value of 36 deg at 2.0°K and a maximum value of 45 deg at about 9°K. For rubidium, Θ has aminimum value of 50 deg at 3.3°K and a maximum value of 56 deg at about 9°K. Manchester[4] has reported Θ values for rubidium between 1.2° and 4.2°K. He finds an approximately constant Θ below 1.6°K and a minimum value of 51.2 deg at 2.8°K. His results were not corrected for the electronic contribution. The subtraction of an electronic term from the specific heat would make Θ rise at lower temperatures and might shift the location of the minimum to a slightly higher temperature, but it could not account for the difference in absolute values of Θ minimum found in these experiments.

Dauphinee *et al.*[5] found Θ values of 61 deg for rubidium at 25°K and 44 deg for cesium at 20°K. These results suggest the existence of at least one more minimum in the Θ vs temperature curve for each metal between 12° and 20° or 25°K.

Bauer[6] and Bhatia[7] have calculated the vibrational spectra of body-centered cubic lattices, using the elastic constants of sodium. Their results are expressed in terms of Θ vs temperature curves which typically show a high Θ at 0°K with a minimum at low temperatures followed by an approximately constant Θ at higher temperatures. These curves are similar to, but less complicated than, those from the experiments on rubidium and cesium.

ACKNOWLEDGMENT

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Effect of Quadrupolar Polarizability upon Field Gradient in Tetragonal Lattices*

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In the course of investigating sources of electric field gradient in the body-centered tetragonal structure of indium, a study of the effect of quadrupole moments induced in the ions themselves has been made. An eight-figure table covering a wide range of c/a values and giving the axial field gradient per unit axial quadrupole moment in a tetragonal lattice of quadrupolarly polarized ions has been constructed. The effects of the ions at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and those at (0,0,0) have been listed separately in the interest of versatility.

Using a rough estimate of the quadrupolar polarizability of the indium ion, the net effect of the induced moments in this material is shown to be small. Larger effects could be expected in other substances.

I. INTRODUCTION

In a recent article,[1] R. R. Hewitt and the author investigated nuclear quadrupole resonance and possible sources of the electric field gradient (EFG) in metallic indium. One possible source, however, was made the subject of a separate investigation and is reported in the present article. That source is the effect of the quadrupole moments induced in the ions themselves.

The principal result of the present work is a detailed table (Table I) of the axial EFG per unit axial quadrupole moment generated in a tetragonal lattice of quadrupolarly polarized ions. This table, which separates the effects of the ions at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ from those at (0,0,0) and which covers the range $0.50\leqslant c/a\leqslant 3.20$, is intended to apply not only to indium but to a variety of tetragonal structures including compounds as well as elements. The extensive numerical work involved in the construction of this table and in other calculations discussed in this article was performed on an IBM 1620 automatic digital computer maintained by the Biometrical Laboratory of the Citrus Research Center and Agricultural Experiment Station located at this campus of the University of California.[2]

Since the quadrupole moment induced in the ions depends upon the total EFG present and at the same time helps to determine this quantity, the total EFG must be found by solving a simple algebraic equation containing the quantity F_Q given in Table I, the quadrupolar polarizability, and the EFG due to primary sources, e.g., the monopole moments of the ions and the electron density in the interionic space. The only information presently available on the quadrupolar polarizability of the In^{3+} ion is, unfortunately, in the form of a rough estimate. On the basis of this estimate, it is found that the effect of the induced quadrupole

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[1] R. R. Hewitt and T. T. Taylor, Phys. Rev. **125**, 524 (1962).

[2] This laboratory is under the direction of Dr. Morris J. Garber, whose willingness to assist at all times is greatly appreciated.

moments in indium is such as to make the total EFG exceed the primary EFG by about 1%. As long as it is small, this percentage figure is roughly proportional to the polarizability and will have to be revised if the latter is revised. The effect could easily be greater in substances having more fortunate c/a ratios, as Table I shows. It could also be greater in compounds in which the ions at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are of a different species from those at (0,0,0).

Gaussian units are used throughout this article.

II. CALCULATION OF THE ELECTRIC FIELD GRADIENT IN A LATTICE OF QUADRUPOLAR SOURCES

Since the object of this section is to calculate the EFG at a given ion site due to quadrupole moments in all the other ions, the model employed will consist of an infinite lattice of identical nonoverlapping charge aggregations or sources each of which produces an external potential having only an axial quadrupole component. It is important to realize that the charge density distribution of a source is not fully determined by the multipolar composition of its external potential, therefore there exists some latitude within which one may vary the model for the charge density within the confines of a given source without changing the essential character of that source as manifested by its external effects. The model actually used consists of a surface density proportional to $P_2(\cos\theta)$ upon a small sphere whose radius s_1 is adjustable within limits; the derivation of the Fourier series representation for a lattice of such spheres is detailed in Appendix A. The ordinary point charge cluster model is unsatisfactory because it has, in addition to the intended moment, a whole series of higher moments which disappear only as the limit of infinite charges and zero relative displacements is reached.

According to the nomenclature of reference 1, the external potential of a source is represented in spherical harmonics as follows:

$$V=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} B_l^m r^{-(l+1)} P_l^{|m|}(\cos\theta)\exp(\mathrm{im}\phi). \quad (2.1)$$

The B_l^m coefficients are related to, or may simply be regarded as, the multipole moments of the source. If the latter has density ρ_s, then the following can be shown to be consistent with (2.1):

$$B_l^m=\frac{(l-|m|)!}{(l+|m|)!}\int \rho_s r^l P_l^{|m|}(\cos\theta)\exp(-\mathrm{im}\phi)d\tau. \quad (2.2)$$

In the same system of nomenclature, a potential which is Laplacian and regular in a neighborhood of the origin is represented as follows:

$$V=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_l^m r^l P_l^{|m|}(\cos\theta)\exp(\mathrm{im}\phi). \quad (2.3)$$

From the usual definitions of the axial quadrupole moment and the EFG, it is evident that $eQ_0=2B_2^0$ and that $eq_0=2C_2^0$, respectively. Here, the zero subscripts are used to emphasize that eQ_0 is the quadrupole moment externally induced in the ion, not the nuclear quadrupole moment and that eq_0 is the EFG in which the ion as a whole is situated, not the EFG at the site of the nucleus. In the immediate problem, the B_2^0 moment of the ions is regarded as given and the contribution which it makes to the total C_2^0 coefficient is the quantity sought. To avoid cumbersome nomenclature, this contribution is simply called C_2^0 in what follows.

The method of reference 1 gives the EFG contribution in terms of a sum over reciprocal lattice vectors $\mathbf{h}$. From Eq. (A16) in that reference, one has:

$$C_2^0=-B_2^0 r_1^{-5}(\tfrac{7}{2})_n/n! \\ -\tfrac{4}{3}\pi\sum_{\mathbf{h}} A(\mathbf{h})\Lambda_{n+\frac{5}{2}}(2\pi h r_1)P_2(\cos\theta_{\mathbf{h}}). \quad (2.4)$$

Here, the first term on the right-hand side, in which B_2^0 appears explicitly, is included only if an ion belonging to the lattice being summed is present at the origin. Thus, this term is included in calculating the effects of the ions at (0,0,0) but is omitted in calculating the effects of those at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The purpose of this term is to subtract the self-field of the ion at the origin. The notation $(z)_n$ means $\Gamma(n+z)/\Gamma(z)$ and the function $\Lambda_\nu(z)$ is related to the Bessel function of the first kind as follows:

$$\Lambda_\nu(z)=\Gamma(1+\nu)(2/z)^\nu J_\nu(z). \quad (2.5)$$

The quantity n in (2.4) may in principle be set equal to any non-negative integer but, for practical reasons, small values are not suitable. Most of the calculations were performed with $n=31$. The distance parameter r_1 must be chosen so that a sphere of this radius contains all the charge belonging to the ion at the origin and none of the charge belonging to any other ion.

For a tetragonal lattice, the reciprocal lattice vector $\mathbf{h}$ has the rectangular components p_1/a, p_2/a, and p_3/c, where the p_j are integers. From Appendix A, the Fourier coefficients for a lattice of quadrupolar sources located at the (0,0,0) positions become:

$$A(\mathbf{h})=-(4\pi^2h^2B_2^0/3a^2c)\Lambda_{\frac{5}{2}}(2\pi h s_1)P_2(\cos\theta_{\mathbf{h}}). \quad (2.6)$$

For a lattice of similar sources located at the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ positions,

$$A(\mathbf{h})=-(-1)^{p_1+p_2+p_3}(4\pi^2h^2B_2^0/3a^2c) \\ \times\Lambda_{\frac{5}{2}}(2\pi h s_1)P_2(\cos\theta_{\mathbf{h}}). \quad (2.7)$$

When these expressions are used in conjunction with (2.4), r_1 and s_1 must be chosen so that $s_1<r_1<(r_0-s_1)$ where r_0 is the nearest-neighbor distance. Actually it was found most convenient to take $s_1>0$ but yet so small that $\Lambda_{\frac{5}{2}}(2\pi h s_1)$ could be set equal to unity for all h values used in the calculation; there is no practical difference between choosing s_1 in this way and setting it equal to zero but there are theoretical advantages

Table I. Calculated values of a^5 times the axial electric field gradient per unit axial quadrupole moment in a tetragonal lattice of quadrupolarly polarized ions. Lattice parameters are a, a, c.

c/a	$F_{Q,0,0,0}$	$F_{Q,\frac{1}{2},\frac{1}{2},\frac{1}{2}}$	$F_{Q,\text{total}}$
0.50	398.42502	−11.43216	386.99286
0.60	160.89894	−21.95906	138.93988
0.70	76.013832	−31.129064	44.884768
0.78	46.181511	−35.958563	10.222948
0.80	41.348966	−36.768814	4.580152
0.82	37.233091	−37.422443	−0.189352
0.84	33.718776	−37.923710	−4.204934
0.86	30.711170	−38.278198	−7.567028
0.88	28.131761	−38.492561	−10.360800
0.90	25.915290	−38.574277	−12.658987
0.92	24.007291	−38.531444	−14.524153
0.94	22.362143	−38.372583	−16.010440
0.96	20.941498	−38.106476	−17.164978
0.98	19.713021	−37.742025	−18.029004
1.00	18.649360	−37.288123	−18.638763
1.02	17.727321	−36.753556	−19.026235
1.04	16.927180	−36.146915	−19.219735
1.06	16.232124	−35.476527	−19.244403
1.08	15.627792	−34.750396	−19.122604
1.10	15.101891	−33.976161	−18.874270
1.12	14.643877	−33.161067	−18.517190
1.14	14.244691	−32.311938	−18.067247
1.16	13.896538	−31.435164	−17.538626
1.18	13.592700	−30.536695	−16.943995
1.20	13.327377	−29.622039	−16.294662
1.22	13.095558	−28.696269	−15.600711
1.24	12.892907	−27.764026	−14.871119
1.26	12.715668	−26.829537	−14.113869
1.28	12.560583	−25.896625	−13.336042
1.30	12.424825	−24.968730	−12.543905
1.32	12.305939	−24.048924	−11.742985
1.34	12.201787	−23.139930	−10.938143
1.36	12.110512	−22.244147	−10.133635
1.38	12.030495	−21.363666	−9.333171
1.40	11.960325	−20.500290	−8.539965
1.42	11.898772	−19.655560	−7.756788
1.44	11.844763	−18.830770	−6.986007
1.46	11.797362	−18.026988	−6.229626
1.48	11.755748	−17.245075	−5.489327
1.50	11.719207	−16.485705	−4.766498
1.52	11.687114	−15.749378	−4.062264
1.54	11.658920	−15.036442	−3.377522
1.56	11.634148	−14.347102	−2.712954
1.58	11.612378	−13.681443	−2.069065
1.60	11.593243	−13.039433	−1.446190
1.70	11.527118	−10.176897	1.350221
1.80	11.492278	−7.857261	3.635017
1.90	11.473869	−6.012958	5.460911
2.00	11.464121	−4.568268	6.895853
2.20	11.456204	−2.592416	8.863788
2.40	11.453966	−1.446676	10.007290
2.60	11.453333	−0.797810	10.655523
2.80	11.453153	−0.436258	11.016895
3.00	11.453101	−0.237088	11.216013
3.20	11.453087	−0.128264	11.324823

related to the convergence properties of the Fourier series.

The dimensionless quantity $F_Q = a^5 C_2^0 / B_2^0$ was calculated[3] with the aid of (2.4), (2.6), and (2.7) for a large number of c/a ratios; it is tabulated in Table I and presented graphically in Fig. 1.

III. EFFECT OF QUADRUPOLAR POLARIZABILITY

In introducing the term "quadrupolar polarizability," one postulates a relationship, linear at least in the small, of the form:

$$eQ_0 = \alpha e q_0, \tag{3.1}$$

where α, whose dimensions are L^5, is the quadrupolar polarizability and eq_0 is the total EFG in the environment of the ion due to all causes. If eq_{0p} represents the EFG due to primary sources such as those mentioned in the introduction and discussed in reference 1, one may say that:

$$eq_0 = eq_{0p} + a^{-5} F_Q \alpha e q_0, \tag{3.2}$$

where the second term represents the effect considered here, namely the EFG due to the quadrupole moments of the ions. Note that the second term is related, through the polarizability, to the total EFG present. By simple algebra, one obtains:

$$eq_0 = (1 - a^{-5} F_Q \alpha)^{-1} eq_{0p}, \tag{3.3}$$

and it is seen that the effect of quadrupolar polarizability takes the form of a numerical factor which multiplies the primary EFG to yield the total EFG.

It is interesting to estimate this factor for metallic indium since this article was inspired by an investigation of that material. In a private communication, E. G. Wikner has suggested a value of −1 Å^5 for the quadrupolar polarizability of the In^{3+} ion; this is quite reasonable since the same quantity for a perfectly conducting sphere of radius R is $-R^5$. Using $a = 3.25$ Å, $c/a = 1.52$, and $F_Q = -4.06$ from Table I, one finds that $(1 - a^{-5} F_Q \alpha)$ is approximately equal to 0.99 and therefore, in indium the total EFG is greater than the primary EFG by about 1%. If the various sources of primary EFG ever become accurately calculable (as the effect of the monopole moments of the ions now is), then the result just obtained, although small, will come within the scope of experimental verifiability.

An inspection of Tables I and II (Table II is discussed in Appendix B) shows that for both monopole and quadrupole sources of EFG, the ions at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are opposed in their effects to the ions at (0,0,0). Moreover, the c/a ratio of indium is not well suited to the

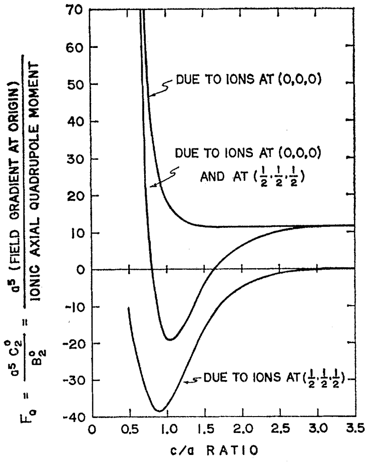

Fig. 1. Graphical presentation of the data of Table I as a function of c/a ratio.

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[3] The author is indebted to Mr. Earl H. Hygh for constructing tables of the Λ function of orders 67/2 and 69/2.

TABLE II. Calculated values of a^3 times the axial electric field gradient per unit monopole moment in a tetragonal lattice of ions in a uniform compensating background. Lattice parameters are a, a, c.

c/a	$F_{M,0,0,0}$	$F_{M,\frac{1}{2},\frac{1}{2},\frac{1}{2}}$	$F_{M,\text{total}}$
0.50	30.08204082	−8.08765794	21.99438288
0.60	15.24693343	−6.17616421	9.07076922
0.70	7.936051229	−4.415074892	3.520976337
0.78	4.572315066	−3.088470732	1.483844334
0.80	3.936895536	−2.770614541	1.166280995
0.82	3.363191029	−2.459108516	0.904082513
0.84	2.843509001	−2.154366965	0.689142036
0.86	2.371244875	−1.856783459	0.514461416
0.88	1.940711609	−1.566722715	0.373988894
0.90	1.546998772	−1.284514721	0.262484051
0.92	1.185855494	−1.010450717	0.175404777
0.94	0.853592830	−0.744780749	0.108812081
0.96	0.547002004	−0.487712492	0.059289512
0.98	0.263285682	−0.239411120	0.023874562
1.00	0.000000000	0.000000000	0.000000000
1.02	−0.244994492	0.230437970	−0.014556522
1.04	−0.473574480	0.451858522	−0.021715958
1.06	−0.687389343	0.664253827	−0.023135516
1.08	−0.887891423	0.867650038	−0.020241385
1.10	−1.076361928	1.062104683	−0.014257245
1.12	−1.253933164	1.247703954	−0.006229210
1.14	−1.421607637	1.424559988	0.002952351
1.16	−1.580274525	1.592808151	0.012533626
1.18	−1.730723889	1.752604390	0.021880501
1.20	−1.873658972	1.904122672	0.030463700
1.22	−2.009706855	2.047552538	0.037845683
1.24	−2.139427699	2.183096776	0.043669077
1.26	−2.263322791	2.310969242	0.047646451
1.28	−2.381841537	2.431392820	0.049551283
1.30	−2.495387570	2.544597532	0.049209962
1.32	−2.604324077	2.650818798	0.046494721
1.34	−2.708978454	2.750295845	0.041317391
1.36	−2.809646388	2.843270254	0.033623866
1.38	−2.906595433	2.929984653	0.023389220
1.40	−3.000068143	3.010681542	0.010613399
1.42	−3.090284827	3.085602237	−0.004682590
1.44	−3.177445979	3.154985946	−0.022460033
1.46	−3.261734410	3.219068947	−0.042665463
1.48	−3.343317130	3.278083877	−0.065233253
1.50	−3.422347008	3.332259115	−0.090087893
1.52	−3.498964245	3.381818258	−0.117145987
1.54	−3.573297666	3.426979674	−0.146317992
1.56	−3.645465876	3.467956139	−0.177509737
1.58	−3.715578277	3.504954535	−0.210623742
1.60	−3.783735971	3.538175618	−0.245560353
1.70	−4.098255858	3.654200261	−0.444055597
1.80	−4.375489784	3.702195178	−0.673294606
1.90	−4.622283483	3.700028244	−0.922255239
2.00	−4.843721519	3.661890222	−1.181831297
2.20	−5.225315673	3.519111389	−1.706204284
2.40	−5.542873718	3.333360354	−2.209513364
2.60	−5.811449939	3.136926972	−2.674522967
2.80	−6.041621446	2.945996239	−3.095625207
3.00	−6.241092822	2.767769596	−3.473323226
3.20	−6.415627220	2.604696617	−3.810930603

production of a large EFG. It is possible, then, that in substances other than indium and especially in tetragonal crystals in which the ions at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are of a different species from those at (0,0,0) or in which they are missing altogether, the effect considered here could be appreciably larger than 1%.

APPENDIX A. FOURIER REPRESENTATION OF A LATTICE OF MULTIPOLAR SOURCES

The summation method used in this article requires that the charge density configuration associated with an infinite lattice of axial quadrupolar sources be expressed as a Fourier series. In the interest of generality, however, this Appendix treats the problem of constructing a Fourier representation for a lattice of identical sources each of which generates an external potential consisting of any single multipole component.

As discussed earlier, there is some latitude in the choice of a model for the charge density of the sources. For convenience, a spherical shell model has been chosen; the results which follow from this choice are detailed below.

Figure 2 illustrates a typical source with density $\rho_s(\mathbf{s})$ where $\mathbf{s}$ is the relative displacement vector from the point O' with respect to which the multipolar composition of the source is to be reckoned. The configuration is shown in relationship to a typical crystal unit cell defined by the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The displacement of O' with respect to O is indicated by the vector $\mathbf{r}'$. In general, the Fourier coefficient is given by

$$A(\mathbf{h})=\tau_0^{-1}\int_{\tau_0}\rho_s\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})d\tau,\tag{A1}$$

where τ_0 is the volume of the unit cell. Since $\mathbf{r}=\mathbf{r}'+\mathbf{s}$, one has

$$A(\mathbf{h})=\tau_0^{-1}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}')\int\rho_s\exp(-2\pi i\mathbf{h}\cdot\mathbf{s})d\tau.\tag{A2}$$

In other words, the Fourier coefficient is simply the product of a position factor, $\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}')$, and the Fourier transform of the source density with respect to O'. The latter may be expanded by the use of Eq. (A5) of reference 1, whereupon:

$$\begin{aligned}A(\mathbf{h})=\tau_0^{-1}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}')\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^l(2l+1)\\ \times[(l-|m|)!/(l+|m|)!]P_l^{|m|}(\cos\theta_{\mathrm{h}})\exp(\mathrm{i}m\phi_{\mathrm{h}})\\ \times\int\int\int\rho_s j_l(2\pi hs)P_l^{|m|}(\cos\theta)\\ \times\exp(-\mathrm{i}m\phi)s^2\sin\theta d\theta d\phi ds.\end{aligned}\tag{A3}$$

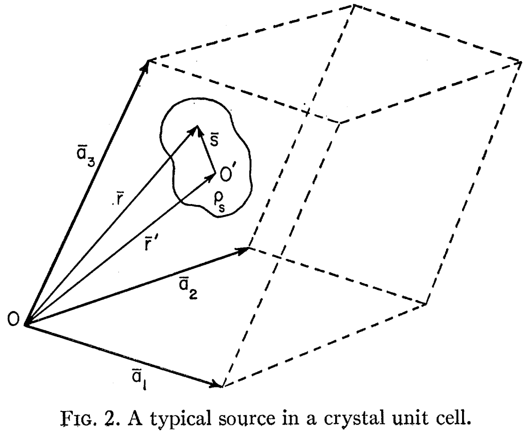

FIG. 2. A typical source in a crystal unit cell.

The charge density is chosen to reside upon a spherical shell of radius s_1 and to be given analytically by:

$$\rho_s=[(2l'+1)B_{l'}^{m'}/4\pi]s^{-(l'+2)}\delta(s-s_1)P_{l'}^{|m'|}(\cos\theta)\times\exp(\mathrm{i}m'\phi). \quad (A4)$$

For any value of s_1, this distribution satisfies the hypothesis that its external potential shall have but a single multipolar component and, as substitution in (2.2) shows, the multipole moment of this source is simply $B_{l'}^{m'}$. The fact that this distribution is complex is no cause for concern since, in any practical situation, it will always appear in superposition with its conjugate. When this ρ_s is substituted into (A3), the summations disappear by orthogonality and the Fourier coefficient acquires a factor whose angular dependence in reciprocal space reflects the angular dependence of the source in real space:

$$A(\mathbf{h})=\tau_0^{-1}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}')B_{l'}^{m'}(-i)^{l'}(2l'+1)\times s_1^{-l'}j_{l'}(2\pi hs_1)P_{l'}^{|m'|}(\cos\theta_{\mathbf{h}})\exp(\mathrm{i}m'\phi_{\mathbf{h}}). \quad (A5)$$

In the final form, it will prove convenient to introduce the Λ-function notation. The radius s_1 remains as an adjustable parameter, and the Fourier coefficient becomes

$$A(\mathbf{h})=\tau_0^{-1}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}')B_{l'}^{m'}\frac{(2l'+1)(-2\pi ih)^{l'}}{2^{l'}(\frac{3}{2})_{l'}}\times\Lambda_{l'+\frac{1}{2}}(2\pi hs_1)P_{l'}^{|m|'}(\cos\theta_{\mathbf{h}})\exp(\mathrm{i}m'\phi_{\mathbf{h}}). \quad (A6)$$

The results quoted in Eqs. (2.6) and (2.7) follow immediately.

APPENDIX B. CHECKING PROCEDURES

The results given in Table I were subjected to three checking procedures. These will be discussed briefly.

(1) Table I was originally calculated with the arbitrary integer n in (2.4) set equal to 31. The calculations were repeated with n set equal to 32 for thirteen representative values of c/a ranging from 0.50 to 3.20. Disagreements were never greater than unity in the least significant figure quoted.

(2) The asymptotic forms of the entries in Table I as c/a tends to zero or to infinity were calculated by summations in real space. Using (C7) from Appendix C, F_Q may be written as a sum over the coordinates of the ith ion with the term corresponding to the ion at the origin delected:

$$F_Q=6\sum_i{}'(a/r_i)^5P_4(\cos\theta_i). \quad (B1)$$

As c/a tends to zero, the effects of all ions except those on the z axis become negligible. $F_{Q,\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ tends to zero and

$$F_{Q,\mathrm{total}}\rightarrow F_{Q,0,0,0}\rightarrow 6(a/c)^5P_4(1)\sum_{n=-\infty}^{\infty}{}'|n|^{-5}. \quad (B2)$$

The sum is twice $\zeta(5)$, the Riemann zeta function of argument 5, whose numerical value is 1.036927755. It follows that

$$F_{Q,\mathrm{total}}\rightarrow F_{Q,0,0,0}\rightarrow 12.443133(a/c)^5. \quad (B3)$$

As c/a tends to infinity, on the other hand, only those ions which lie in the xy plane are important. Again $F_{Q,\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ tends to zero and the other two quantities become asymptotic to a plane sum:

$$F_{Q,\mathrm{total}}\rightarrow F_{Q,0,0,0}\rightarrow 6P_4(0)\sum_{m,n=-\infty}^{\infty}{}'(m^2+n^2)^{-\frac{5}{2}}. \quad (B4)$$

This plane sum was evaluated by a combined summation and integration technique which yielded the value 5.09025821. Since $P_4(0)=\frac{3}{8}$,

$$F_{Q,\mathrm{total}}\rightarrow F_{Q,0,0,0}\rightarrow 11.453081. \quad (B5)$$

An inspection of Table I shows that the asymptotic forms given by (B3) and (B5) are realistic.

(3) It was found that the EFG due to a lattice of monopoles in a uniform compensating background and that due to a lattice of quadrupoles could be calculated at the same time with very little program complication. This is true because the only substantial modification required in changing from the quadrupole to the monopole calculation is the substitution of $P_2(\cos\theta_{\mathbf{h}})$ for $h^2[P_2(\cos\theta_{\mathbf{h}})]^2$. It was therefore decided that $F_M=a^32C_2^0/B_0^0$ should be calculated simultaneously with F_Q in order that the former could be compared with the published results of deWette.[4] The F_M coefficients so calculated are given in Table II. $F_{M,\mathrm{total}}$ compares directly with $a^3Z^{-1}q_{tcp}$ in the reference cited whereas $F_{M,0,0,0}$ must be compared with $8\pi a/3c+a^3S^{\mathrm{tetr}}{}_{0,0,0}$ and $F_{M,\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ with $8\pi a/3c+a^3S^{\mathrm{tetr}}{}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$. The agreement between the corresponding sets of results is excellent.

APPENDIX C. RELATIONSHIPS AMONG LATTICE SUMS

Tara P. Das has pointed out in a private communication that F_Q, the quantity calculated here, is equivalent within a multiplying factor to the axial hexadecapolar term in an expansion of the potential at the origin due to a lattice of monopoles; it is similarly equivalent to the potential at the origin due to a lattice of hexadecapolarly polarized ions. It will be interesting to derive the general relationship of which these are specific cases.

Figure 3 illustrates an axial multipole source of moment $B_{l'}^0$ located at O' and an observer located at O. It is desired to investigate at the origin the C_l^0 component of the potential produced by the source. If this potential can be found as a function of z with x and y set to zero, it will be a simple matter to find C_l^0, since

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[4] F. W. de Wette, Phys. Rev. 123, 103 (1961).

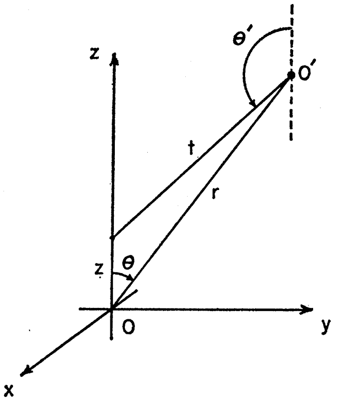

FIG. 3. An axial multipole source at O' shown in relationship to an observer at O.

the latter is simply the Maclaurin coefficient in the expansion of $V(0,0,z)$ at O. The relationship,[5]

$$r^{-(l+1)}P_l(\cos\theta)=\frac{(-1)^l}{l!}\frac{\partial^l}{\partial z^l}\left(\frac{1}{r}\right), \tag{C1}$$

will be very useful here. One has:

$$V(0,0,z)=B_{l'}^0 t^{-(l'+1)}P_{l'}(\cos\theta'); \tag{C2}$$

$$V(0,0,z)=B_{l'}^0\frac{(-1)^{l'}}{l'!}\frac{\partial^{l'}}{\partial z^{l'}}\left(\frac{1}{t}\right). \tag{C3}$$

It follows that

$$C_l^0=B_{l'}^0\frac{(-1)^{l'}}{l'!l!}\left[\frac{\partial^{l'+l}}{\partial z^{l'+l}}\left(\frac{1}{t}\right)\right]_{t=r}. \tag{C4}$$

Equation (C1) may now be invoked again and,

$$C_l^0=B_{l'}^0\frac{(-1)^{l'}(-1)^{l'+l}(l'+l)!}{l'!l!}r^{-(l'+l+1)} \times P_{l'+l}(\cos[\pi-\theta]). \tag{C5}$$

Finally

$$\frac{C_l^0}{B_{l'}^0}=(-1)^{l'}\binom{l'+l}{l}r^{-(l'+l+1)}P_{l'+l}(\cos\theta), \tag{C6}$$

where $\binom{l'+l}{l}$ indicates the lth binomial coefficient in an expansion of order $l'+l$.

When one has an infinite lattice of identical sources, the quantity $C_l^0/B_{l'}^0$ can frequently be related to a real space sum with the term corresponding to the ion at the origin deleted:

$$\frac{C_l^0}{B_{l'}^0}=(-1)^{l'}\binom{l'+l}{l}\sum_i{}' r_i^{-(l'+l+1)}P_{l'+l}(\cos\theta_i). \tag{C7}$$

This sum converges absolutely[6] for all cases in which $l'+l\geqslant 3$, although the rapidity of convergence is not always satisfactory from a computational point of view. In these cases, $C_l^0/B_{l'}^0$ is rigorously given by (C7) and many interesting relationships among lattice sums are immediately deducible. The following, for instance, are particularly relevant to the present article:

$$C_4^0/B_0^0=-C_3^0/4B_1^0=C_2^0/6B_2^0=-C_1^0/4B_3^0=C_0^0/B_4^0. \tag{C8}$$

When $l'+l=2$, the convergence is not absolute and an especially interesting situation arises. Tolerably satisfactory results can be obtained from (C7) by making sure to stop the summation at a spherical boundary concentric with the origin, provided that the sources are either monopoles or quadrupoles. When the sources are dipoles, however, the bound surface density due to the unsummed dipoles just beyond the sphere where summation stops creates the familiar Lorentz field which is independent of the size of the sphere. Since $C_1^0=-E_z$, the Lorentz field contributes negatively to C_1^0/B_1^0 and the latter may be written:

$$\frac{C_1^0}{B_1^0}=-2\sum_{\substack{i,\text{ large}\\ \text{sphere}}}{}' r_i^{-3}P_2(\cos\theta_i)-\frac{4\pi N_d}{3\tau_0}, \tag{C9}$$

where N_d is the number of dipole sources per unit cell in the crystal and τ_0 is the volume of the unit cell. The set of relationships for $l'+l=2$ becomes

$$\frac{C_2^0}{B_0^0}=\frac{-1}{2}\left[\frac{C_1^0}{B_1^0}+\frac{4\pi N_d}{3\tau_0}\right]=\frac{C_0^0}{B_2^0}. \tag{C10}$$

When the quantities C_2^0/B_0^0, C_1^0/B_1^0, and C_0^0/B_2^0 are calculated by the method of reference 1 using the Fourier coefficients derived in Appendix A of this article, the results are in agreement with (C10), hence there is no need to "correct" the C_1^0/B_1^0 so calculated for the Lorentz field. Only when one attempts to calculate C_1^0/B_1^0 by a real space sum must the correction for the Lorentz field be applied.

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[5] W. Magnus and F. Oberhettinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 50.

[6] The result is independent of the order in which the terms are summed.