Electric Field Gradient in the Arsenic Structure*

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The electric field gradients at an ion site per monopole moment and per quadrupole moment of all other ions are calculated for a body-centered rhombohedral structure over a wide range of parameter values. Similar calculations specifically applicable to the elements arsenic, antimony, and bismuth, for which the body-centered ion is slightly displaced, are also performed.

I. INTRODUCTION

THE experimental observation[1] of the nuclear quadrupole resonance spectrum in antimony focusses attention upon the electric field gradient (EFG) at an ion site in the crystalline structure characteristic of this material, that is, in what is commonly known as the arsenic structure. Following Pearson,[2] the latter may be described as rhombohedral with two ions per unit cell at positions $(\bar{v},\bar{v},\bar{v})$ and (v,v,v). Although the sites of these two ions are equivalent, they are here designated I and II, respectively, strictly for reference purposes. In the present article, the origin of coordinates is located at a type I site with the positive z axis passing through the nearest type II site and coincident with the threefold axis of symmetry. A description in terms of an hexagonal unit cell containing three ions at type I sites and three at type II sites is also possible and, for some purposes, is preferable; Table I summarizes the two descriptions in the coordinate system just delineated. The structure may also be regarded as two interpenetrating and slightly distorted cubic close packed lattices.

This article investigates the axial EFG at a given ion site due to nonoverlapping sources at all other sites in a uniform compensating background charge density, a configuration known as the ionic model. It is primarily concerned with the EFG due to the monopole moments or net charges of the sources. The lattice sums necessary to calculate the EFG due to quadrupole moments induced in the sources are also included, however, for completeness, even though estimates of the quadrupolar polarizability of the ions in question are not yet available. The axial hexadecapolar potential component (fourth z derivative of potential) due to monopole moments of the sources can also be calculated from this second type of sum according to Eq. (3.2), below. Following a nomenclature used earlier by Hewitt and Taylor,[3,4] the ionic model contribution to the EFG is denoted $2C_2^0$, and the monopole and axial quadrupole moments of the sources are denoted B_0^0 and $2B_2^0$, respectively. These notations are consistent with the use of C_l^m as the coefficient of $r^l P_l^{|m|}(\cos\theta)\exp(im\phi)$ in an expansion of the Laplacian portion of the potential in a neighborhood of the origin due to all charge not associated with the source at the origin and with the use of B_l^m as the coefficient of $r^{-(l+1)}P_l^{|m|}(\cos\theta)\exp(im\phi)$ in an expansion of the potential due to the source itself. The fraction $2C_2^0/B_0^0$ is understood to mean the contribution to the total EFG at an ion site per ionic charge due to the charges on all other ions; similarly C_2^0/B_2^0 is understood to mean the contribution to the total EFG per quadrupole moment due to the quadrupole moments of all other ions.

The numerical calculations reported in this paper were performed on an IBM 1620 computer.

Gaussian units are used throughout this article.

TABLE I. Crystallographic positions of ions in the arsenic structure.

Ion	Position in rhombohedral unit cell	Positions in hexagonal unit cell
I	(0,0,0)	(0,0,0), $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$
II	$(2v,2v,2v)$	$(0,0,2v)$, $(\frac{2}{3},\frac{1}{3},\frac{1}{3}+2v)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3}+2v)$

II. RESULTS

Two types of calculation are undertaken in the research reported here. The first of these is based upon an

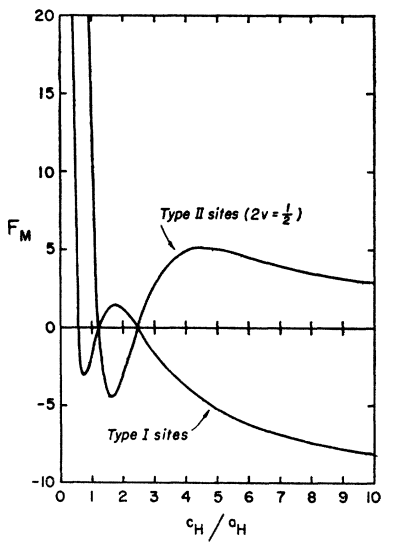

FIG. 1. Graphical presentation of $F_{M,\mathrm{I}}$ and $F_{M,\mathrm{II}}$ as functions of c_H/a_H.

* Supported in part by the National Science Foundation.
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[1] R. R. Hewitt and B. F. Williams, Phys. Rev. **129**, 1188 (1963).
[2] W. B. Pearson, *Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, New York, 1958), p. 124.
[3] R. R. Hewitt and T. T. Taylor, Phys. Rev. **125**, 524 (1962).
[4] T. T. Taylor, Phys. Rev. **127**, 120 (1962).

TABLE II. Values (calculated from the ionic model) of a_H^3 times the axial electric field gradient per unit monopole moment in an idealized arsenic structure with $2v=1/2$.

c_H/a_H	$F_{M,\mathrm{I}}$	$F_{M,\mathrm{II}}$	$F_{M,\mathrm{total}}$
0.2	528.48	4134.65	4663.13
0.3	129.75	1198.17	1327.92
0.4	39.202	489.274	528.476
0.5	10.665	239.025	249.690
0.6	0.647	129.103	129.750
0.7	−2.5957	73.4166	70.8209
0.8	−3.1484	42.3507	39.2023
0.9	−2.6523	23.8835	21.2312
1.0	−1.8135	12.4782	10.6647
1.1	−0.94164	5.31060	4.36896
1.2	−0.16906	0.81588	0.64682
$(3/2)^{1/2}$	0.00000	0.00000	0.00000
1.3	0.45462	−1.93292	−1.47830
1.4	0.91883	−3.51449	−2.59566
1.5	1.23159	−4.30524	−3.07365
1.6	1.40936	−4.55780	−3.14844
1.7	1.47176	−4.44588	−2.97412
1.8	1.43874	−4.09108	−2.65234
1.9	1.32908	−3.57961	−2.25053
2.0	1.15966	−2.97312	−1.81346
2.1	0.94511	−2.31583	−1.37072
2.2	0.69779	−1.63944	−0.94165
2.3	0.42793	−0.96651	−0.53858
2.4	0.14381	−0.31286	−0.16905
$6^{1/2}$	0.00000	0.00000	0.00000
2.5	−0.14800	0.31066	0.16266
2.6	−0.44236	0.89698	0.45462
2.7	−0.73533	1.44177	0.70644
2.8	−1.02398	1.94281	0.91883
2.9	−1.30616	2.39939	1.09323
3.0	−1.58037	2.81196	1.23159
3.1	−1.84561	3.18177	1.33616
3.2	−2.10127	3.51064	1.40937
3.3	−2.34703	3.80076	1.45373
3.4	−2.58281	4.05457	1.47176
3.5	−2.80868	4.27465	1.46597
3.6	−3.02485	4.46359	1.43874
3.7	−3.23159	4.62397	1.39238
3.8	−3.42924	4.75832	1.32908
3.9	−3.61818	4.86905	1.25087
4.0	−3.79880	4.95846	1.15966
4.1	−3.97150	5.02870	1.05720
4.2	−4.13669	5.08180	0.94511
4.3	−4.29476	5.11962	0.82486
4.4	−4.44608	5.14388	0.69780
4.5	−4.59104	5.15616	0.56512
4.6	−4.72996	5.15789	0.42793
4.7	−4.86319	5.15040	0.28721
4.8	−4.99105	5.13485	0.14380
4.9	−5.11382	5.11233	−0.00149
5.0	−5.23179	5.08378	−0.14801
5.5	−5.75820	4.87785	−0.88035
6.0	−6.19754	4.61716	−1.58038
6.5	−6.56949	4.34409	−2.22540
7.0	−6.88836	4.07968	−2.80868
7.5	−7.16474	3.83322	−3.33152
8.0	−7.40658	3.60778	−3.79880
8.5	−7.61997	3.40337	−4.21660
9.0	−7.80964	3.21861	−4.59103
9.5	−7.97936	3.05158	−4.92778
10.0	−8.13210	2.90031	−5.23179

TABLE III. Values (calculated from the ionic model) of a_H^5 times the axial electric field gradient per unit axial quadrupole moment in an idealized arsenic structure with $2v=1/2$.

c_H/a_H	$F_{Q,\mathrm{I}}$	$F_{Q,\mathrm{II}}$	$F_{Q,\mathrm{total}}$
0.2	38885.	1205429.	1244314.
0.3	5117.	158743.	163860.
0.4	1193.6	37691.2	38884.8
0.5	349.7	12391.3	12741.0
0.6	88.14	5028.64	5116.78
0.7	−12.68	2371.02	2358.34
0.8	−55.61	1249.17	1193.56
0.9	−73.463	713.021	639.558
1.0	−78.876	428.614	349.738
1.1	−77.449	263.575	186.126
1.2	−72.0616	160.2003	88.1387
$(3/2)^{1/2}$	−70.3311	140.6223	70.2912
1.3	−64.4355	91.2691	26.8336
1.4	−55.7205	43.0392	−12.6813
1.5	−46.7166	8.1354	−38.5812
1.6	−37.9704	−17.6357	−55.6061
1.7	−29.8306	−36.7997	−66.6303
1.8	−22.4930	−50.9699	−73.4629
1.9	−16.0403	−61.2408	−77.2811
2.0	−10.4761	−68.4001	−78.8762
2.1	−5.7537	−73.0456	−78.7993
2.2	−1.7973	−75.6517	−77.4490
2.3	1.4822	−76.6073	−75.1251
2.4	4.1769	−76.2384	−72.0615
$6^{1/2}$	5.3215	−75.6526	−70.3311
2.5	6.3748	−74.8215	−68.4467
2.6	8.1567	−72.5922	−64.4355
2.7	9.5940	−69.7513	−60.1573
2.8	10.7484	−66.4688	−55.7204
2.9	11.6722	−62.8875	−51.2153
3.0	12.4093	−59.1259	−46.7166
3.1	12.9960	−55.2814	−42.2854
3.2	13.4619	−51.4323	−37.9704
3.3	13.8313	−47.6406	−33.8093
3.4	14.1237	−43.9543	−29.8306
3.5	14.3548	−40.4090	−26.0542
3.6	14.5374	−37.0304	−22.4930
3.7	14.6814	−33.8357	−19.1543
3.8	14.7950	−30.8352	−16.0402
3.9	14.8844	−28.0336	−13.1492
4.0	14.9549	−25.4310	−10.4761
4.1	15.0103	−23.0243	−8.0140
4.2	15.0540	−20.8077	−5.7537
4.3	15.0883	−18.7735	−3.6852
4.4	15.1153	−16.9126	−1.7973
4.5	15.1365	−15.2152	−0.0787
4.6	15.1532	−13.6710	1.4822
4.7	15.1663	−12.2693	2.8970
4.8	15.1766	−10.9997	4.1769
4.9	15.1847	−9.8520	5.3327
5.0	15.1910	−8.8162	6.3748
5.5	15.2073	−5.0043	10.2030
6.0	15.2122	−2.8029	12.4093
6.5	15.2137	−1.5563	13.6574
7.0	15.2141	−0.8592	14.3549
7.5	15.2142	−0.4726	14.7416
8.0	15.2143	−0.2594	14.9549
8.5	15.2143	−0.1421	15.0722
9.0	15.2143	−0.0778	15.1365
9.5	15.2143	−0.0425	15.1718
10.0	15.2143	−0.0233	15.1910

idealized arsenic structure with $2v=\frac{1}{2}$, that is, upon a body-centered rhombohedral structure, and has as its object the tracing of the behavior of the EFG over a wide range of c_H/a_H where c_H and a_H are the lattice parameters in the hexagonal description. This calculation parallels work of a similar nature in the tetragonal[4,5] and in the hexagonal close packed lattices.[5] Tables II and III give the dimensionless quantities $F_M=a_H^3 2C_2^0/B_0^0$ and $F_Q=a_H^5 C_2^0/B_2^0$, respectively, as functions of c_H/a_H. These data are also presented graphically in Figs. 1 and 2. In both presentations, the effects of ions at type I sites and type II sites are listed separately in the interest of versatility. The special entries at $c_H/a_H=(3/2)^{1/2}$ and

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

TABLE IV. Crystal structure parameters for arsenic, antimony, and bismuth.

Chemical symbol	T (°K)	c_H (Å)	a_H (Å)	c_H/a_H	$2v$
As[a]	Room	10.54	3.762	2.803	0.452
Sb[b]	4.2	11.222	4.3007±0.0002	2.6093±0.0003	0.46724±0.00004
	78	11.232	4.3012±0.0002	2.6114±0.0003	0.46728±0.00004
	298	11.274	4.3084±0.0002	2.6167±0.0003	0.46698±0.00013[c]
Bi[d]	4.2	11.807	4.5333±0.0005	2.6044±0.0002	0.46812±0.00003
	78	11.818	4.5345±0.0005	2.6062±0.0003	0.46801±0.00003
	296±2				0.4680 ±0.0002
	304	11.862	4.5461±0.0002	2.6091±0.0002	

[a] From Pearson (reference 2).
[b] From Barrett, Cucka, and Haefner (reference 6).
[c] This tolerance estimated by the authors using data from reference 6.
[d] From Barrett (reference 7).

$(6)^{1/2}$ correspond to rhombohedral angles of 90° and 60°, that is, to situations in which the total structure may be thought of as body-centered cubic and simple cubic, respectively. The null values taken by F_M at these points are to be expected from the high symmetry of the lattice.

Some interesting relationships which extend the utility of Tables II and III are deducible from the nature of the crystal structure. The first of these is based upon the fact that a simple rhombohedral lattice is equivalent to a body-centered rhombohedral lattice with c_H twice as great. Letting F stand for either F_M or F_Q, one has

$$F_{\mathrm{I}}(c_H/a_H)=F_{\mathrm{total}}(2c_H/a_H). \tag{2.1}$$

Similar considerations make it possible to calculate the EFG produced by ions at the rhombohedral positions $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ or $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ from data already available. If these two sites are designated III and IV, respectively, then for the quantities considered here it follows that

$$F_{\mathrm{III}}(c_H/a_H)=F_{\mathrm{IV}}(c_H/a_H)=\tfrac{1}{2}F_{\mathrm{II}}(\tfrac{1}{2}c_H/a_H). \tag{2.2}$$

The second type of calculation applies specifically to the three elements arsenic, antimony, and bismuth. The

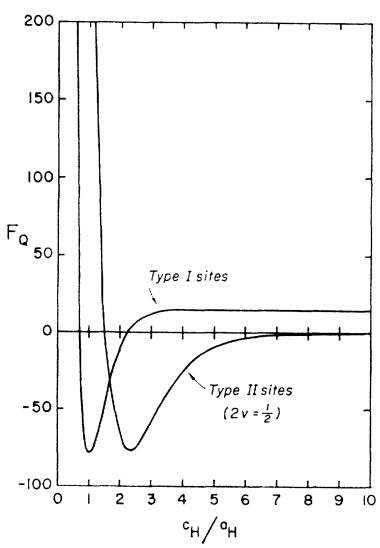

FIG. 2. Graphical presentation of $F_{Q,\mathrm{I}}$ and $F_{Q,\mathrm{II}}$ as functions of c_H/a_H.

TABLE V. Values (calculated from the ionic model) of a_H^3 times the axial electric field gradient per unit monopole moment for the elements antimony and bismuth.

c_H/a_H	$F_{M,\mathrm{I}}$	$2v$	$F_{M,\mathrm{II}}$
2.59	−0.412932	0.4655	−0.301554
		0.4660	−0.269320
		0.4665	−0.237519
		0.4670	−0.206154
		0.4675	−0.175225
		0.4680	−0.144736
		0.4685	−0.114687
		0.4690	−0.085080
		0.4695	−0.055916
2.60	−0.442362	0.4655	−0.249923
		0.4660	−0.217532
		0.4665	−0.185578
		0.4670	−0.154062
		0.4675	−0.122986
		0.4680	−0.092351
		0.4685	−0.062159
		0.4690	−0.032411
		0.4695	−0.003110
2.61	−0.471777	0.4655	−0.198589
		0.4660	−0.166046
		0.4665	−0.133941
		0.4670	−0.102278
		0.4675	−0.071056
		0.4680	−0.040279
		0.4685	−0.009947
		0.4690	0.019938
		0.4695	0.049374
2.62	−0.501174	0.4655	−0.147556
		0.4660	−0.114863
		0.4665	−0.082611
		0.4670	−0.050803
		0.4675	−0.019440
		0.4680	0.011477
		0.4685	0.041946
		0.4690	0.071965
		0.4695	0.101533
2.63	−0.530550	0.4655	−0.096826
		0.4660	−0.063986
		0.4665	−0.031591
		0.4670	0.000358
		0.4675	0.031860
		0.4680	0.062913
		0.4685	0.093516
		0.4690	0.123666
		0.4695	0.153363

TABLE VI. Values (calculated from the ionic model) of a_H^5 times the axial electric field gradient per unit axial quadrupole moment for the elements antimony and bismuth.

c_H/a_H	$F_{Q,\mathrm{I}}$	$2v$	$F_{Q,\mathrm{II}}$
2.59	7.9951	0.4655	−64.4018
		0.4660	−64.6607
		0.4665	−64.9149
		0.4670	−65.1645
		0.4675	−65.4096
		0.4680	−65.6501
		0.4685	−65.8860
		0.4690	−66.1175
		0.4695	−66.3446
2.60	8.1567	0.4655	−64.3013
		0.4660	−64.5561
		0.4665	−64.8063
		0.4670	−65.0520
		0.4675	−65.2931
		0.4680	−65.5297
		0.4685	−65.7618
		0.4690	−65.9895
		0.4695	−66.2128
2.61	8.3149	0.4655	−64.1951
		0.4660	−64.4459
		0.4665	−64.6921
		0.4670	−64.9338
		0.4675	−65.1710
		0.4680	−65.4037
		0.4685	−65.6319
		0.4690	−65.8558
		0.4695	−66.0753
2.62	8.4696	0.4655	−64.0836
		0.4660	−64.3303
		0.4665	−64.5724
		0.4670	−64.8101
		0.4675	−65.0433
		0.4680	−65.2721
		0.4685	−65.4965
		0.4690	−65.7165
		0.4695	−65.9323
2.63	8.6211	0.4655	−63.9667
		0.4660	−64.2093
		0.4665	−64.4474
		0.4670	−64.6810
		0.4675	−64.9103
		0.4680	−65.1351
		0.4685	−65.3556
		0.4690	−65.5718
		0.4695	−65.7838

structure parameters given in Table IV for these substances were obtained, respectively, from Pearson[2]; from Barrett, Cucka, and Haefner[6]; and from Barrett.[7] Since such parameters are always subject to determination at new temperatures, the authors chose (in the cases of antimony and bismuth) to present accurately calculated results in the form of Tables V and VI which cover a substantial range of parameter values. The grain size of these tables was selected so that three or four figure accuracy can be obtained by linear interpolation, and accuracy equal to that of the entries themselves, by methods employing second differences. Fortunately, the structure parameters of antimony and bismuth are very similar, so that one set of tables suffices for both. Since the parameters for arsenic are relatively poorly known, only single rough values of F_M and F_Q are given for this substance. Table VII summarizes the specific results obtained for the three materials.

[6] C. S. Barrett, P. Cucka, and K. Haefner (to be published).
[7] C. S. Barrett, Australian J. Phys. 13, 209 (1960).

III. METHOD OF CALCULATION

The method employed here is that reported by Hewitt and Taylor,[3] which involves a summation over reciprocal lattice vectors **h**. If $A(\mathbf{h})$ denotes the Fourier coefficient of a charge density corresponding to a lattice of monopoles in a uniform compensating background, then

$$C_2^0/B_0^0 = -(4\pi/3)\sum_{\mathbf{h}} [A(\mathbf{h})/B_0^0] \times \Lambda_{n+5/2}(2\pi h r_1) P_2(\cos\theta_{\mathbf{h}}). \quad (3.1)$$

The quantity C_2^0/B_2^0 is calculated with the aid of an equivalence derived by Taylor[4]:

$$C_2^0/B_2^0 = 6C_4^0/B_0^0, \quad (3.2)$$

and C_4^0/B_0^0 can be calculated from the same set of Fourier coefficients used in (3.1). Thus

$$C_4^0/B_0^0 = (4\pi/105)\sum_{\mathbf{h}} [A(\mathbf{h})/B_0^0](2\pi h)^2 \times \Lambda_{n+9/2}(2\pi h r_1) P_4(\cos\theta_{\mathbf{h}}). \quad (3.3)$$

The $\Lambda_\nu(z)$ function which appears above is equivalent to $\Gamma(1+\nu)(2/z)^\nu J_\nu(z)$, and n is an arbitrary non-negative integer (see reference 3). The quantity r_1 is a parameter with the dimensions of length and may be set equal to any distance less than r_0, the nearest neighbor distance, without affecting the final result. Quantities such as real space distance, reciprocal space distance, and $\cos\theta_{\mathbf{h}}$, which are geometrical in character, are derived in a general fashion in this section with detailed formulas reserved for appendixes.

Since both the rhombohedral and the hexagonal systems involve nonorthogonal coordinates, the language of generalized coordinate transformations, including tensor notation, is useful. Let $\mathbf{a}_j$, $j=1, 2, 3$, be the primitive translation vectors of a given crystal lattice and let $\mathbf{b}^k$, $\mathbf{b}^k\cdot\mathbf{a}_j=\delta_j^k$, be the primitive translation vectors of the corresponding reciprocal lattice.[8] The writing of a displacement vector **r** as a linear combination of the vectors $\mathbf{a}_j$ is equivalent to a coordinate transformation between the components of **r** in the rectangular system and the components of **r** in a system defined by the $\mathbf{a}_j$ basis, that is, in the crystal system. In what follows, **r** is written in terms of its contravariant components r^i in the rectangular system or u^i in the crystal system, and a reciprocal vector **h**, in terms of its covariant components h_j in the rectangular system or p_j in the crystal system. The usual summation convention is used, and the transformation from one system to the other and vice versa is effected through tensors com-

[8] C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 49.

TABLE VII. Specific results obtained for the elements arsenic, antimony, and bismuth. Values for arsenic were specially calculated; values for antimony and bismuth were interpolated from Tables V and VI. Central values of structure parameters (without tolerances) from Table IV were employed.

Chemical symbol	T (°K)	$F_{M,\mathrm{I}}$	$F_{M,\mathrm{II}}$	$F_{M,\mathrm{total}}$	$F_{Q,\mathrm{I}}$	$F_{Q,\mathrm{II}}$	$F_{Q,\mathrm{total}}$
As	Room	−1.033	−0.388	−1.421	10.78	−55.01	−44.23
Sb	4.2	−0.46972	−0.09086	−0.56058	8.304	−65.057	−56.753
	78	−0.47589	−0.07750	−0.55339	8.337	−65.050	−56.713
	298	−0.49148	−0.06902	−0.56050	8.419	−64.842	−56.423
Bi	4.2	−0.45531	−0.06210	−0.51741	8.227	−65.531	−57.304
	78	−0.46060	−0.05942	−0.52002	8.255	−65.457	−57.202
	304	−0.4691	−0.0450	−0.5141	8.30	−65.42	−57.12

posed of the rectangular components of the primitive translation vectors. Thus

$$r^k = u^i a_j{}^k; \quad u^i = r^k b^i{}_k; \tag{3.4}$$

$$h_j = p_k b^k{}_j; \quad p_k = h_j a_k{}^j. \tag{3.5}$$

Evidently u^i and p_j are dimensionless, and, for vectors from the origin to lattice points, they are integers. The "first unit cell" of the crystal is here understood to mean the cell in which $0 \leqslant u^i < 1$ for all j; in this cell, the u^i are equivalent to the usual triads of numbers employed to designate crystallographic positions. Summation over $\mathbf{h}$ as required in (3.1) and (3.3) amounts to a summation over integral values of p_1, p_2, and p_3.

Distances in real space or reciprocal space are obtained from appropriate metric tensors. Thus $r^2 = g_{jk} u^i u^k$ and $h^2 = g^{ik} p_j p_k$, where

$$g_{jk} = a_j{}^m a_k{}^n \delta_{mn}; \tag{3.6}$$

$$g^{ik} = b^i{}_m b^k{}_n \delta^{mn}. \tag{3.7}$$

Since $\cos\theta_{\mathbf{h}} = h_3/h$,

$$\cos\theta_{\mathbf{h}} = p_k b^k{}_3 [g^{ik} p_j p_k]^{-1/2}. \tag{3.8}$$

For a lattice of point charges in a uniform compensating background, the Fourier coefficient becomes proportional to the crystal structure factor, that is, to a sum over terms of the form $\exp(-2\pi i \mathbf{h}\cdot\mathbf{r}_n)$ where $\mathbf{r}_n$ is the displacement vector from the origin to the nth ion within the first unit cell. The dot product is an invariant equal to $h_j(r_n)^j$ or to $p_j(u_n)^j$, and the Fourier coefficient may be written

$$\begin{aligned} A(\mathbf{h}) &= 0, & \mathbf{h} &= 0; \\ &= B_0{}^0 \tau_0{}^{-1} \sum_{n=1}^{N} \exp[-2\pi i p_j (u_n)^j], & \mathbf{h} &\neq 0. \end{aligned} \tag{3.9}$$

where N is the total number of ions in the first unit cell and τ_0 is the volume of that cell. The latter is given by

$$\tau_0 = |a_j{}^k|. \tag{3.10}$$

Specific derivations for the rhombohedral and the hexagonal structures are listed in Appendixes A and B, respectively.

IV. CHECKING PROCEDURES

The results given in Tables II, III, V, and VI were subjected to three checking procedures.

(1) As indicated earlier, the number n in Eqs. (3.1) and (3.3) may be set equal to any non-negative integer. All entries in the tables mentioned were recalculated with a changed value of n and the results compared. Agreement extended to three or four more figures than are actually quoted in the tables.

(2) The asymptotic forms of F_M and F_Q as c_H/a_H tends to zero or to infinity were calculated by summations in real space and were found consonant with the entries in Tables II and III. As c_H/a_H tends to zero, the lattice reduces effectively to a single line of point sources and the sum becomes related to a value of the Riemann zeta function. As c_H/a_H tends to infinity, on the other hand, the lattice reduces to a planar distribution of point sources. Summation over these leads to the following:

$$F_{M,\mathrm{I}} \to F_{M,\mathrm{total}} \to -11.0341754; \tag{4.1}$$

$$F_{Q,\mathrm{I}} \to F_{Q,\mathrm{total}} \to 15.21427168. \tag{4.2}$$

The result of (4.1) was calculated by van der Hoff and

TABLE VIII. Values of $a_j{}^k/a_R$ for the rhombohedral unit cell.

k	$j=1$	$j=2$	$j=3$
1	$\sin\theta$	$-\frac{1}{2}\sin\theta$	$-\frac{1}{2}\sin\theta$
2	0	$\frac{1}{2}\sqrt{3}\sin\theta$	$-\frac{1}{2}\sqrt{3}\sin\theta$
3	$\cos\theta$	$\cos\theta$	$\cos\theta$

TABLE IX. Values of $a_R b^i{}_k$ for the rhombohedral unit cell.

k	$j=1$	$j=2$	$j=3$
1	$\frac{2}{3}\csc\theta$	$-\frac{1}{3}\csc\theta$	$-\frac{1}{3}\csc\theta$
2	0	$\frac{1}{3}\sqrt{3}\csc\theta$	$-\frac{1}{3}\sqrt{3}\csc\theta$
3	$\frac{1}{3}\sec\theta$	$\frac{1}{3}\sec\theta$	$\frac{1}{3}\sec\theta$

Benson[9]; that of (4.2), by the authors. The reasonableness of these forms, especially in the latter case where the interaction is of shorter range and the asymptotic value more quickly approached, is clearly discernible.

(3) All quantities in Tables II, III, V, and VI were calculated using the hexagonal description of the crystal structure. In a representative number of cases, however, the calculations were also performed using the rhombohedral description. Agreement of the same order as that mentioned in paragraph (1) above was reached.

APPENDIX A: THE RHOMBOHEDRAL UNIT CELL

The rhombohedral unit cell is characterized by a single length parameter a_R and by the angle α between any two $\mathbf{a}_j$ vectors. Each $\mathbf{a}_j$ vector makes an angle θ with the z axis, where

$$\cos\theta=[(1+2\cos\alpha)/3]^{1/2}, \tag{A1}$$

and the vector $\mathbf{a}_1$ lies in the xz plane. Components of the tensors $a_j{}^k$ and $b^j{}_k$ are obtainable from Tables VIII and IX respectively. Metric expressions for displacements from the origin to points in real space and in reciprocal space are given, respectively, as follows:

$$r^2=a_R{}^2\{[(u^1)^2+(u^2)^2+(u^3)^2][1-\cos\alpha]+[u^1+u^2+u^3]^2\cos\alpha\}; \tag{A2}$$

$$h^2=\{a_R{}^2(1-\cos\alpha)(1+2\cos\alpha)\}^{-1}\{[p_1{}^2+p_2{}^2+p_3{}^2]\times[1+2\cos\alpha]-[p_1+p_2+p_3]^2\cos\alpha\}. \tag{A3}$$

Other useful quantities are

$$\cos\theta_{\mathbf{h}}=(p_1+p_2+p_3)/ha_R[3(1+2\cos\alpha)]^{1/2}; \tag{A4}$$

$$\tau_0=a_R{}^3(1-\cos\alpha)[1+2\cos\alpha]^{1/2}. \tag{A5}$$

The Fourier coefficients for a lattice of ions at type I sites and for $\mathbf{h}\neq 0$ are given by

$$A_{\mathrm{I}}(\mathbf{h})=B_0{}^0\tau_0{}^{-1}; \tag{A6}$$

for a lattice of ions at type II sites and $\mathbf{h}\neq 0$,

$$A_{\mathrm{II}}(\mathbf{h})=A_{\mathrm{I}}(\mathbf{h})\exp[-4\pi iv(p_1+p_2+p_3)]. \tag{A7}$$

APPENDIX B: THE HEXAGONAL UNIT CELL

The hexagonal unit cell is characterized by the lattice parameters a_H, a_H, and c_H; the vector $\mathbf{a}_1$ is taken to lie along the x axis. Components of the tensors $a_j{}^k$ and $b^j{}_k$ are obtainable from Tables X and XI, respectively.

[9] B. M. E. van der Hoff and G. C. Benson, Can. J. Phys. **31**, 1087 (1953).

TABLE X. Values of $a_j{}^k/a_H$ for the hexagonal unit cell.

k	$j=1$	$j=2$	$j=3$
1	1	$-\frac{1}{2}$	0
2	0	$\frac{1}{2}\sqrt{3}$	0
3	0	0	c_H/a_H

TABLE XI. Values of $a_H b^j{}_k$ for the hexagonal unit cell.

k	$j=1$	$j=2$	$j=3$
1	1	0	0
2	$\frac{1}{3}\sqrt{3}$	$\frac{2}{3}\sqrt{3}$	0
3	0	0	a_H/c_H

Metric expressions for displacements from the origin to points in real space and in reciprocal space are given respectively as follows:

$$r^2=a_H{}^2[(u^1)^2-u^1u^2+(u^2)^2]+c_H{}^2(u^3)^2; \tag{B1}$$

$$h^2=[4/3a_H{}^2][p_1{}^2+p_1p_2+p_2{}^2]+p_3{}^2/c_H{}^2. \tag{B2}$$

Other useful quantities are

$$\cos\theta_{\mathbf{h}}=p_3/hc_H; \tag{B3}$$

$$\tau_0=a_H{}^2c_H\sqrt{3}/2. \tag{B4}$$

The Fourier coefficients for a lattice of ions at type I sites and for $\mathbf{h}\neq 0$ are given by either of the following equivalent expressions:

$$A_{\mathrm{I}}(\mathbf{h})=B_0{}^0\tau_0{}^{-1}\{1+\exp[-2\pi i(\tfrac{2}{3}p_1+\tfrac{1}{3}p_2+\tfrac{1}{3}p_3)]+\exp[-2\pi i(\tfrac{1}{3}p_1+\tfrac{2}{3}p_2+\tfrac{2}{3}p_3)]\}; \tag{B5}$$

$$A_{\mathrm{I}}(\mathbf{h})=3B_0{}^0\tau_0{}^{-1},\quad \text{if 3 divides } (p_2-p_1+p_3),$$
$$=0,\quad \text{if 3 does not divide } (p_2-p_1+p_3). \tag{B6}$$

The Fourier coefficients for a lattice of ions at type II sites and for $\mathbf{h}\neq 0$ are

$$A_{\mathrm{II}}(\mathbf{h})=A_{\mathrm{I}}(\mathbf{h})\exp(-4\pi ivp_3). \tag{B7}$$

APPENDIX C: TRANSFORMATION BETWEEN RHOMBOHEDRAL AND HEXAGONAL UNIT CELLS

The following formulas were found useful and are included for reference:

$$a_H=a_R 2\sin(\alpha/2); \tag{C1}$$

$$(c_H/a_H)=[3(1+2\cos\alpha)/2(1-\cos\alpha)]^{1/2}; \tag{C2}$$

$$\cos\alpha=[2(c_H/a_H)^2-3]/[2(c_H/a_H)^2+6]. \tag{C3}$$