Calculations of Electric Field Gradients and g Factors for a Single Crystal of Paramagnetic $CuCl_2 \cdot 2H_2O$

D. V. G. L. Narasimha Rao and A. Narasimhamurty

Department of Physics, Andhra University, Waltair, India

(Received 1 May 1963; revised manuscript received 11 June 1963)

The electric field gradient tensor at the chlorine site in a single crystal of $CuCl_2 \cdot 2H_2O$ has been evaluated using the point-charge model and also considering the effects of induced dipoles. The quadrupole coupling constant, asymmetry parameter, and orientation of the principal axes of the field gradient tensor with respect to the crystalline a,b,c axes are also calculated. The theoretical quadrupole resonance frequency, assuming the antishielding factor of the Cl^- ion to be -56.6, comes out as 6.8 Mc/sec which is to be compared with the observed value of 9.05 Mc/sec. The calculated asymmetry parameter and orientation of the principal axes could not be checked for want of an experimental investigation on the Zeeman effect. Using the same model, g factors of the paramagnetic Cu^{++} ion are evaluated considering spin-orbit interaction by calculating the electrostatic potential at the Cu^{++} site and the consequent crystal-field splittings. The agreement between the theoretical and experimental g factors is better than in the case of the chlorine nuclear quadrupole resonance (NQR) frequency, perhaps due to the fact that the final g values calculated are less sensitive to the percentage covalent character. The contribution of induced dipoles is noted to be significant in both cases. The effect of the paramagnetic Cu^{++} ions on the chlorine NQR, particularly in the antiferromagnetic region (below 4°K), is discussed and the importance of careful experimental investigations to detect the Zeeman splittings even in the absence of an external magnetic field analogous to the zero-field nuclear resonance is indicated.

INTRODUCTION

THE evaluation of electric field gradients in ionic crystals has been of growing interest in recent years. A knowledge of the electric field gradient q is necessary to obtain an estimate of the nuclear quadrupole moment Q from the observed quadrupole coupling constant eqQ. Alternatively, if a reliable value of Q is available from an independent source, q could be calculated, say, in crystals for which quadrupole resonance of the nucleus is observed. The value of q so obtained could be compared with values calculated on the basis of various models for the charge distribution in the crystal lattice. In ionic crystals, the individual ions are assumed to a first approximation to have spherical symmetry and the quadrupole coupling with their own nuclei vanishes. The electric field gradients at a nucleus would thus originate solely from charges external to the ion. In the absence of more sophisticated models, all the calculations to date are based on the point-charge model.

There is, however, an additional contribution to the quadrupole coupling due to the distortion of the spherical electronic shell of the ion by the external charges. The net electric field gradient seen by the nucleus is shown to be[1] $q_{external}(1-\gamma_\infty)$, where γ_∞ is called the antishielding factor. Bersohn[2] obtained good agreement between the calculated and observed eQq values in the case of Cu^+ in cuprite and Al^{3+} in Al_2O_3 using the theoretical values of γ_∞. Investigations on the volume dependence of q in crystals and the validity of the point-charge model for the distribution of electric charge in an ionic solid were carried out, notably by

Bersohn,[2] Bernheim and Gutowsky, and co-workers.[3,4] It has been shown by Burns[5] that γ_∞ multiplies the unshielded value of q produced not only by an external charge but also the effects produced by all the external moments, and some of these are shown to be significant in alkali halide gases.

The antishielding factor has also been used with varying degrees of success in other calculations such as (1) field gradients produced by the method of ultrasonic waves as was done by Proctor and co-workers[6] in order to study the resulting electric quadrupole transitions, (2) nuclear quadrupole spin-lattice relaxation times in terms of an ionic model by Van Kranendonk,[7] and (3) the modification of Van Kranendonk's ionic model by Wikner et al.[8] by introducing the effect of induced electric dipole moments associated with optical modes of the lattice vibrations.

This article presents calculations for the paramagnetic single crystal of $CuCl_2 \cdot 2H_2O$ of (1) the electric field gradient tensor at the chlorine site and hence the quadrupole coupling constant eqQ and asymmetry parameter η, (2) the electrostatic potential due to the crystalline environment at the paramagnetic Cu^{++} ion and evaluation of crystal-field splittings and g factors. These calculations have been possible for $CuCl_2 \cdot 2H_2O$ since, for this crystal, a number of other data required in the calculations are available in the literature: (a) The positions of the various atoms are known from

[1] R. M. Sternheimer, Phys. Rev. **95**, 736 (1954).
[2] R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

[3] R. A. Bernheim and H. S. Gutowsky, J. Chem. Phys. **32**, 1072 (1960).
[4] G. G. Belford, R. A. Bernheim, and H. S. Gutowsky, J. Chem. Phys. **35**, 1032 (1961).
[5] G. Burns, Phys. Rev. **115**, 367 (1959).
[6] W. G. Proctor and W. Robinson, Phys. Rev. **104**, 1344 (1956).
[7] J. Van Kranendonk, Physica **20**, 781 (1954).
[8] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960).

TABLE I. Principal values of q tensor and direction cosines with respect to the crystalline axes.

q tensor in xyz system[a] (in units of 10^{14} esu)			Principal values[b]	Direction cosines with respect to abc axes[b]		
−0.2917	0	−0.0552	q_{XX} −0.3043	±0.975	0	±0.223
(−0.0254)	(0)	(+0.3275)	(−0.5710)	(±0.782)	(0)	(±0.623)
0	0.3503	0	q_{YY} −0.0499	∓0.223	0	±0.975
(0)	(−0.0025)	(0)	(+0.2146)	(∓0.623)	(0)	(±0.782)
−0.0552	0	−0.0625	q_{ZZ} +0.3533	0	1	0
(+0.3275)	(0)	(+0.0277)	(+0.3558)	(0)	(1)	(0)

[a] Values in parenthesis indicate contribution of induced dipoles.
[b] Values in parenthesis are obtained if the contribution of induced dipoles is neglected.

x-ray diffraction[9]; (b) the nuclear magnetic resonance of the water protons, the relaxation times, and electron paramagnetic resonance of Cu^{++} ion were already investigated down to liquid-helium temperatures by the Leiden school,[10] and an antiferromagnetic transition was observed at 4.3°K; (c) the nuclear quadrupole resonance (NQR) of Cl was measured by Robinson *et al.*[11] in the temperature range 300–4°K.

CALCULATION OF THE FIELD GRADIENT

$CuCl_2 \cdot 2H_2O$ belongs to the bipyramidal class of the orthorhombic system with two molecules in the unit cell. The various atoms in the unit cell are in the general positions[9]:

Cu— (000); ($\frac{1}{2}$,$\frac{1}{2}$,0);

O— ($0uv$); ($0\bar{u}0$); ($\frac{1}{2}$, $\frac{1}{2}+u$, 0); ($\frac{1}{2}$, $\frac{1}{2}-u$, 0);

Cl— ($u0v$); ($\bar{u}0\bar{v}$); ($\frac{1}{2}-u$, $\frac{1}{2}$, v); ($\frac{1}{2}+u$, $\frac{1}{2}$, v);

with $u = 0.25$ and $v = \frac{3}{8}$.

There are three mutually perpendicular twofold axes of symmetry and three planes of symmetry passing through these axes. The two Cu^{++} ions and all the four Cl^- ions in the unit cell are crystallographically equivalent. As the Cu^{++} ions carry two units of charge, they produce a considerable electric field in the neighborhood and the induced moments in the chlorines and oxygens may not be negligible. The effective dipoles at the respective lattice points are obtained from the equation

$$\mu_{\text{eff}} = \mu_{\text{permanent}} + \alpha F, \tag{1}$$

where the induced dipole is given by αF, α being the polarizability of the ion and F being the effective electrostatic field at the lattice site. The permanent dipole moment of water[12] is assumed as 1.87 Debye units.

The xyz coordinate system is conveniently chosen to coincide with the crystalline abc axes ($x\|a,y\|b,z\|c$) with

the origin at Cl. The electric field F is a resultant of the effect of both charges and effective dipole moments associated with all the neighbors. The components of the electric field at a point (x,y,z) due to an ideal point charge e at (0,0,0) are evavulated using the equations:

$$F_x = ex/r^3, \quad F_y = ey/r^3, \quad F_z = ez/r^3, \tag{2}$$

where r is the distance of the point from the charge. Similarly, the effect of an ideal point dipole m at (0,0,0) [13] with components m_x, m_y, m_z is given as[14]

$$F_x = \frac{3x^2 - r^2}{r^5} m_x + \frac{3xy}{r^5} m_y + \frac{3xz}{r^5} m_z,$$

$$F_y = \frac{3xy}{r^5} m_x + \frac{3y^2 - r^2}{r^5} m_y + \frac{3yz}{r^5} m_z, \tag{3}$$

$$F_z = \frac{3xz}{r^5} m_x + \frac{3yz}{r^5} m_y + \frac{3z^2 - r^2}{r^5} m_z.$$

As all the four Cl ions in the unit cell are equivalent, they see the same field and hence have the same value for the effective dipole moment. A similar situation holds for all the waters in the unit cell. The electric field at a Cu^{++} ion is zero due to symmetry and hence $\mu_{\text{eff}} = 0$ at the Cu sites.

Assuming the polarizability values[15] as $\alpha_{H_2O} = 1.48 \times 10^{-24}$ cc, $\alpha_{Cl} = 3.01 \times 10^{-24}$ cc, and knowing the position coordinates of the various ions, a set of simultaneous equations of type (1) are formulated. The effective field F is obtained by a summation over all the neighboring ions which give significant contribution (not less than 1% of the nearest neighbor). The final values obtained by solving the equations are $m_x = 1.53$ Debye units, $m_y = 0$, $m_z = 2.88$ Debye units for the Cl sites and $\mu_x = 0$, $\mu_y = 4.66$ Debye units, $\mu_z = 0$ at the water sites.

[9] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951).
[10] G. E. G. Hardiman, J. J. Paulis, W. Van Der Lugt, and W. P. A. Hass, Physica, 23, 907 (1957).
[11] W. A. Robinson, W. J. O'Sullivan, and W. W. Simmons, Bull. Am. Phys. Soc. 6, 105 (1961).
[12] L. G. Wesson, *Tables of Electric Dipole Moments* (Technology Press, Cambridge, Massachusetts, 1948).

[13] In the actual calculation, the effects at the point (x,y,z) of charges and dipoles at respective points (x_i,y_i,z_i) are obtained by suitably transforming the Eqs. (2) to (5), i.e., by substituting $x - x_i$ for x, $y - y_i$ for y, etc.
[14] C. J. F. Bohcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Inc., Houston, Texas, 1962).
[15] Landolt-Bornstein, *Physikalich-Chemischen Tabellen* (Julius Springer-Verlag, Berlin, 1923).

Thus, a model is set up by designating each lattice point with the respective charge and effective dipole and both these contribute to the electric field gradient tensor. The components of q could be easily obtained by suitable differentiation of Eqs. (2) and (3); $q_{xx}=\partial F_x/\partial x$, $q_{yy}=\partial F_y/\partial y$, etc. The q's in this article are actual field gradients whereas conventionally they are the negative of field gradients.

We have the general formulas written as

Effect of charges:

$$q_{xx}=(e/r^3)(1-3x^2/r^2), \quad q_{xy}=-3exy/r^5,$$
$$q_{yy}=(e/r^3)(1-3y^2/r^2), \quad q_{yz}=-3eyz/r^5, \qquad (4)$$
$$q_{zz}=(e/r^3)(1-3z^2/r^2), \quad q_{zx}=-3ezx/r^5.$$

Effect of dipoles:

$$q_{xx}=\frac{3(r^2-5x^2)(xm_x+ym_y+zm_z)}{r^7}+\frac{6xm_x}{r^5},$$

$$q_{yy}=\frac{3(r^2-5y^2)(xm_x+ym_y+zm_z)}{r^7}+\frac{6ym_y}{r^5},$$

$$q_{zz}=\frac{3(r^2-5z^2)(xm_x+ym_y+zm_z)}{r^7}+\frac{6zm_z}{r^5},$$

$$q_{xy}=\frac{3(xm_y+ym_x)}{r^5}-15xy\frac{(xm_x+ym_y+zm_z)}{r^7}, \qquad (5)$$

$$q_{yz}=\frac{3(ym_z+zm_y)}{r^5}-15yz\frac{(xm_x+ym_y+zm_z)}{r^7},$$

$$q_{zx}=\frac{3(zm_x+xm_z)}{r^5}-15zx\frac{(xm_x+ym_y+zm_z)}{r^7}.$$

The q's are obtained by a summation over all neighboring ions which give a significant contribution—not less than 1% of the nearest neighbor. The complete field gradient tensor (shown in Table I) at the Cl⁻ site is evaluated in the xyz system to facilitate a calculation of the asymmetry parameter and orientation of the principal axes of q with respect to the crystalline axes in addition to the quadrupole coupling constant. q_{yy} (parallel to the b axis of the crystal) happens to be a principal value and also the one along which the field gradient is maximum. The trace of the tensor ($q_{xx}+q_{yy}+q_{zz}$) is zero to within 3 in 1000. The matrix is easily diagonalized. The principal values and their direction cosines with respect to the crystalline a, b, c axes are shown in Table I. The contributions of the induced dipoles to the components q_{xx}, q_{yy}, $\cdots$, are also listed in the Table. It may be observed that the effect of the induced dipoles is significant particularly in the case of q_{zz} and q_{zx}.

The principal values are designated according to the convention q_{zz} is maximum and $q_{xx}>q_{yy}$ so that the
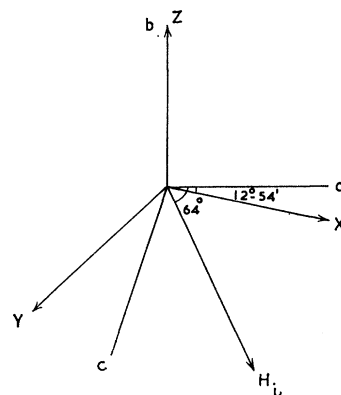

FIG. 1. Orientation of principal axes of the field gradient with respect to the crystalline axes system.

quadrupole coupling constant is given by eQq_{zz} and the asymmetry parameter $\eta=(q_{xx}-q_{yy})/q_{zz}=0.72$. q_{zz} is parallel to the b axis and q_{xx}, q_{yy} lie in the ac plane (Fig. 1). Assuming the quadrupole moment[2] of Cl³⁵ to be -0.085×10^{-24} cm² and an antishielding factor $\gamma_\infty=-56.6$, the theoretical quadrupole coupling constant $(eQq_{zz}/h)(1-\gamma_\infty)$ comes out to be 12.5 Mc/sec. For $I=\frac{3}{2}$ the quadrupole resonance frequency[16] is expected at $\nu=\frac{1}{2}(eQq_{zz}/h)(1-\gamma_\infty)(1+\eta^2/3)^{1/2}=6.8\,\text{Mc/sec}$ which is to be compared with the observed value[8] of 9.05 Mc/sec. The deviation between the predicted and observed resonance frequencies may be attributed to (1) the uncertainty in the theoretical γ_∞ and (2) departure of the bonding from an ideal ionic model and the presence of covalent character. The comparison is expected to be better in the case of the asymmetry parameter and the orientation of the principal values q_{xx}, q_{yy}, q_{zz} with respect to the crystalline-axes system, because these are independent of the assumed γ_∞. Unfortunately this is not possible for lack of data on the Zeeman effect of the pure quadrupole resonance of chlorine in CuCl₂·2H₂O. It has been a general observation[17] that the agreement between the calculated (using the theoretical γ_∞) and experimental values of eQq is good in the case of positive ions but far from satisfactory in the case of negative ions—particularly for halogens. The crystalline environment might modify the free-ion wave function used in calculating γ_∞. Some second-order calculations[5] of the polarizabilities and antishielding factors using a direct substitution method indicate that, for alkali halide gas calculations, perturbation theory is applicable to the alkali ions but not to the easily deformable halide ions. This is probably the reason that the ionic model has always yielded poor results for the halide ions. Ultrasonic measurements[18] and second-order broadening effects[19] also point to the same conclusion. One significant factor to be noted in the present case is that the value of γ_∞ for Cl⁻ necessary

[16] Neglecting the contribution of induced dipoles, the values obtained are $\nu=10.3$ Mc/sec and $\eta=0.25$.
[17] G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961).
[18] E. F. Taylor and N. Bloembergen, Phys. Rev. 113, 431 (1959).
[19] E. Otsuka and J. Kawamura, J. Phys. Soc. (Japan) 12, 1071 (1957).

TABLE II. Crystalline field parameters in terms of the charge, dipole moment, and position coordinates of the ion at the lattice point.

	Contribution due to charge nature	Contribution due to dipolar character[a]
A_2^0	$e(\pi/5)^{1/2}(3z_1^2-r_1^2)r_1^{-5}$	$2(\pi/5)^{1/2}[(3\mu_z z_1-d)-(5d/2r_1^2)(3z_1^2-r_1^2)]r_1^{-5}$
$A_2^{\pm2}$	$e(3\pi/10)^{1/2}(x_1\mp iy_1)^2 r_1^{-5}$	$(6\pi/5)^{1/2}[(x_1\mp iy_1)(\mu_x\mp i\mu_y)-(5d/2r_1^2)(x_1\mp iy_1)^2]r_1^{-5}$
A_4^0	$e(\pi^{1/2}/12)(35z_1^4-30z_1^2r_1^2+3r_1^4)r_1^{-9}$	$(\pi^{1/2}/3)[(35z_1^3\mu_z-15\mu_z z_1 r_1^2-15dz_1^2+3dr_1^2)$ $-(9d/4r_1^2)(35z_1^4-30z_1^2r_1^2+3r_1^4)]r_1^{-9}$
$A_4^{\pm2}$	$\tfrac{1}{6}e(5\pi/2)^{1/2}(x_1\mp iy_1)^2(7z_1^2-r_1^2)r_1^{-9}$	$\tfrac{1}{3}(5\pi/2)^{1/2}[(x_1\mp iy_1)(\mu_x\mp i\mu_y)(7z_1^2-r_1^2)+(x_1\mp iy_1)^2(7\mu_z z_1-d)$ $-(9d/2r_1^2)(x_1\mp iy_1)^2(7z_1^2-r_1^2)]r_1^{-9}$
$A_4^{\pm4}$	$(1/12)e(35\pi/2)^{1/2}(x_1\mp iy_1)^4 r_1^{-9}$	$\tfrac{1}{3}(35\pi/2)^{1/2}[(x_1\mp iy_1)^3(\mu_x\mp i\mu_y)-(9d/4r_1^2)(x_1\mp iy_1)^4]r_1^{-9}$

[a] $d=x_1\mu_x+y_1\mu_y+z_1\mu_z$.

to get agreement with the observed resonance frequency is a little more than the theoretical value, whereas most of the previous calculations need a value of γ_∞ less than the theoretical value. (The contracted wave functions of Burns and Wikner[17] give $\gamma_\infty=-27.04$.) This may be attributed to the effects of covalent character in the Cu—Cl bond. Assuming that the Cu—Cl bond is a resonance hybrid of the two structures-ionic Cu$^+$—Cl$^-$ and covalent Cu:Cl—the covalent character[20] may be estimated as $\approx 5\%$.

CALCULATIONS OF g FACTORS

The same model of the crystal lattice is used for calculating the g factors of the paramagnetic Cu^{++} ion. The procedure essentially involves (1) calculation of the electrostatic potential at the Cu^{++} site due to the neighboring environment and hence obtaining the Stark energy splittings of the configurational ground manifold, and (2) introducing the spin-orbit interaction and the interaction with the external magnetic field as perturbations which further split the lowest Stark energy level. Full details of the method were reported in a previous paper elsewhere.[21]

The nearest neighbors of the Cu^{++} ion are four Cl$^-$ ions lying in the crystallographic ac plane and two water molecules along the b axis. The symmetry of the electrostatic field near the central Cu^{++} site is rhombic. Assuming that the crystalline field potential satisfies Laplace's equation, it can be expanded in spherical harmonics as

$$V_{cryst}=\sum_{n,m} A_n^m r^n Y_n^m(\theta,\phi).$$

In employing this expression for the determination of

the potential-energy matrix elements between two d-electron wave functions (i.e., integrals of the type $\int \chi^* V_{cryst}\psi d\tau$), the terms in V_{cryst} which need to be considered can be reduced as follows:

1. With χ and ψ denoting two d-electron wave functions, the density $\chi^*\psi$ expanded in spherical harmonics does not contain harmonics for which $n>4$. If U is a spherical harmonic for which $n>4$, the integral $\int \chi^* U\psi\, d\tau$ vanishes by the orthogonality relations for spherical harmonics. Hence, all terms for which $n>4$ need not be considered in the expansion of V_{cryst}.

(2) The product $\chi^*\psi$ is unchanged by the substitution $x,\ y,\ z\rightarrow -x,\ -y,\ -z$, whereas U reverses sign if n is odd. Hence, all terms for which n is odd give zero matrix elements.

(3) The term with $n=0$ is a constant and shifts all the levels of a given configuration by the same amount and hence has no theoretical importance.

(4) V_{cryst} should exhibit the same symmetry as the surroundings of the central paramagnetic ion. If there is a p-fold symmetry about the z axis, only these terms in V_{cryst} will be nonvanishing for which m is either 0 or an integral multiple of p.

(5) Since V_{cryst} is to be real, $A_n^m=(A_n^{-m})^*$. Thus, for a rhombic field, the potential operator has the form

$$V_{cryst}=A_2^0 r^2 Y_2^0+A_2^{\pm2}r^2 Y_2^{\pm2}+A_4^0 r^4 Y_4^0$$
$$+A_4^{\pm2}r^4 Y_4^{\pm2}+A_4^{\pm4}r^4 Y_4^{\pm4}.$$

To calculate the crystalline field parameter A_n^m the following procedure is adopted:
Considering an ion at (x_1,y_1,z_1) associated with charge e and effective dipole moment components $\mu_x,\ \mu_y,\ \mu_z$, the potential V at (r,θ,ϕ) near the origin is given as

$$V=\frac{e}{[r^2+r_1^2-2r(x_1\sin\theta\cos\phi+y_1\sin\theta\sin\phi+z_1\cos\theta)]^{1/2}}+\frac{(r\sin\theta\cos\phi-x_1)\mu_x+(r\sin\theta\sin\phi-y_1)\mu_y+(r\cos\theta-z_1)\mu_z}{[r^2+r_1^2-2r(x_1\sin\theta\cos\phi+y_1\sin\theta\sin\phi+z_1\cos\theta)]^{3/2}}.$$

[20] The estimated covalent character would be a little more if γ_∞ is assumed (Ref. 17) to be -27.04 for Cl$^-$ ion in calculating q for the ionic structure.
[21] A. Narasimhamurty and D. Premaswarup, J. Sci. Ind. Res. (India) (to be published).

TABLE III. Values of Crystal-field parameters (in cm^{-1}).
$\langle r^2 \rangle_{av} = 0.9 \times 10^{-16}$. $\langle r^4 \rangle_{av} = 1.32 \times 10^{-32}$ (Ref. 21).

	Contribution due to charges and permanent dipole moment	Contribution due to induced dipoles	Total value
$A_2{}^0 \langle r^2 \rangle_{av}$	5330	20 000	25 330
$A_2{}^{\pm2} \langle r^2 \rangle_{av}$	1130	12 770	13 900
$A_4{}^0 \langle r^4 \rangle_{av}$	−1330	−3970	−5300
$A_4{}^{\pm2} \langle r^4 \rangle_{av}$	−7140	−7890	−15 030
$A_4{}^{\pm4} \langle r^4 \rangle_{av}$	−6870	−10 280	−17 150

This can be expanded in spherical harmonics as

$$V = \sum_{n,m} A_n{}^m r^n Y_n{}^m (\theta,\phi).$$

Equating these two expressions, and employing the orthonormal properties of spherical harmonics, $A_n{}^m$ can be expressed in terms of the position coordinates of an ion with respect to the Cu^{++} as origin and the associated charge and dipole moments. Only those combinations of n, m which correspond to nonvanishing terms in V_{cryst} need be considered. The final expressions are shown in Table II. Direct effect of only the nearest four chlorines and two waters is considered, the indirect effect of distant neighbors is considered only through the effective dipole moments. Values of $A_n{}^m$ are shown in Table III. The contribution of induced dipoles is quite significant in all the cases.

The elements of the energy matrix may be written as

$$\int \phi_{n,l}{}^{ml'*} V_{cryst} \phi_{n,l}{}^{ml''} d\tau,$$

where

$$\phi_{n,l}{}^{ml} = R_n{}^L(r) Y_l{}^{ml}(\theta,\phi).$$

Since the configurational ground state of the Cu^{++} ion $(3d^9)$ is ^2D, the associated five degenerate wave functions are given by $m_l = 2$, 1, 0, −1, −2 for $n = 3$ and $L = 2$. The energy matrix is formed and the eigenvalues and eigenstates are obtained by solving the secular determinant. The crystal-field splittings are illustrated in Fig. 2.

The g values are calculated from the relations

$$g_i = 2 - 2\lambda \sum_{n \neq 0} \frac{\langle 0|L_i|n \rangle \langle n|L_i|0 \rangle}{E_n - E_0},$$

where λ is the spin-orbit coupling constant. As the eigenstates and the associated eigenvalues in the presence of the crystalline electric field are known, the g factors can be expressed in terms of the matrix elements of L—the orbital angular momentum operator.

The theoretical g factors along the crystalline axes are shown in Table IV, along with the observed values[22] for comparison. The agreement between the calculated

[22] H. J. Gerritsen, R. Okkes, B. Bölger, and C. J. Gorter, Physica 21, 629 (1955).
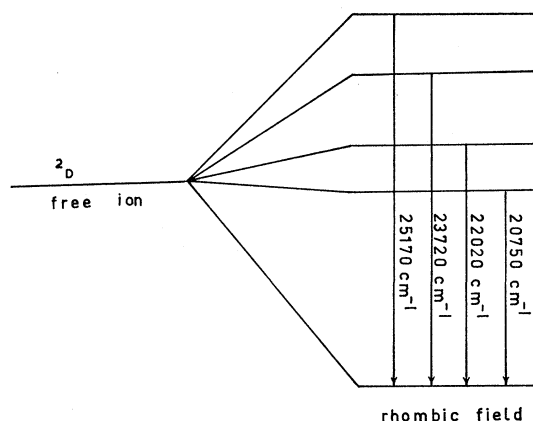

rhombic field

FIG. 2. Crystal field splittings of paramagnetic Cu^{++} ion.

and observed g values seems to be better than in the case of the quadrupole resonance frequency perhaps because of the fact that the final g values calculated are less sensitive (though values of $A_n{}^m$ are quite sensitive) to the percentage covalent character. The g values obtained by neglecting the contribution of induced dipoles which are also shown in Table IV indicate the significance of induced dipoles.

EFFECT OF THE PARAMAGNETIC Cu^{++} ON THE Cl QUADRUPOLE RESONANCE

$CuCl_2 \cdot 2H_2O$ becomes antiferromagnetic below 4.3°K. Approximate magnetostatic calculations of the internal magnetic field H_i at the Cl site due to the Cu spins (which are aligned parallel to $\pm a$ axis according to Hardiman et al.[10]) yield a value of $H_i \approx 1600$ Oe at 0°K effective in the ac plane. It should be noted that the value may be significantly modified due to effects of electron transfer. The Zeeman splitting due to H_i at 4°K is estimated to be about 600 kc/sec[23] whereas only a broadening of 200 kc/sec has been observed at this temperature. Hardiman et al.[10] mentioned that their attempts to detect the Cl^{35} nuclear resonance in the antiferromagnetic state were not fruitful (1.2–4.2°K),

TABLE IV. Theoretical and experimental g values.

g values	Theoretical (a) Neglecting contribution of induced dipoles	(b) Considering induced dipoles	Experimental
g_a	3.26	2.18	2.19
g_b	2.02	2.01	2.03
g_c	3.06	2.24	2.25

[23] The calculation is very approximate and is based on the equation $\mu_0 - \langle \mu \rangle = c\mu_0 T^4$ which holds in the region 1.2°K $< T$ < 3.5°K. Assuming T^5 dependence in the region 3.5–4°K, the expected splitting is about 400 kc/sec.

although the external field was varied between 0–10 000 Oe and the frequency between 5 to 40 Mc/sec. No explanation was suggested. It might perhaps be possible to observe the effect of H_i on the quadrupole resonance of Cl [35,37] at these low temperatures. Nevertheless, it would be interesting to undertake careful experiments particularly in the region 1–4°K on NQR and Zeeman effect. As the asymmetry parameter is large, all the four Zeeman components corresponding to the tran-

sition $(\pm\frac{3}{2}) \rightarrow (+ -)$ may be observed even in zero field.

ACKNOWLEDGMENTS

Paramagnetic Susceptibility of Metallic Lithium and Sodium by Electron Spin Resonance Saturation*

RICHARD HECHT†

IBM Watson Laboratory, Columbia University, New York, New York

(Received 12 June 1963)

The total conduction electron spin moment of lithium and sodium dispersions has been measured in polarizing fields of about 10 G. The steady-state change in sample polarization at electron spin resonance was detected and then extrapolated to the limit of full saturation. Surprisingly, it was found that because the rf fields were linearly polarized and comparable to the polarizing field, the saturation level did not increase monotonically with rf field strength. The data were in good fit with saturation curves derived by means of numerical integration of the modified Bloch equation. The conduction electron spin susceptibility X_s for lithium at 300°K was $(1.96\pm0.10)\times10^{-6}$ cgs volume units. The relative values of X_s in lithium were the same at 300, 77, and 1.5°K, within an estimated uncertainty of 3%, and the relative values of X_s in sodium were the same at 77 and 1.5°K, within an estimated uncertainty of 5%.

I. INTRODUCTION

DIRECT measurements of conduction electron spin susceptibility X_s were first made by Schumacher and Slichter[1] on lithium and sodium at 77°K. Their method was later refined by Schumacher and Vehse,[2] who extended the measurements on sodium to 4.2°K. As expected, the values found for X_s were higher than those predicted by Pauli[3] in the free-electron approximation, because the exchange interaction favors spin alignment. The best agreement is with the values of X_s calculated by Bohm and Pines,[4] and by Shimizu.[5]

In addition to permitting a comparison with theory, knowledge of X_s is useful in estimating the interaction between conduction electrons and nuclear spins. In particular, the average probability density P_F of Fermi level electrons at the nuclear site can be inferred from the Knight shift,[6] which is proportional to the product

$P_F X_s$. Moreover, knowledge of X_s permits a surer test of the Korringa relation[7] connecting X_s, the Knight shift, the electronic specific heat, and that part of the nuclear relaxation rate associated with the contact hyperfine field. For these reasons, it seemed worthwhile to repeat the measurements of X_s by a different method.

In the present experiment, a transverse linearly polarized rf field at electron spin resonance is applied to a longitudinally polarized sample, and the resulting change in longitudinal electron spin moment is detected. Only the average, steady-state response is observed. The change in moment is proportional to the degree of saturation Z, defined by $Z = 1 - \langle M_z \rangle / X_s H_0$, where H_0 is the polarizing field strength, and $\langle M_z \rangle$ is the longitudinal spin magnetization at resonance. The original electron spin moment is inferred by extrapolating the detected signal to the limit $Z = 1$. To do this, the data must be fitted to the computed dependence of Z on rf field strength, based on the modified Bloch equation.[8] These computations are essential, for we find that Z does not increase monotonically with the rf field strength, but shows broad local maxima owing to the fact that the rf field is linearly polarized and comparable to H_0.

* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University.

† Present address: RCA Laboratories, Princeton, New Jersey.

[1] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1957).

[2] R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297, (1963).

[3] W. Pauli, Ann. Physik **41**, 81 (1927).

[4] D. Pines, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. I, p. 367.

[5] Masao Shimizu, J. Phys. Soc. Japan **15**, 2220 (1960).

[6] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press Inc., New York, 1956), Vol. II, p. 105.

[7] J. Korringa, Physica **16**, 601 (1950).

[8] R. K. Wangsness, Phys. Rev. **98**, 927 (1955).