the experimental points seems satisfactory, considering that both the area and γ were assumed to remain constant. This agreement would seem to indicate the reasonableness of the space charge explanation of the negative characteristics. The lowering of the breakdown voltage is also given by the calculations with reasonable accuracy.

At the largest experimentally measured current, the field at the cathode is calculated to be seven percent higher than the average applied field. Thus, for the currents for which experimental data are available, the E/p values are well within the region for which Eq. (3), with the values of the constants A and B as used, is valid, namely $18 < E/p < 22$ volt (cm mm Hg)$^{-1}$.

Although the assumed discharge area for the calcu-

lations is 17 cm², the illuminated area (image of the arc) of the cathode was only about 10 cm², but this is a lower limit if the possibility of reflections of ultraviolet light from the anode and walls onto the cathode is considered. The previously mentioned glow covering the entire anode suggests possibly a much larger discharge area. The calculations are not too sensitive to the precise area chosen. This may be seen in Fig. 4 where calculations are shown for the largest value of I_0 for 34 as well as for 17 cm². Taking all of the above factors into consideration, 17 cm² is not an unreasonable area to assume, although the proper value is somewhat uncertain. In fact, it seems reasonable to assume that the effective discharge area varies somewhat with current even below breakdown.

Cubic Field Splitting of D Levels in Metals

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The splitting of the fivefold degeneracy of free atom d electron states by nonspherical components of a crystalline field is calculated. The crystal potential employed is that of a lattice of positive point charges screened by a uniform distribution of electrons. The calculation is done to first order in the cubic field, using hydrogenic electron wave functions. The triply degenerate d state is lowered with respect to the doubly degenerate one in both body-centered and face-centered cubic lattices. Numerical results are given for both lattices. Finally, analytic atomic wave functions are used to estimate the splitting in iron and copper at the observed lattice spacing. The crystal field splitting of these levels is found to be much smaller than the overlap splitting as obtained in previous calculations for both materials.

I. INTRODUCTION

IN a recent calculation, perturbation theory was used to study d bands in the body-centered cubic lattice.[1] The crystal potential employed was that produced by a lattice of point charges of atomic number Z and lattice parameter a, screened by a uniform distribution of valence electrons. The energy of an electron state in this potential can be expressed as (atomic units throughout)

$$E = (Z/a)f(Za)$$

where $f(Za)$ is a function proportional to $(Za)^{-1}$ for small Za. The parameter Za is a measure of the tightness of the binding, and the perturbation calculation reported contained the first three terms in the expansion of the function $f(Za)$ for certain interesting states. The calculation could only be expected to be valid for

small Za, but the apparent behavior of the series for large Za led to the conjecture that the d bands in this limit would split into two sub-bands. Within the model considered, such a split could arise only from the departure of the crystal potential around a lattice site from spherical symmetry.

The situation is similar in many respects to that considered in crystal field theory, in which the presence of cubic terms in the crystal potential produces a split of the fivefold degeneracy of the d states of a single electron into a triply degenerate state T_{2g} and a doubly degenerate state E_g.[2] We estimate this splitting for a metal. The calculation, which utilizes the ideas of the tight-binding approximation, considers the potential produced by the lattice of point charges previously mentioned; it can probably be generalized to more complicated situations.

To understand the physical situation in more detail,

[1] J. Callaway, Phys. Rev. **115**, 346 (1959). For a review of energy band calculations, see J. Callaway in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7.

[2] A recent review of crystal field theory is given by W. Moffitt and C. J. Ballhausen, Ann. Revs. Phys. Chem. **7**, 107 (1956).

consider a hypothetical cubic metal with both s and d electrons, such that the s electrons are distributed reasonably uniformly throughout the atomic cell, but the d electrons are rather tightly bound so that d wave functions on the atomic sites overlap only slightly. The degeneracy of the d levels of the isolated atom would be broken both by the overlaps of the wave functions and by the nonspherical components of the crystal field. For very tightly bound d functions, we would expect the crystal field splitting to be large compared to the overlap splitting. The d levels would then form two sub bands. This is essentially the model which Mott and Stevens[3] have proposed for the body-centered transitions metals. One of the principal reasons for undertaking this calculation was to determine whether the Mott-Stevens model could reasonably be expected to apply to iron. None of the existing energy band calculations for iron supports the Mott-Stevens model[1]; however, all the calculations have neglected crystal field effects.

One of the problems in a tight-binding calculation of energy bands is to determine the expectation value of the crystal potential using atomic wave functions on a single site. This quantity, which is often considered to be the same for all the states in the band, actually contains the crystal field effects in which we are interested. If for simplicity we consider hydrogenic d electron radial wave functions:

$$R_d = (\alpha^7/6!)^{\frac{1}{2}} r^2 e^{-\frac{1}{2}\alpha r} \qquad (1)$$

the appropriate dimensionless parameter characterizing the physical situation is αa ($\alpha = 2Z/3$ for a Coulomb potential). We will later be able to obtain the crystal field splitting for more general wave functions consisting of sums of terms of this form. Large values of αa correspond to small overlap and tight binding. While both the overlap splitting and the cubic field splitting go to zero as $\alpha a \to \infty$, the overlap splitting goes exponentially while the cubic field depends on $(\alpha a)^{-4}$ as we will show. Thus, for sufficiently large αa the cubic field will dominate.

The problem of crystal field effects in metals has previously been discussed by Leigh.[4] He considered a similar model of the crystal potential, but quite different wave functions. He estimated d band splittings at the observed interatomic spacing only, in iron and copper. The present calculation is of greater generality.

This calculation also contains substantial improvements with respect to conventional crystal field studies which are made possible by the use of a simple model of the crystal potential. We use an expression for the potential which is exact for this model, and do not restrict ourselves to a multipole expansion valid only at distances from the central atom less than the nearest neighbor distance. The use of simple radial functions

makes it possible to obtain explicit expressions for all radial integrals, which are conventionally regarded as parameters to be determined from experimental data. Finally, we have evaluated all the pertinent lattice sums.

II. THEORY

The use of a simple lattice model and approximate d electron wave functions permits us to estimate the cubic field effects for a large range of the appropriate parameters. To be precise, we wish to calculate the difference in the energies of the d states of $\Gamma_{25'}$ (xy, yz, zx) symmetry and those of Γ_{12} symmetry (x^2-y^2, $3z^2-r^2$)[5] (t_{2g} and e_g respectively in another notation), of a single electron in a potential field produced by a lattice of positive point charges (atomic number Z) screened by a uniform distribution of electrons so that each cell is electrically neutral. The calculation is the first order in the cubic field only. Spin-orbit coupling is neglected. We define

$$\Delta E = E(\Gamma_{25'}) - E(\Gamma_{12}) = \int \left[|\psi(\Gamma_{25'})|^2 \right.$$
$$\left. - |\psi(\Gamma_{12})|^2 \right] V(\mathbf{r}) d\tau. \qquad (2)$$

ΔE defined by (2) is the negative of the quantity called $10 \, Dq$ in the literature of crystal field theory. We put

$$\psi(\Gamma_{25'}) = R_d(r) \mathcal{K}_{2,25'}(\theta,\phi),$$
$$\psi(\Gamma_{12}) = R_d(r) \mathcal{K}_{2,12}(\theta,\phi), \qquad (3)$$

where R_d is given by (1) and $\mathcal{K}_{l,i}$ functions are the appropriate kubic harmonics[6] (order l and representation Γ_i). For example we have

$$\mathcal{K}_{2,25'} = \left(\frac{15}{4\pi}\right)^{\frac{1}{2}} \frac{xy}{r^2}; \quad \mathcal{K}_{2,12} = \frac{1}{2}\left(\frac{15}{4\pi}\right)^{\frac{1}{2}} \frac{(x^2-y^2)}{r^2}. \qquad (4)$$

Then

$$\Delta E = \int R_d{}^2(r) [\mathcal{K}^2{}_{2,25'}(\theta,\phi) - \mathcal{K}^2{}_{2,12}(\theta,\phi)] V(\mathbf{r}) d\tau. \qquad (5)$$

Since $V(\mathbf{r})$ belongs to the completely symmetric (Γ_1) representation of the cubic point group, it follows that if $V(\mathbf{r})$ is expanded in kubic harmonics, the only ones which appear are the $\mathcal{K}_{l,1}$. From the orthonormality properties of the spherical harmonics it follows we need only consider coefficients of $\mathcal{K}_{4,1}$.

$$\mathcal{K}_{4,1} = \frac{5}{4}\left(\frac{21}{4\pi}\right)^{\frac{1}{2}} \left(\frac{x^4+y^4+z^4}{r^4} - \frac{3}{5}\right). \qquad (6)$$

[3] N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957).
[4] R. S. Leigh, Proc. Phys. Soc. (London) **71**, 33 (1958).

[5] Notation according to L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).
[6] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

We then deduce

$$\Delta E = -\frac{5}{2(21\pi)} \int R_d{}^2(r)\mathcal{K}_{4,1}(\theta,\phi)V(\mathbf{r})d\tau. \quad (7)$$

We use the Fourier series expression for $V(\mathbf{r})$

$$V(\mathbf{r}) = \sum b(\mathbf{K}_n) \exp(i\mathbf{K}_n \cdot \mathbf{r}), \quad (8)$$

where $\mathbf{K}_n$ is a reciprocal lattice vector,

$$\mathbf{K}_n = (2\pi/a)(n_1,n_2,n_3),$$
$$b(\mathbf{K}_n) = -8\pi Z/\Omega_0 \mathbf{K}_n{}^2 = -2Za^2/\pi\Omega_0\mathbf{n}^2. \quad (9)$$

Ω_0 is the volume of the unit cell.

In evaluating (7) we make use of the fact that the kubic harmonics are linear combinations of spherical harmonics of order l; for example,

$$\mathcal{K}_{4,1} = (7/12)^{\frac{1}{2}}[Y_{40} + (5/14)^{\frac{1}{2}}(Y_{44}+Y_{4-4})], \quad (10)$$

where the Y_{lm} are normalized spherical harmonics as given, for example, by Bethe and Salpeter.[7] Also, the Fourier transform of a spherical harmonic is proportional to the same spherical harmonic in k space:

$$\int e^{i\mathbf{k}\cdot\mathbf{r}} Y_{lm}(\theta,\phi)d\Omega = 4\pi i^l j_l(kr) Y_{lm}(\theta_k,\phi_k) \quad (11)$$

where k, θ_k, ϕ_k are the spherical polar components of $\mathbf{k}$. Thus if we substitute (8) into (7) and perform the integration over solid angle, we obtain

$$\Delta E = -10(\pi/21)^{\frac{1}{2}} \sum b(\mathbf{K}_n)\mathcal{K}_{4,1}(\theta_k,\phi_k)$$
$$\times \int R_d{}^2(r)j_4(kr)r^2dr. \quad (12)$$

The radial integral can be done for the radial d function given by (1):

$$\int r^6 e^{-\alpha r} j_4(kr)dr = \frac{32(5!)\alpha}{k^8(1+\alpha^2/k^2)^6}. \quad (13)$$

If we substitute (13) and (9) into (12), we find after some rearrangement

$$\Delta E = \frac{1280}{3}\frac{\pi Z}{\Omega_0\alpha^4}\left(\frac{\pi}{21}\right)^{\frac{1}{2}} \sum \frac{\mathbf{K}_n{}^2}{(1+\mathbf{K}_n{}^2/\alpha^2)^6}\mathbf{K}_{4,1}(\theta_k,\phi_k). \quad (14)$$

Some further simplification is possible using (9) and the explicit representation of the kubic harmonics. The type of lattice (body-centered cubic or face-centered cubic) is involved in (14) through the expression giving the cell volume in terms of the lattice parameter and in the choice of reciprocal lattice vectors $\mathbf{K}_n$. For the body-centered lattice $(\Omega_0 = a^3/2)$,

[7] H. A. Bethe and E. Salpeter in *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1957), Vol. 35, p. 91.

we have finally

$$\Delta E = \frac{400}{3\pi}\frac{Z}{a}\left(\frac{2\pi}{\alpha a}\right)^4 \sum \frac{\mathbf{n}^2}{(1+4\pi^2\mathbf{n}^2/\alpha^2 a^2)^6}$$
$$\times \left(\frac{n_1{}^4+n_2{}^4+n_3{}^4}{\mathbf{n}^4} - \frac{3}{5}\right) \quad (15)$$

while for the face-centered lattice, the numerical coefficient is greater by a factor of two. The procedure used here may also be applied to more complicated crystal potentials by suitable choice of the coefficients $b(\mathbf{k}_n)$ in (8).

The series in (5) is not difficult to evaluate for moderate values of αa; however for large αa (say $\alpha a > 20$) the convergence of (15) is slow.

For large values of αa, it is necessary to transform the series to a more rapidly convergent form. This can be done in the following manner.

We define the function

$$f(\mathbf{h}) = \sum_{\mathbf{K}_n} g(\mathbf{h}-\mathbf{K}_n) \quad (16a)$$

where

$$g(\mathbf{h}) = \mathbf{h}^2(1+\mathbf{h}^2/\alpha^2)^{-6}\mathcal{K}_{4,1}(\theta_h,\phi_h). \quad (16b)$$

Then

$$\Delta E = \frac{1280}{3}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\frac{\pi Z}{\Omega_0\alpha^4}f(0). \quad (17)$$

$f(\mathbf{h})$ is periodic function of $\mathbf{h}$ and thus may be expanded in a Fourier series in the direct lattice.

$$f(\mathbf{h}) = \sum_{\mathbf{R}_n} a(\mathbf{R}_n) \exp(-i\mathbf{h}\cdot\mathbf{R}_n). \quad (18)$$

$\mathbf{R}_n$ is a direct lattice vector. The coefficients $a(\mathbf{R}_n)$ are given by

$$a(\mathbf{R}_n) = [\Omega_0/(2\pi)^3] \int f(\mathbf{h}) \exp(i\mathbf{h}\cdot\mathbf{R}_n)d\mathbf{h}. \quad (19)$$

With the use of (16), (19) may be expressed as

$$a(\mathbf{R}_n) = [\Omega_0/(2\pi)^3] \int_\infty g(\mathbf{h}) \exp(i\mathbf{h}\cdot\mathbf{R}_n)d\mathbf{h}. \quad (20)$$

Then using (11) and (16), we have

$$a(\mathbf{R}_n) = \frac{\Omega_0}{2\pi^2}\mathcal{K}_{4,1}(\theta_R,\phi_R) \int_0^\infty \frac{h^4 j_4(hR_n)}{(1+h^2/\alpha^2)^6}dh. \quad (21)$$

With the use of (15), we transform the integral over h to the form

$$\int_0^\infty \frac{h^4 j_4(hR)}{(1+h^2/\alpha^2)^6}dh = \frac{\alpha^{11}}{32(5!)}$$
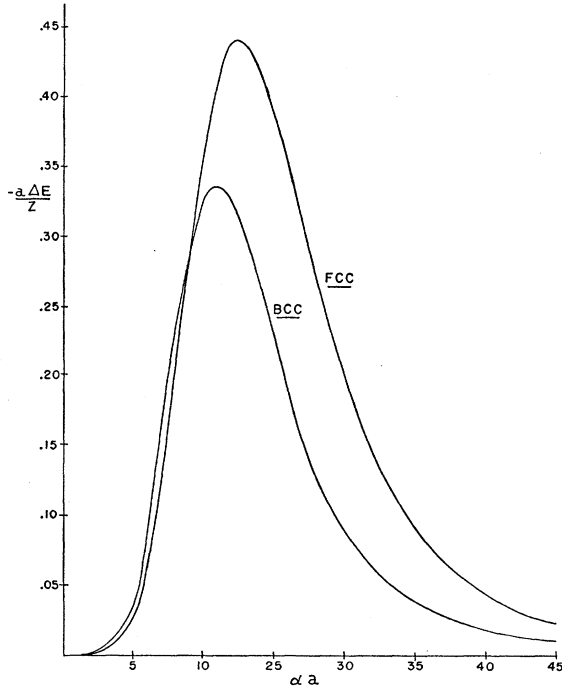$$\times \int_0^\infty \int_0^\infty r^6 e^{-\alpha r} j_4(hr) j_4(hR)dhdr.$$

FIG. 1. The cubic field splitting $a\Delta E/Z$ is shown for body-centered cubic and face-centered cubic lattices, based on the numerical data of Table I.

This integral over h can now be done,[8] leaving an elementary integral over r. We obtain

$$\frac{\pi \alpha^{11}}{576(5!)}\left(R^{-5}\int_0^R r^{10}e^{-\alpha r}dr + R^4 \int_R^\infty re^{-\alpha r}dr \right)$$

$$=\frac{105\pi}{2R^5}[1-\Phi(\alpha R)]; \quad \Phi(x)=e^{-x}\left[\sum_{s=0}^{8}\frac{x^s}{s!}+\frac{9x^9}{10!}\right].$$

But, from (17) and (18)

$$\Delta E=\frac{1280}{3}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\frac{\pi Z}{\Omega_0\alpha^4}\sum a(\mathbf{R}_n)$$

$$=\frac{11\,200Z}{a^5\alpha^4}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\sum\left(\frac{a}{R_N}\right)^5 \mathcal{K}_{4,1}(\theta_R,\phi_R)[1-\Phi(\alpha R_N)]$$

where in the last line we have introduced the lattice parameter explicity. Then using (6) for $\mathcal{K}_{4,1}$ we finally have

$$\Delta E=\frac{7000}{(\alpha a)^4}\frac{Z}{a}\sum\left(\frac{a}{R_N}\right)^5[1-\Phi(\alpha R_n)]$$

$$\times(R_{N1}^4+R_{N2}^4+R_{N3}^4-\tfrac{3}{5}R_N^4)/R_N^4. \quad (24)$$

Since $\Phi(\alpha R_n)$ is an exponentially decreasing function,

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[8] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. II, p. 47.

for large αa we may write

$$\Delta E=\frac{7000}{(\alpha a)^4}\frac{Z}{a}\sum\left(\frac{a}{R_N}\right)^5$$

$$\times(R_{N1}^4+R_{N2}^4+R_{N3}^4-\tfrac{3}{5}R_N^4)/R_N^4. \quad (25)$$

Equation (25) may also be obtained more directly by a multipole expansion, as is shown in Appendix 1.

III. RESULTS

It is not necessary to employ sophisticated methods to evaluate the lattice sum in (25) unless great precision is desired. These sums have been carried out approximately for the body-centered and face-centered cubic lattices. The results are -2.131 and -5.163, respectively, with an accuracy of about ±0.003 in each case. Thus we have

$$a\Delta E/Z=-1.492\times10^4(\alpha a)^{-4} \text{ for the bcc,}$$
$$a\Delta E/Z=-3.614\times10^4(\alpha a)^{-4} \text{ for the fcc.} \quad (26)$$

Numerical results for the splitting $a\Delta E/Z$ are presented in Table I and shown graphically in Fig. 1, based on evaluation of (15) and (26). We can conclude that the cubic field splitting tends to lower the energies of functions of the type $\Gamma_{25'}$ with respect of those of Γ_{12} symmetry for all values of the relevant parameters.

A check on the numerical work is provided by the agreement between the values of $a\Delta E/Z$ computed for the bcc lattice for $(\alpha a)^2=12\pi^2$. The sum of the series (15), including 102 different reciprocal lattice vectors is a $aE/Z=-0.0653$. Equation (26) yields for this value of αa; -0.0664. The agreement is already quite good; and inclusion of the function $\Phi(\alpha R_n)$ in the lattice sum using Eq. (24) gave $aE/Z=-0.0653$. A similar agreement between (15) and (24) was found for the fcc lattice at $\alpha a=8\pi$.

It is possible to use these results to make a reasonable estimate of the contribution of the cubic field to the Γ_{25}, Γ_{12} separation in iron at the actual lattice spacing. Of course, d-electron wave functions are more complicated than the simple form (1), but it appears to be possible to express free atom d functions in the form

$$R_d=r^2\sum_i N_i e^{-\frac{1}{2}\alpha_i r}. \quad (27)$$

In recent calculations, four terms are included in the sum.[9,10]

ΔE can then be found as a sum of term of the form (15) or (26) provided the change in normalization of the basic functions is properly included. This calculation has been carried out for iron with two different electron wave functions: that found by Lowdin and Appel[9]; and the one determined for the average of all configurations based on d^8 by Watson.[10]

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[9] P. O. Lowdin and K. Appel, Phys. Rev. 103, 1746 (1956).

[10] R. E. Watson, Technical Report 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (June 15, 1959) (unpublished).

TABLE I. The cubic field splitting a $\Delta E/Z$ is given for body-centered cubic and face-centered cubic lattices as a function of αa. The evaluation is based on Eqs. (15) and (24) of the text. For values of αa greater than those given in the table, the simple formula of Eq. (26) will generally suffice.

$(\alpha a/2\pi)^2$	αa	$a\Delta E/Z$ (bcc)	$a\Delta E/Z$ (fcc)
0.0	0.000	−0.00000	−0.0000
0.5	4.443	−0.02351	−0.01245
1.0	6.283	−0.1187	−0.08174
1.5	7.695	−0.2228	−0.1867
2.0	8.886	−0.2938	−0.2873
3.0	10.883	−0.3344	−0.4110
4.0	12.566	−0.3034	−0.4391
5.0	14.050	−0.2538	−0.4146
6.0	15.391	−0.2063	−0.3695
8.0	17.771	−0.1353	−0.2748
10.0	19.869	−0.0918	−0.2011
12.0	21.766	−0.0653	−0.1493
16.0	25.133	−0.0373	−0.0886

We find $E=-0.094Z$ (ev) using the Lowdin function and $E=-0.128Z$ (ev) using the Watson function. The number of free electrons is contained as a parameter in the results, but it is probably reasonable to take $Z=1$. The difference of the results given is of significance only insofar as it indicates the sensitivity of the calculated splitting to the compactness of the wave functions. We can conclude that the cubic field splitting is of the order of $-0.1Z$ ev at the observed interatomic spacing. This would appear to be considerably smaller than the d bandwidth,[1] for any reasonable value of Z, and is in essential agreement with the result of Leigh, obtained in a cruder calculation.[4] These considerations do not support application of the Mott-Steven d-band model applied to iron.

We have also estimated ΔE for copper by the same procedure, using an analytic wave function for Cu⁺ from Lowdin and Appel. The result is a cubic field splitting $-0.03Z$ ev at the observed interatomic spacing. The splitting is smaller than in iron because of the greater compactness of the Cu⁺ wave functions.

APPENDIX

We give here a derivation of Eq. (25) based on the conventional multipole expansion of the crystal potential. This furnishes a check on the algebra involved in the derivation of that equation. The expansion can be obtained without difficulty, following the work of DeWette and Nijboer.[11] We note first that in the crystal model considered here the uniform distribution of negative charge can contribute only to the spherically symmetric part of the potential, so that we may consider only the point charges. Let these be located at lattice vectors R_λ. Then

$$V(\mathbf{r}) = -2Z \sum_\lambda |\mathbf{r} - \mathbf{R}_\lambda|^{-1} \qquad (A\text{-}1)$$

(except for the contribution from the negative charge).

[11] F. W. DeWette and B. R. A. Nijboer, Physica 24, 1105 (1958).

We use the expansion

$$|\mathbf{r} - R_\lambda|^{-1} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r^l}{R_\lambda^{l+1}}$$
$$\times Y_{lm}^*(\theta,\phi) Y_{lm}(\theta_R,\phi_R) \qquad (A\text{-}2)$$

which is valid for r smaller than the nearest neighbor distance. We are only interested in the part of the expansion involving $l=4$, which we call V_4. The lattice constant a is also introduced;

$$V_4 = -\frac{2Z}{a}\left(\frac{4\pi}{9}\right)\frac{r^4}{a^4} \sum_m \left[Y_{4m}^*(\theta,\phi) \sum_{R_\lambda} \left(\frac{a}{R_\lambda}\right)^5 \right.$$
$$\left. \times Y_{4m}(\theta_R,\phi_R) \right]. \qquad (A\text{-}3)$$

On account of the symmetry of the crystal, the sums in (20) must produce the kubic harmonic $\mathcal{K}_{4,1}$. It is found that

$$V_4 = -\frac{2Z}{a}\left(\frac{r}{a}\right)^4 \mathcal{K}_{4,1}(\theta,\phi)B \qquad (A\text{-}4)$$

where B is a numerical coefficient

$$B = \frac{4\pi}{9}\left(\frac{12}{7}\right)^{\frac{1}{2}} \sum_{R_\lambda} Y_{40}(\theta_R,\phi_R)\left(\frac{a}{R_\lambda}\right)^5. \qquad (A\text{-}5)$$

With the use of (A-4), the explicit representation of the radial function, and the orthonormality of the kubic harmonics, ΔE, as given by Eq. (7) may be evaluated:

$$\Delta E = \frac{2.52\times 10^4}{(21\pi)^{\frac{1}{2}}} \frac{BZ}{a(\alpha a)^4}. \qquad (A\text{-}6)$$

We must now evaluate B. Since the atoms are in "cubic" positions, the sum of Y_{40} over all the atoms of a given type [say those located at $R_\lambda = a(3,2,1)$] is proportional to the kubic harmonic $\mathcal{K}_{4,1}$. We find that

$$B = \frac{5}{18}(21\pi)^{\frac{1}{2}} \sum_{R_\lambda} \left(\frac{a}{R_\lambda}\right)^5$$
$$\times (R_1^4 + R_2^4 + R_3^4 - \tfrac{3}{5}R_\lambda^4)/R_\lambda^4. \qquad (A\text{-}7)$$

Equation (23) is substituted in (A-6) to obtain

$$\Delta E = \frac{7000}{(\alpha a)^4} \frac{Z}{a} \sum_{R_\lambda} \left(\frac{a}{R_\lambda}\right)^5$$
$$\times (R_1^4 + R_2^4 + R_3^4 - \tfrac{3}{5}R_\lambda^4)/R_\lambda^4. \qquad (A\text{-}8)$$

Equation (A-8) agrees exactly with (25) of the text.

If we replace Eq. (A-2) by the complete multipole expansion which has radial dependence R_λ^l/r^{l+1} for $r>R_\lambda$. we obtain, by a similar procedure, Eq. (24). This result demonstrates the complete equivalence of the procedures based on the Fourier series and on the multipole expansion of the crystal potential.