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PHYSICAL REVIEW B

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Soft-Sphere Model for Nuclear Quadrupole Resonance: Rare-Earth Trichlorides under Hydrostatic Pressure*

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Nuclear quadrupole resonance of Cl³⁵ in five hexagonal rare-earth trichlorides under hydrostatic pressure up to 5×10^3 kg/cm² showed a decrease in frequency ν with increase in pressure. The normalized pressure coefficients $\nu_0^{-1} (\partial \nu / \partial P)_T$ varied smoothly between the extremes $(-5.586 \pm 0.020) \times (10^{-6} \text{ cm}^2/\text{kg})$ and $(-3.855 \pm 0.016) \times (10^{-6} \text{ cm}^2/\text{kg})$ for CeCl₃ and GdCl₃, respectively. The negative sign suggested a model with a significant overlap contribution to the electric field gradient and a soft-sphere model was developed in analogy to the Born-Mayer model of inter-ionic repulsive forces. This model proved adequate to explain the systematic variations in ν_Q with compound and was consistent with the pressure dependence of ν . The use of pressure data as a critical test for the model must await reliable compressibility data for the compounds. Pressure data for monoclinic ErCl₃ and YbCl₃ are also presented.

I. INTRODUCTION

Nuclear quadrupole resonance (NQR) measures the electric field gradient (EFG) at a nucleus whose quadrupole moment is known (and nonzero).¹⁻³ The EFG is a traceless second-rank tensor characterized by a magnitude q with sign, by an asymmetry parameter $0 \le \eta \le 1$ that describes departure from cylindrical symmetry, and by the orientation of its principal axes in space. The EFG components can be expressed in spherical-tensor notation as

$$q_{m} = \frac{1}{e} \int \frac{\rho_{c}(r) Y_{2}^{m}(\theta, \phi)}{r^{3}} d^{3}r , \qquad (1)$$

where ρ_c is the charge density in the neighborhood of the nucleus, e is the charge of an electron, and Y_2^m is a spherical harmonic. From Eq. (1), two

features clearly emerge: (a) Only those components of ρ_c having the symmetry of $Y_2^m(\theta, \phi)$ can contribute to the EFG. This requirement explicitly eliminates any contribution from the spherically symmetric part of ρ_c . (b) The weighting function r^{-3} significantly decreases the importance of distant charge density. The practical consequence of these features is a domination of the EFG at the nucleus of a given ion by the outer, distorted electron cloud of that same ion.

Models for the mechanisms whereby distortions are introduced into the spherical ions have been proposed, but have not led to very satisfactory descriptions of the experimental results. The basic $model^{1}$ is the point-ion model in which the *i*th ion is replaced by an appropriate point charge $z_i e$, where z_i is the valence of ion *i*. Each ion gives a cylindrically symmetric contribution to the EFG at the ion of interest. The contribution is directed along the ion-ion axis, and has a magnitude $q_i = 2z_i/r_i^3$ where r_i is the distance of the *i*th ion. This applied EFG distorts the charge distribution of the ion of interest and Sternheimer⁴ has shown that the resulting nonspherical charge distribution adds a contribution $-\gamma_{\infty}(2z_i/r_i^3)$, so that the total EFG contribution from the *i*th ion is $q_i = (1 - \gamma_{\infty})(2z_i/r_i^3)$. The contribution from each ion in the crystal is then rotated into a common coordinate system and summed to yield the total EFG. The early review article by Cohen and Reif¹ describes four major modifications to the above model: (i) The ions should have higher electric multipole moments as a consequence of being polarized by their environment; (ii) ion-ion overlap should modify the EFG; (iii) the Sternheimer parameter γ_{∞} should vary as the local environment of the ion is changed; and (iv) charge transfer from an ion leaves holes in the previously spherically symmetric closed shells, and thus yields a covalent-type contribution to the EFG.

Various of these modifications have been utilized in subsequent work. The large polarizabilities (which also should vary greatly with environment) of the anions have seriously impaired the dependability of models based upon calculated higher electric moments.⁵ Overlap integrals have been evaluated in KCl by Das and Karplus⁶ and have been shown to give rise to a dominant. but difficult to evaluate, contribution to the EFG at Cl⁻. More recently, overlap contributions have been calculated for metal ions in several oxides.⁷⁻⁹ These direct calculations of overlap contributions require an independent determination of some kind of shielding constant akin to the Sternheimer γ_{∞} . For highly distortable anions, this introduces a large uncertainty. Burns and Wikner¹⁰ evaluated the Sternheimer γ_{∞} in Cl⁻ using wave functions that were appropriate to a crystalline environment and obtained $\gamma_{\infty} = -30$ in contrast to the value -56.6 calculated by Sternheimer for a free Cl⁻ ion. Finally, Bersohn and Shulman¹¹ evaluated the EFG at anions in transition-metal salts as being due to charge-transfer covalency. Such charge-transfer effects, important in many "ionic salts," will be ignored in this work. They will need to be added if the soft-sphere model is extended to more general cases.

In this paper we test and extend an alternative approach, the soft-sphere model, which includes the three above-mentioned effects. Rather than trying to evaluate the various effects explicitly, this model parameterizes the ion-ion interactions in a form suggested by Hartree-Fock (HF) calculations for closed shells diatomic molecules. This procedure is not only similar to Gilbert's¹² approach in evaluating the repulsive forces in the Born-Mayer model for alkali halides, it also utilizes empirical relationships obtained by Gilbert. The name, softsphere model, follows Gilbert's usage. For the present, we limit our considerations to ionic solids which at first approximation are considered to consist of spherical ions. The test employed is the ability of the model to predict the EFG behavior as observed by NQR. As the above discussion indicates, EFG behavior is a sensitive indicator of departures from sphericity which occur in real crystals. This sensitivity is not without disadvantages and, for the purposes of the present paper, the dependence of the EFG upon local environment dictates two limitations.

First, the ions in ionic solids must be further classified. The anions such as O^{-2} and the halides are very deformable because the outer electrons are so loosely bound (in fact, O^{-2} does not exist in the free state); are tractable in terms of local environment parameters; and thus are excellent candidates for consideration. Polyatomic radicals such as SO_4^{-2} and NO_3^{-} require extensive local environment parameters and thus are excluded from consideration. As a matter of convenience we consider only closed-shell ions at this time, which excludes the transition-metal ions, but not the anions in transition-metal salts.

Second, a plethora of potential EFG behavior exists and the enumeration and subsequent classification of these possibilities is not our intent. Therefore, we choose to present the model as it developed in relation to explicit experimental systems. This choice provides a natural limitation of material and permits the presentation of concise motivations for a number of procedures which were invoked. This manner of presentation does not imply any limit of the model's applicability.

The ideal experimental system would be totally ionic, would have been extensively studied so that detailed knowledge of all relevant parameters is available, and would display an obvious departure from the behavior expected of a system obeying the point-charge model with an antishielding factor. The hexagonal rare-earth trichlorides satisfy several of these requirements. The compounds appear to be highly ionic, and whatever chemical properties of the rare-earth ions enter the problem are expected to be only slowly varying. Moreover, elements from the first half of the rare-earth sequence form a series of isomorphic compounds whose geometries (i.e., ion-ion distances and angles) vary slowly as a function of cation species and thus there is the possibility of studying systematic trends. During some preliminary studies on GdCl₃ we discovered the NQR frequency for Cl³⁵ decreased as a function of applied pressure. This behavior is clearly at variance with expected behavior-the point-charge antishielding model predicting the fre-

739

TABLE I.	Crystal structure data for hexagonal rare-				
earth trichlorides.					

Compound	A (Å)	C (Å)	u	v	V/cell (Å ³)
LaCl ₃ ^a	7.4779	4.3745	0.38741	0.30155	211.84 ^b
CeCl ₃ °	7.452	4.328	0.38753	0.30160	208.14
PrCl ₃ °	7.425	4.283	0.38765	0.30164	204,49
NdCl ₃ ^a	7.3988	4.2423	0.38777	0.30167	201.12
SmCl ₃ ^c	7.384	4.164	0.38852	0,30172	196.62
EuCl ₃ ^a	7.3746	4.1323	0.38911	0.30174	194.63
GdCl ₃ ^a	7.3663	4.1059	0.38929	0.30153	192.95

^aData from Morosin (1968).

^bMorosin's value is incorrect.

^cEstimated from Morosin's data.

quency scales as r^{-3} . We have completed measurements of the Cl³⁵ NQR frequency as a function of pressure for five hexagonal compounds involving elements from the first half of the rare-earth series and these data are combined with existing NQR data¹³ to provide an experimental test of our model.

Unfortunately, the final predictions of the softsphere model for the pressure dependence of NQR behavior scale with compressibility. The general lack of compressibility data unites with inconsistencies associated with existing elastic constants for



FIG. 1. Crystal structure of GdCl₃. All ions lie on mirror planes and two mirror planes are depicted in this figure. The Cl⁻ ion of interest is "0" on the lower plane. This ion has three nearest-neighbor Gd^{3*} ions: One in the same plane at *a* and one each at *b* in planes above and below the plane containing "0". A pair of near-neighbor Cl⁻ ions are in the same plane at *c* and three more pairs are in neighboring planes at *d*, *d*, and *e*. The ion coordinates are listed in Table II.

 $LaCl_3$ to postpone use of the high-pressure data as a critical test of the model. However, the softsphere model seems to make genuine progress in understanding the NQR properties at 1-atm pressure and we present it now for that reason.

II. CRYSTAL STRUCTURE

The crystal structure of the series LaCl₃ through GdCl₃, as well as for UCl₃, is hexagonal, $P6_3/m$, and has been analyzed by Morosin¹⁴ for the trichlorides of La, Nd, Eu, and Gd. Table I gives his results, together with our interpolated values (following his prescription) for the rest of the compounds of interest here. Table II and Fig. 1 show the structure of GdCl₃. All ions lie on mirror planes perpendicular to the c axis. This requires that one of the principal axes of the EFG at each Cl⁻ ion be along the c axis. This is always found to be the x principal axis. All three CI⁻ ions are chemically equivalent, that is, the principal values of the EFG are the same at each ion (and therefore all Cl³⁵ nuclei have the same pure quadrupole frequency) but the Cl⁻ ions are magnetically inequivalent, there being three sites whose z principal axes differ in direction by 120° . The positive and negative ends of the principal axes are equivalent, so there is a z axis every 60° . In addition, the crystals lack a twofold axis in the mirror plane, so the directions along the c axis are inequivalent, but this cannot be discerned experimentally except with x-ray intensity measurements. This introduces a twofold uncertainty in the orientation of the crystals and makes the correct assignment of an observed zprincipal axis to a given ion unfeasible. For these reasons, we have not concerned ourselves with the orientation of the EFG beyond the requirement that its x axis is along the crystal c axis.

III. EXPERIMENTAL TECHNIQUES

With one exception the single crystals were prepared by vacuum distilling Lindsay rare-earth trichloride powder into a Vycor growing tube which was detached under vacuum and lowered through a gradient furnace. The exception, SmCl₃, was not

TABLE II. Ion coordinates for $GdCl_3$. Listed above are the coordinates for various ions relative to a given Cl^- ion. The ions are labeled in Fig. 1 and all distances are in Å.

Species	Label	R	x	Y	Z
Gd ³⁺	a	2.9177	-2.6863	1.1388	0,0000
Gd ³⁺	b	2.8223	1.5666	1,1388	± 2.0529
C1-	c	3.3546	3,3361	0.3514	0.0000
C1-	с	3.3546	1.3637	3.0649	0.0000
C1-	d	3.3169	-2.4834	-0.7873	±2.0529
C1-	d	3.3169	1.9236	-1.7570	± 2.0529
Cl	е	3.2643	-1.1197	2.2775	±2.0529

TABLE III. Nuclear quadrupole frequency and pressure data for hexagonal rare-earth trichlorides. ν_Q is the frequency at one atmosphere of pressure and the room temperature represents an ambient laboratory temperature which was never measured. Uncertainties in ν_Q are standard deviations from at least five observations and uncertainties in the derivatives result from a least-squares fit to the pressure dependence. ν_0 is the frequency at zero pressure which is obtained by extrapolating the pressure-dependent data.

		0 K	77	K (au)	Room temperature	
Compound	4.	ν _Q (kHz)	ν _Q (kHz)	$\frac{\nu_0^{-1} \left(\frac{\partial \nu}{\partial P}\right)_T}{(10^{-6} \text{ cm}^2/\text{kg})}$	ν _Q (kHz)	$\frac{\nu_0^{-1} \left(\frac{\partial \nu}{\partial P} \right)_T}{(10^{-6} \text{ cm}^2/\text{kg})}$
LaCl ₃	0.50 ± 0.02^{a}	4167 ± 1^{a}				
CeCl ₃		$4387 \pm 1^{\texttt{b}}$	4377.2 ± 0.3	-5.586 ± 0.020	4341.0 ± 1.0	
PrCl ₃	0.4937°	4566.7 ± 0.1^{d}	4561.9 ± 0.8	-5.136 ± 0.023		
NdCl ₃		4729.0 ± 0.3^{b}	4722.3 ± 0.3	-4.794 ± 0.018	4676.4 ± 0.3	-4.85 ± 0.03
$SmCl_3$		5033.0 ± 0.5^{b}	5026.8 ± 0.5	-4.252 ± 0.031	$\textbf{4975.6} \pm \textbf{0.4}$	-4.24 ± 0.06
GdCl ₃	0.4265 ^c	5315 ± 1^{e}	5307.6 ± 0.3	-3.855 ± 0.016	5248.4 ± 0.3	-3.73 ± 0.03

^aE. H. Carlson and H. S. Adams, J. Chem. Phys. <u>51</u>, 388 (1969).

^bB. W. Mangum and D. B. Utton, Bull. Am. Phys. Soc. <u>12</u>, 1043 (1967).

^cJ. P. Hessler, thesis (Michigan State University, 1971)

distilled but melted in a HCl stream. The hydroscopic crystals were stored under mineral oil. Samples were diamond sawed and cleaved to hexagonal prisms about 1 cm long and 2 mm in diameter having their axis along the c axis, and were then coated with GE7031 cement.

Coherent free-induction decay signals were put through an rf phase-sensitive detector¹⁵ and displayed on an oscilloscope. The frequency was measured with a HP5245L frequency counter.

The BeCu pressure cell¹⁶ was made in two pieces with the pressure seal employing three stainlesssteel rings coated with indium. The upper half of the cell was connected to $\frac{5}{16}$ -in.-o.d. by $\frac{1}{16}$ -in.-o.d. stainless-steel high-pressure tubing by a standard cone seal. The spectrometer lead was extracted from the pressure cell through the high-pressure tube, which itself served as the ground return. The lead emerged from the room-temperature highpressure region through a U-shaped tube, approximately 50 cm long filled with Dow Corning 704 oil frozen in liquid nitrogen.

The pressure medium was helium gas driven through a 10:1 intensifier from an oil-driven piston. Pressure was measured with a Bourdon gauge, stated by the manufacturers to have $\pm 2\%$ accuracy. The gauge calibration was checked against manganin resistance data.

Data was taken by first cycling the sample to 5×10^3 kg/cm² at room temperature, and the room-temperature frequencies as a function of pressure were recorded if signals could be seen. The pressure was reduced to about 1×10^3 kg/cm², and the cell was immersed in liquid nitrogen. Thirty minutes were allowed for initial establishment of thermal equilibrium between the temperature bath and

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^dW. E. Hughes, C. G. Montgomery, W. G. Moulton, and E. H. Carlson, J. Chem. Phys. <u>41</u>, 3470 (1964).

^eE. H. Carlson, Bull. Am. Phys. Soc. <u>11</u>, 377 (1966).

the sample. Subsequently, a 10-min period between pressure change and frequency measurements was employed. It should be noted that the frequency changes usually tracked the pressure changes and the waiting period was not essential. In all cases except YbCl₃, the pressure was cycled at least once to check for hysteresis. None was ever observed.

IV. EXPERIMENTAL RESULTS

The data for the Cl³⁵ frequencies in the hexagonal trichlorides were fit by least squares to the equation $\nu(P) = \nu_0 + mP$, where *m* is $(\partial \nu / \partial P)_T$. No departure from linearity could be seen for $\nu(P)$ and *m* was negative. The results at 77 K and room temperature are tabulated with earlier 4.2-K data in Table III. The values for LaCl₃ are from Carlson and Adams, ¹³ and for η from Hessler.¹⁷ ν_Q is the frequency at 1 atm. The uncertainty in the ν_Q frequencies is the standard deviation of at least five measurements. The uncertainties in ν_0 and *m* are obtained from the least-squares fit. There appears to be a small zero error in the pressure gauge. The normalized pressure coefficient $\nu_0^{-1}(\partial \nu / \partial P)_T$ at 77 K is plotted vs compound in Fig. 2.

V. THEORY

A. Pure Quadrupole Frequency

The soft-sphere model begins with the usual assumption that the EFG at a nucleus can be written as a sum of ion-pair interactions. Each ion-pair gives a cylindrically symmetric contribution to the EFG along the ion-ion radius vector. In summing the total EFG, the contribution from each ion-pair must be rotated into a common coordinate system.

The soft-sphere model relies on a parametrized



FIG. 2. Normalized pressure coefficients of nuclear quadrupole frequency vs atomic number.

form of the ion-pair interaction. The interaction depends on the internuclear separation R as well as the ion species, and is taken to be the sum of two terms:

$$q = q_{\rm pc} + q_{\rm ov} \,. \tag{2}$$

The first term is referred to as the "point-charge" contribution and varies as r^{-3} . The second term is referred to as the "overlap" contribution and has an exponential dependence on r. The justification for this form of the interaction is given in Sec. V A 1.

The q_{pc} term depends only on the properties of the ion at the origin and contains a single parameter. The q_{ov} term depends on the properties of both ions and contains at least two parameters. The form that this parametrization takes and the values chosen for the parameters are discussed in Sec. VA 2.

1. Two-Ion Interaction

For instruction in the form of the two-ion interaction we utilized a number of HF calculations in alkali halide molecules by Matcha.¹⁸ The EFG's in all of these molecules have the same general form as a function of internuclear separation. At large separation the EFG at the nucleus of interest approaches the point-charge value with Sternheimer⁴ antishielding

$$q = (1 - \gamma_{\infty})(2 z/r^3) , \qquad (3)$$

where $\gamma_{\rm e}$ is the antishielding parameter for the ion of interest and z is the valence of the other ion. As the ions approach each other, they are mutually polarized by each other's Coulomb fields and some higher multipole contributions appear. When the charge distributions begin to overlap, a negative contribution to q appears which dominates the EFG at the molecular equilibrium separation. This behavior was also observed in a set of self-consistentfield calculations¹⁹ using a Gaussian lobe basis for the series of molecules F_2^{-2} , NeF⁻, and NaF.

Since the ion-ion separations in solids are somewhat larger than in diatomic molecules, and since Matcha's treatment of KCl was carried to a somewhat larger relative separation than the other alkali halides, we analyzed it in detail in an attempt to obtain a more quantitative description of the above behavior. From Matcha's value of the EFG at the Cl⁻ nucleus we subtracted a point-charge term (3) with $\gamma_{\infty} = -56.6$, which is the value calculated by Sternheimer⁴ and others³ for a free Cl⁻ ion. We have referred to the difference as "the overlap" contribution, $q_{ox}(r)$, although it also includes polarization and shielding effects. A plot of these various contributions for KCl is shown in Fig. 3. On a semilog curve, the three points with the largest r fit a straight line. We assume then, that for relatively large r, the overlap term can be written in the form

$$q_{\rm ov}(r) = -F \exp[(R_{\rm KC\,1} - r)/\rho_{\rm K\,C1}], \qquad (4)$$

where R_{KC1} is a radius parameter and ρ_{KC1} is a softness parameter for the K^{*} and Cl⁻ ions. *F* is a strength parameter which is not independent of R_{KC1} . We choose $R_{\text{KC1}} = 5.101$ bohr by a method which is discussed in Sec. VA 2 and obtain F = 0.9239 a.u. and $\rho_{\text{KC1}} = 0.7674$ bohr.

The exponential form for the "overlap" term has a close resemblance to the Born-Mayer potential for hard-core repulsive forces between ion pairs:

$$U_{ij} = f \rho_{ij} \exp[(R_{ij} - r) / \rho_{ij}].$$
 (5)

Gilbert¹² used spectroscopic data to evaluate the parameters in (5) for alkali halide monomers. He found that the radius and softness parameters approximately obeyed the additivity conditions R_{ij} = $R_i + R_j$ and $\rho_{ij} = \rho_i + \rho_j$, where R_i and ρ_i are parameters for individual ions. We have exploited this resemblence by assuming that similar additivity rules hold in the "overlap" term (4).

2. Choice of Parameters

Gilbert¹² published a set of radius and softness parameters for alkali and halide ions, which are listed here as a part of Table IV. Our first attempt to apply the soft-sphere model to $GdCl_3$ gave very poor results, but is nevertheless worth discussing in some detail. We took chloride parameters from

TABLE IV. Comparison of ionic parameters determined from the Gilbert (G) and the Hartree-Fock-Slater (HFS) procedures. The ionic radius R and the softness ρ are given in bohrs. The residual electronic charge outside a sphere of radius $R_{\rm HFS}$ is also listed.

Ion	R (G)	R (HFS)	ρ (G)	ρ (HFS)	Residual charge
Li ⁺	1.31	1.306	0.131	0.2047	0.08
Na ⁺	1.80	1.801	0.150	0.2481	0.17
K*	2.35	2,361	0.200	0.3304	0.36
\mathbf{Rb}^{*}	2.59	2,590	0.217	0.3690	0.52
Cs⁺	2.87	2,880	0.245	0.4176	0.73
F-	2.59	2,230	0.338	0.4172	0.64
C1-	3.59	2.739	0.449	0.4947	1.01
Br ⁻	3.90	2.896	0.488	0.5277	1.20
I-	4.37	3.140	0.546	0.5803	1.50
La ⁺³		2.636		0.3267	0.42
Ce ⁺³		2.608		0.3204	0.42
Pr^{+3}		2.581		0.3148	0.40
Nd ⁺³		2.556		0.3096	0.37
Pm ^{*3}		2.531		0.3048	0.38
Sm^{+3}		2.507		0.3004	0.36
Eu ⁺³		2.484		0.2962	0.34
Gd ⁺³		2.462		0.2923	0,32

Gilbert, namely, $R_{C1} = 3.59$ bohr and $\rho_{C1} = 0.449$ bohr, and used the free-ion value for the chloride antishielding parameter -56.6. We estimated the gadolinium radius parameter at about 2 bohr using the crystallographic hard-sphere radii of Templeton and Dauben²⁰ as a guide, and guessed at a softness parameter of about 0.2 to 0.3 bohr. We used an overlap strength F in the vicinity of 1.0 a.u., and tried to vary R_{Gd} , ρ_{Gd} , and F to fit the observed quadrupole frequency and asymmetry parameter.

Even with three parameters available to fit two data points, the model gave very poor results. The calculated frequency was too large by a factor from 2 to 3, and the orientation of the EFG was incorrect. At the time the cause of this failure was difficult to ascertain, but the lesson from the failure was clear. A systematic method for fixing the individual ion parameters was essential.

We expected to find a close relationship between the individual ion parameters of the soft-sphere model and the charge density of the outer parts of the ion. We tested this expectation by using a Herman-Skillman Hartree-Fock-Slater (HFS) program²¹ to calculate the charge densities of all the ions of interest. The results, to be published elsewhere in detail, ²² showed that the charge density of an ion ρ_c behaved in an approximate exponential manner near the edge of the ion:

$$\rho_c \simeq \exp[K + (R_0 - r)/\rho] \text{ a.u.}$$
(6)

Here r is the distance from the nucleus, R_0 is some characteristic radius for the ion, and ρ describes the rate of change of $\ln \rho_c$ with r. If $K \equiv -4.3$ then R_0 fit the Gilbert radii for the alkali ions (but not the halides).

We used these HFS calculations to define radius and softness parameters for all ions of interest. We choose $\ln\rho_c(R_i) = -4.300$ to define the characteristic HFS radius, R_i (HFS) of an ion, and the appropriate slope at the HFS radius to define the HFS softness parameter ρ_i (HFS). The HFS parameters so defined are compared with Gilbert's parameters in Table IV. In addition, the HFS parameters for rare-earth ions are listed. Note that the charge outside a sphere of radius R_i (HFS) is of the order of 0.5 electron for all ions.

In connection with the discussion relating to parameters used for Fig. 3, the value of R_{KC1} was assumed to be 5.101 bohr. It is now evident that this choice is based on the additivity rule $R_{KC1} = R_{K} + R_{C1}$ and the HFS radii for K^{*} and Cl⁻. Note that



FIG. 3. Soft-sphere model for KCl. The circles are Matcha's calculations (Ref. 18) as a function of internuclear distance R. Curve A is a point-charge curve having the form $q_A = 2(1-\gamma)/R^3$ with $\gamma = -56.6$. Curve B is generated by subtracting curve A from the calculated points of Matcha and fitting the resultant points to the form q_B $= -F \exp [R_{\rm KC1} - R)/\rho_{\rm KC1}]$. This curve is the "overlap term". Curve C is the sum of curves A and B. The discrepancy between curve C and the calculations for molecules occur far from the distances of interest: R_e , equilibrium distance in the molecule; $R_{\rm HFS}$, the sum of HFS calculated radii for K⁺ and Cl⁻ ions; and $R_{\rm xtal}$, the K-Cl equilibrium distance in KCl crystals. All quantities are atomic units.



FIG. 4. Calculated nuclear quadrupole frequency vs compound. The curves are straight lines drawn through the predictions for each compound using the soft-sphere model (parameter sets A, B, C) and the point-charge model (P). In each instance, the parameters were adjusted to fit the data for GdCl₃. The circles are observed values. The parameter sets A, B, and C are defined in Table V.

 $\rho_{\text{KC1}} = 0.7674$ bohr for Fig. 3 compares with $\rho_{\text{K}}(\text{HFS}) + \rho_{\text{C1}}(\text{HFS}) = 0.8251$ bohr. We regarded the close agreement as an indication that we were on the right track.

3. Application of Soft-Sphere Model

The Cartesian components of the EFG in the softsphere model are given by

$$q_{ij} = \sum_{\alpha} \frac{\left(q_{pc}^{\alpha} + q_{ov}^{\alpha}\right) \left(3 x_i^{\alpha} y_j^{\alpha} - r_{\alpha}^2 \delta_{ij}\right)}{2 r_{\alpha}^2} , \qquad (7)$$

where r_{α} is the distance to ion α with coordinates $(x_1^{\alpha}, x_2^{\alpha}, x_3^{\alpha})$. The point-charge term q_{pc}^{α} is given by

$$q_{\rm pc}^{\alpha} = 2Z_{\alpha}(1-\gamma)/r_{\alpha}^{3}, \qquad (8)$$

where Z_{α} is the valence of ion α and γ is the antishielding parameter for the ion at the origin. We treat γ as a free parameter and expect that its value should be somewhat less than the free-ion value for Cl⁻. Approximately 20 000 ions are included in the point-charge sum over a neutral sphere of radius 50 Å. The convergence was tested by comparison with a 100-Å sum; the results differed by less than 1 part in 10⁴ for each EFG component. The overlap term $q_{\alpha y}^{\alpha}$ is given by

$$q_{ov}^{\alpha} = -F \exp\left(\frac{R_{C1} + R_{\alpha} - r_{\alpha}}{\rho_{C1} + \rho_{\alpha}}\right) \quad , \tag{9}$$

where R_{C1} and ρ_{C1} are the soft-sphere parameters for the Cl⁻ ion at the origin, and R_{α} and ρ_{α} are the soft-sphere parameters for ion α . We treat F as a free parameter and expect its value to be somewhat less than the KCl molecule value as a result of many-ion effects. The overlap term is included for the 11 nearest-neighbor ions (less than 4-Å distant), since for large r our parametrization probably overestimates the overlap contribution.

The soft-sphere parameters for rare-earth ions are taken from the HFS calculations, as is the radius parameter for Cl⁻. There is a slight ambiguity concerning ρ_{Cl} . One choice is to take ρ_{Cl} = 0. 4947 bohr; this choice defines data set A. A second choice is to take $\rho_{Cl} = \rho_{KCl} - \rho_{K}$ and use the values $\rho_{KCl} = 0.7674$ bohr from Fig. 5 and $\rho_{K} = 0.3304$ bohr from HFS to arrive at $\rho_{Cl} = 0.4370$ bohr; this choice motivates data set B, although the calculations were actually made with a slightly different value $\rho_{Cl} = 0.4290$ bohr. Our third choice was arbitrarily to let $\rho_{Cl} = 0.4000$ bohr; this choice defines data set C. For each of the three data sets γ



FIG. 5. Asymmetry parameter vs compound. The curves are straight lines drawn through the predictions for each compound using the soft-sphere model (parameter sets A, B, C) and the point-charge model (P). In the former model, the parameters F and γ were adjusted to fit the data for GdCl₃. In the latter model, η results from geometrical considerations and is independent of γ . The parameter sets A, B, and C are defined in Table V.

TABLE V.	Soft-sphere pa	rameter sets	R_{C1} and ρ_{C1}
are give	n in bohrs and .	F is given in	(bohrs) ⁻³ .

Set	R _{C1}	ρ _{C1}	F	(1 −γ∞)
A	2.740	0.4947	0.4346	28.25
B	2.740	0.4290	0.5695	30.95
С	2.740	0.4000	0.6710	32.99

and F were adjusted so that the soft-sphere model gave the correct chlorine quadrupole resonance frequency and asymmetry parameter in $GdCl_3$ at a pressure of 1 atm. The values of F and γ so obtained are listed in Table V.

The model was then tested by applying it to the other hexagonal rare-earth trichlorides using each of the three data sets in Table V. The only changes are in crystal geometry and rare-earth HFS parameters. The agreement with the experimental values of ν_Q and η is excellent. The detailed results are displayed in Figs. 4 and 5. For data set B, ν_Q and η are predicted to within 2.5 and 0.5%, respective-ly, for all compounds in which these quantities are measured. One systematic flaw appears to be the inability of any of the three data sets to give a rapid enough increase in ν_Q across the series from LaCl₃ to NdCl₃.

The significance of the preceding agreement can be emphasized by briefly considering several points. First, setting F = 0 gives the point-charge model. If $\gamma = -16.59$, this model predicts the correct frequency in GdCl₃, but, as has been previously shown, ¹³ seriously overestimates ν_Q in the remaining compounds. In addition the point-charge model predicts η incorrectly in all of the compounds. The results of a point-charge calculation are also included in Figs. 4 and 5.

Second, using Gilbert's value for the chloride radius (3.59 bohr as opposed to 2.740 bohr from HFS) produces an overlap contribution to the EFG which is dominated by the near-neighbor chlorides. Since they are almost symmetrically located, their contribution tends to cancel, and a very large positive value of F is required to reduce the total EFG and obtain the correct ν_Q and η . However, the EFG then has the wrong orientation, V_{xx} does not lie along the c axis.

Third, an attempt can be made to preserve the free-ion values of γ and F by assuming the HFS values for the gadolinium parameters and adjusting R_{C1} and ρ_{C1} to fit ν_Q and η in GdCl₃. When these chlorine parameters were then applied to PrCl₃ the values of R_{Pr} and ρ_{Pr} necessary to fit the observed ν_Q and η were both drastically less than the assumed values for gadolinium. This is contrary to both our intuition, since we expect that Pr³⁺ is both larger and softer than Gd³⁺, and to the HFS calculations.

Finally, it should be noted that this same general method, with slightly modified details, provides insight into the behavior of $CsPbCl_3$.²³

B. Pressure Dependence

To examine the predictions of the soft-sphere model when the sample is subjected to hydrostatic pressure one needs to know the linear compressibilities α_1 and α_3 along the *a* and *c* axes of the hexagonal crystals, as well as the change in chloride positional parameters *u* and *v* with pressure. None of these are known,²⁴ and hence the model cannot be tested quantitatively. However, we are able to qualitatively test the model by making reasonable assumptions.

We assumed that the bulk compressibility $\beta = 2\alpha_1 + \alpha_3$ was about 7×10^{-6} cm²/kg, which is typical for ionic chlorides, and that u and v were independent of pressure. We defined $r = \alpha_3 / \alpha_1$, as the ratio of strains along the c axis to those along the a and b axes. Then for a number of values of r from 0 to ∞ we calculated the NQR parameters of GdCl₃ as a function of unit cell volume. Since only the change



FIG. 6. Volume dependence of nuclear quadrupole frequency. This figure, for parameter set B, is typical of the volume dependence predicted by the soft-sphere model. The actual behavior depends upon the relation between linear compressibilities and is depicted for various values of r, the ratio of the compressibility along c axis to the compressibility along a axis. r=1 is the isotropic case and r=0 when the c axis is totally incompressible.

in frequency with pressure has been measured, we will not discuss the behavior of the asymmetry parameters here. 25

For the point-charge model, ν_Q increased with decreasing cell volume for all positive values of r, with the slowest increase for r = 0. The reader is reminded that experimentally ν_Q decreased with decreasing cell volume. This constitutes further evidence of the unsuitability of the point-charge model applied to these compounds.

For the soft-sphere model, the dependence of ν_q in GdCl₃ on cell volume and r was similar for the three data sets A, B, and C. That of B is shown in Fig. 6 for several values of r. For large r, ν_q increased as cell volume decreased. However, for small r (less than about 0.5, 1.2 and 1.8 for sets A, B, and C, respectively), ν_q decreased with decreasing cell volume. The results for the other compounds in the series were similar.

Figure 7 shows the normalized frequency shift with cell volume as a function of compound for the three data sets. Values of r have been arbitrarily limited to the range 0.4-0.7, however, the results are similar for larger or smaller values. Also shown in Fig. 7 are the experimental values of the



FIG. 7. Normalized derivative of nuclear quadropole frequency vs compound. The predictions of the softsphere model for parameter sets A, B, and C are represented by the shaded regions. In each instance the ratio of linear compressibilities was assumed to lie within the range 0.4-0.7. The circles are experimental data with an assumed bulk compressibility, $\beta \equiv (7 \pm 1) \times (10^{-6})$ cm²/kg.



FIG. 8. Chlorine nuclear quadrupole frequencies vs pressure at 77 K: ErCl₃.

normalized frequency shift with cell volume. These are calculated from the normalized pressure shifts by assuming $\beta = (7 \pm 1) \times 10^{-6} \text{ cm}^2/\text{kg}$. Data sets *B* and *C* show qualitative agreement with experiment.

VI. CONCLUSION

The soft-sphere model gives remarkable agreement with the NQR experiments in this series of compounds. However, we hesitate to conclude that this agreement indicates the correct set of parameter values have been determined. We reemphasize that this model involves the difference between two large terms, the point-charge contribution and the overlap term, and thus it is very sensitive to the choice of parameters used. Moreover, in the specific series of compounds studied, a given CI⁻ ion has 11 near neighbors which are approximately uniform in their distribution relative to the given ion. This geometrical arrangement causes a substantial cancellation of gradient contributions and intensifies this sensitivity to competing terms. Thus, even though all the parameters seem to be of a physically reasonable magnitude, the extreme sensitivity probably precludes successful transfer of this set of parameters to other compounds with different geometries. Unfortunately, the compounds most of interest in this respect, tetragonal TbCl₃ and the monoclinic series DyCl₃ through LuCl₃, have such poorly determined crystal structures that meaningful computations of this model for them is not posTABLE VI. Pressure data for ErCl_3 and YbCl_3 at 77 K. ν_Q is the frequency at a pressure of 1 atm and the uncertainty represents a standard deviation for at least five observations.

	line	ν _Q (kHz)	$v_0^{-1} \left(\frac{\partial \nu}{\partial P} \right)_T$ (10 ⁻⁶ cm ² /kg)
ErCl ₃	1	4449.2 ± 0.3	1.36 ± 0.05
Ū	2	4508.5 ± 0.3	$\textbf{2.05} \pm \textbf{0.07}$
YbCl ₃	1	4781.1 ± 0.3	0.77 ± 0.07^{a}
	2	4836.0 ± 0.4	1.59 ± 0.01

^aCurve is nonlinear. The slope at zero pressure is given.

sible at present.

The values of F and γ_{∞} are both much less than those obtained in the free KCl molecule and the free Cl⁻ ion, respectively. This seems reasonable because both are dominated by the high distortibility of the outer parts of the Cl⁻ ion in free space. When forming a crystal, it is intuitively appealing to suppose that as one brings ions up to be near neighbors of the Cl⁻ ion, the outer regions of the Cl⁻ ion are distorted and "compressed" and made less able to distort further as more ions are brought up. Thus we expect three-ion and higher many-ion effects to be present, which to first order have resulted in lowering the effective strengths of our two-ion interaction model.

One can envision two routes of improvement for this model and its extension on other than an *ad hoc* basis to additional compounds. First, HF computations in two- and three-ion systems may give insight to better ways to parametrize the problem, probably requiring explicit inclusion of three-ion effects. Second, extension to a wide series of compounds having complete NQR data and well done xray structure analyses should be made. This group of compounds at present is rather small and more experimental work is badly needed.

APPENDIX: MONOCLINIC TRICHLORIDES

Dysprosium trichloride (room-temperature form) through LuCl₃ have the AlCl₃ structure.²⁶ Pressure data obtained for $ErCl_3$ and $YbCl_3$ at 77 K are displayed in Table VI and Figs. 8 and 9. Unfortunately, the positional parameters are not well known,

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FIG. 9. Chlorine nuclear quadrupole frequencies vs pressure at 77 K: YbCl₃.

and so no attempt has been made to apply the softsphere model to these compounds. There are two chemically inequivalent Cl sites in the structure. In both compounds, the frequencies of all lines increased with pressure. In $ErCl_3$, the lines at 77 K disappeared above about 3.7×10^3 kg/cm² and did not reappear when the pressure was lowered. As the critical pressure was approached, the signals lost strength. This loss of signal was not observed at 300 K (where only the stronger, lower frequency line was observed) at pressures up to 4.3×10^3 kg/cm². We suspect that a crystallographic transition takes place to the orthorhombic²⁷ TbCl₃ form. Monoclinic DyCl₃ undergoes such a transition²⁷ when cooled below room temperature at 1 atm. In YbCl₃, the lower frequency line has a nonlinear form vs pressure, while the upper line is linear. The scatter in the $ErCl_3$ data precludes observing whether a similar departure from linearity is present.

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PHYSICAL REVIEW B

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VOLUME 6, NUMBER 3

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Strong-Radio-Frequency-Field Effects in Nuclear Magnetic Resonance and Electron Paramagnetic Resonance

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A change in the rotating-coordinate transformations that are used in making calculations of magnetic-resonance phenomena with large rf fields permits a definition for the quantization axis of the spin system which is continuous in both the driving rf field strength and the departure of the rf frequency from resonance. This modified procedure is used to compute the line narrowing, which is expected in spin-stirring experiments with inhomogeneously broadened systems, as a function of stirring rf field strength. The increase in transverse relaxation time in correlation-time-narrowed inhomogeneously broadened spin systems is calculated. The behavior of the magnetization in the rotating frame in adiabatic fast-passage experiments is predicted. The increase in transverse relaxation time in multiple-pulse experiments in homogeneously broadened systems is calculated. These predictions agree with observations or with exact calculations made with trace-sum methods. It is shown that previous experiments which were predictable and in accord with the usual procedure are also in accord with the modified procedure proposed here.

I. INTRODUCTION

The problem of coupled microscopic magnetic moments in the presence of a strong static magnetic field and a transverse rf field is at the center of the following discussion. There is certainly a wealth of understanding of empirical and analytical aspects of the effect of strong rf fields on the spin-spin interaction in paramagnetic materials.¹⁻¹⁵ However, the theoretical predictions of the behavior of the resonant spin system are difficult to understand physically. In an attempt to understand some recent experimental results of the measurement of spin decoupling in electron paramagnetic systems, the author developed a variant of the usual analytical procedure which allows one to predict some properties of the spin system in a heuristic and more physical fashion. These predictions are applicable to nuclear paramagnetic systems also, and they allow one to make interesting interpretations of some previously reported experimental observations on nuclear resonant systems.

This revised treatment of inhomogeneously