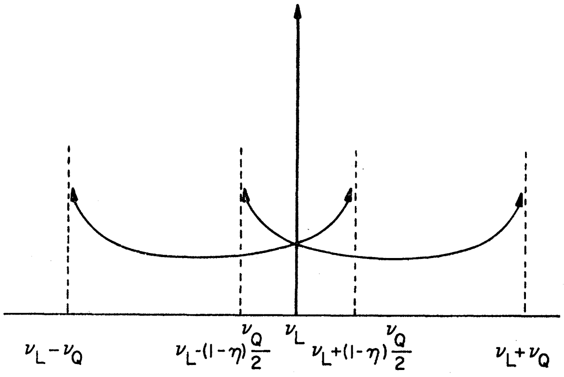

FIG. 7. Shape function of first-order powder pattern for $I=\frac{3}{2}$ and $\eta\neq0$ ($\eta\cong\frac{1}{2}$) when polarizing field is in the plane containing the *c* axes of the crystallites.

The spin-lattice relaxation time of the Be$^9$ resonance in these samples was found to be quite long (estimated to be several minutes) and the resonance saturated even at the lowest rf levels obtainable to the extent that only half of the line could be observed. However, $\gamma$ irradiation (see reference 4) to a dose of about $10^7$ roentgens by means of a cobalt-60 source reduced saturation effects sufficiently to allow the resonance to be easily observed.

## IV. RESULTS AND DISCUSSION

Resonance patterns obtained with the sample cut so that the axis of rotation was in the plane containing the *c* axes (this is the geometry corresponding to Fig. 3) are shown in Figs. 8 and 9 for the two cases $\psi=0$ and $\psi=\pi/2$, respectively. Resonance patterns obtained with the sample cut so that the axis of roation was perpendicular to the plane containing the *c* axes were of the type shown in Fig. 9 for all angles of rotation.

FIG. 8. Recording of the derivative of the Be$^9$ nuclear magnetic resonance absorption when the polarizing field is normal to the plane containing the *c* axes of the crystallites.

The shape function for the resonance pattern displayed in Fig. 8 ($\psi=0$) should be that shown either in Fig. 4 or Fig. 5, depending on whether $\eta=0$ or $\eta\neq0$. Comparison of the resonance pattern with these two shape functions indicates that two possibilities exist. Either $\eta=0$ or $\eta=1$, which would result in single satel-

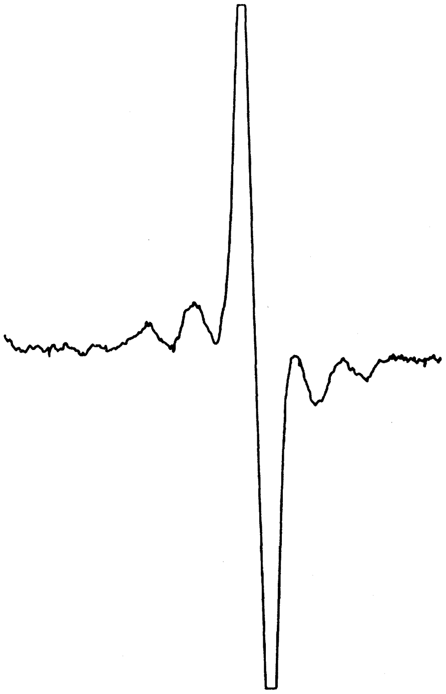

FIG. 9. Recording of the derivative of the Be$^9$ nuclear magnetic resonance absorption when the polarizing field is in the plane containing the *c* axes of the crystallites.

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[9] These samples were supplied by J. D. McClelland and P. D. Johnson of this Laboratory.

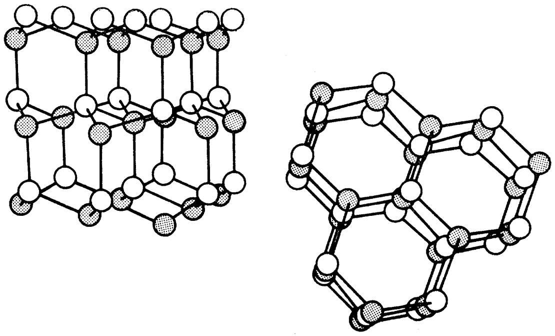

FIG. 10. Two views of the structure of BeO (wurtzite structure).

lite responses at $\nu_L \pm \nu_Q/2$ or $\nu_L \pm \nu_Q$, respectively, with the satellites having a "width" close to the width of the central line. If $\eta$ were nonzero but had some intermediate value there would be a broad response centered at about $\nu_L \pm \nu_Q/2$. Since this is not observed, $\eta$ must be either zero or one. The shape function of the resonance pattern displayed in Fig. 9 ($\psi = \pi/2$) should be that shown either in Fig. 6 or Fig. 7. If $\eta = 1$ were the case there would be satellites only at $\nu_L \pm \nu_Q$ since the responses at $\nu_L \pm (1-\eta)\nu_Q/2$ would be hidden in the central line. Therefore, $\eta$ is not one and must be zero or quite small. If $\eta$ were not zero but small the frequency splitting, as measured at the peak response, of the satellite at $\nu_L \pm (1-\eta)\nu_Q/2$ would be less than half of the frequency splitting of the satellite at $\nu_L \pm \nu_Q$. It is observed experimentally that the splitting at $\nu_L \pm (1-\eta)\nu_Q/2$ is somewhat more than the splitting at $\nu_L \pm \nu_Q$. This is probably due to the fact that the maximum derivative will not occur at exactly the frequency splitting given by the shape function, owing to dipolar broadening effects. This observation and the fact that the width of the satellite response in Fig. 8 is nearly that of the central line both indicate that $\eta$ is zero. Assuming $\eta$ to be zero the quadrupole coupling constant is obtained by averaging the measured frequency splitting of the single satellite response in Fig. 8 and the pair of satellite responses in Fig. 9. This average gives a value for $e^2qQ/h$ of $41 \pm 4$ kc/sec. The error of 4 kc/sec is an estimate of errors due to shifting of the maximum derivative from the shape function positions by dipolar broadening effects.

According to x-ray measurements[5] BeO has the wurtzite structure as shown in Fig. 10. The view on the right, which is almost in the direction of the $c$ axis, shows threefold symmetry about the $c$ axis. From this consideration $\eta$ is expected to be zero,[1] in agreement with the interpretation above.

Assuming the bonds between beryllium and oxygen atoms to be purely ionic, the quadrupole coupling constant can be calculated using the computed value of $q$ and a value[10] of $0.03 \times 10^{-24}$ cm$^2$ for the quadrupole moment, $Q$, of Be$^9$ determined from hyperfine structure measurements. This gives a coupling constant of 4 kc/sec which differs considerably from the value $41 \pm 4$ kc/sec deduced experimentally in this study. However, as pointed out previously, the calculated value of $q$ involves the differences of nearly equal quantities so that small changes in lattice parameters could make appreciable differences in the value obtained. Also, the value of the quadrupole moment determined from the hyperfine structure measurement is somewhat uncertain. Because of this, a comparison of the calculated coupling constant with the experimentally determined coupling constant should be interpreted cautiously and might be taken to indicate only that the bonding is probably more covalent than ionic.

## ACKNOWLEDGMENTS

The author wishes to thank J. D. Strong for the $\gamma$ irradiations and R. H. Shudde for his help in programming the ionic field gradient problem.

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[10] A. Lurio and A. G. Blackman, Bull. Am. Phys. Soc. **5**, 344 (1960).