Computation of Mean Debye Temperature of Cubic Crystals from Elastic Constants. II

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Quimby and Sutton have presented, in an array of equations, an improved, accurate method for computing the mean Debye characteristic temperature of cubic crystals from the elastic constants. The present paper gives an equivalent, simplified, explicit equation. The pertinent integral is also expanded in a Taylor series to the fifth term by a special device and a method of getting the general term made evident. The first two terms of this series constitute Born's equation which is shown to be usually inaccurate since the series is slowly convergent. This series is useful, however, in estimating the correction to the simple equation first mentioned. This correction is analyzed in more detail and extended to values of the anisotropy factor less than unity. Graphs are given permitting rapid calculation of Debye temperatures with an uncertainty due to the approximation made in the method of about 0.1 percent.

INTRODUCTION

In a previous paper by Quimby and Sutton,[1] a method was presented for computing the mean Debye characteristic temperature, Θ_D, of cubic crystals from the elastic constants. It involves the evaluation of an integral

$$Y=\int_0^{4\pi}\left[\sum_i \frac{1}{(C+z_i)^{\frac{3}{2}}}\right]\frac{d\Omega}{4\pi}, \tag{1}$$

where $C=c_{44}/(c_{11}-c_{44})$, c_{jk} are the elastic constants, $d\Omega$ is an element of solid angle, and the z_i are the three real roots of a cubic equation. The z_i depend on the direction cosines for a given direction, α, β, γ, and on $K=(c_{12}+c_{44})/(c_{11}-c_{44})$.

An approximate formula for Y, denoted Y_R, is devised by Quimby and Sutton[1] by a modification of the method of Hopf and Lechner.[2] The function $f(z)=(C+z)^{-\frac{3}{2}}$ is represented by a fifth-degree polynomial $[f(z)]_R$ given by the expression

$$[f(z)]_R=a_0+a_1z+a_2z^2+a_3z^3+a_4z^4+a_5z^5, \tag{2}$$

and the a_i are so adjusted that the value of $[f(z)]_R$ coincides with that of $f(z)$ at six appropriately chosen values of z. Formulas are given for the a_i and a formula is given for Y_R in terms of these a_i. The error involved in the substitution of Y_R for Y in Eq. (1) is evaluated in terms of the anisotropy factor $A=2c_{44}/(c_{11}-c_{12})$ of the crystal, so that a suitable correction can be made.

The foregoing procedure is subject to improvement in two particulars. First, the considerable labor incident to the separate computation of the a_i can be eliminated, with no increase in the complexity of the resultant expression for Y_R. Second, the correction to Y_R in fact depends upon the values of C as well as of A. This circumstance is ignored in reference 1.

The usefulness of the method is further increased by extending the curves for the correction of Y_R to values of A less than unity.

[1] S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953).
[2] L. Hopf and G. Lechner, Verhandl. deut. physik. Ges. **16**, 643 (1914).

EXPLICIT FORM FOR Y_R

If the expressions for the a_i (reference 1) are substituted in the expression for Y_R and the result simplified, it is found that

$$Y_R=3m_0+\frac{1}{1155}\Big\{[12(15-2x)m_1+288m_2+1112.4m_3+825.6m_4+135m_5]+\frac{1}{c}[54(m_5-m_3)+576(m_4-m_2)]+\frac{54}{d}[m_1-m_3]+\frac{1036.8}{f}[m_3-m_4]+\frac{864}{g}[m_2-m_5]\Big\}, \tag{3}$$

where

$$\begin{aligned} m_0&=f(0), & c&=1-2x,\\ m_1&=f(1)-m_0, & d&=3-2x,\\ m_2&=f(x)-m_0, & f&=3-5x,\\ m_3&=f(2x/3)-m_0, & g&=3-7x,\\ m_4&=f(1-x)-m_0, & x&=(1-K)/2.\\ m_5&=f(1-4x/3)-m_0, & & \end{aligned}$$

Table I exhibits the variation of Y_R with x and C. The indicated range of values of x covers all the cubic crystals listed by Hearmon[3] with the exception of Na, K, and $NaClO_3$. C, for the cubic crystals listed by Hearmon,[3] ranges from 0.095 to 1.15 except for Na, K, and beta brass.

A correction to Eq. (3) is shown in Figs. 1 (a) and 1 (b). The method of deriving this correction is discussed in a later section.

The computation of a Debye temperature proceeds directly from the elastic constants by calculating C, K, and x. Equation (3) then yields Y_R. This value of Y_R may then be checked by comparing it with Table I. (Equation (3) must be used since interpolation using

[3] R. F. S. Hearmon, Revs. Modern Phys. **18**, 428 (1946).

Table I is of limited accuracy.) This value of Y_R is then corrected using Fig. 1. The estimation of position of curves of C intermediate to those shown rarely will introduce error over $\pm 0.3\%$ in final Y. The curves themselves may be in error by a like amount, so that the error in the computed mean Θ_D, stemming from the computation, may be about 0.2%.

TAYLOR'S SERIES EXPANSION OF Y

As an aid to the evaluation of the effect of C on the correction to Y_R, it is desired to expand Y in ascending powers of x. If $f(z)$ is represented by a polynomial of the nth degree, there are $n+1$ coefficients a_i to determine. Further, if, instead of forcing agreement with $f(z)$ at $n+1$ *different* points, it is required that

$$a_j=f^j(0)/j!,\ \sum_{i=i}^{n}\frac{i!a_i}{(i-j)!}=f^j(1),\ j=0,1,2\cdots m, \quad (4)$$

where $(m+1)\leq(n+1)/2$ and $f^j(z)$ denotes the jth derivative of $f(z)$, then an equation for Y results whose first $m+1$ terms in powers of x are identical with the first $m+1$ terms of the Taylor expansion for Y (see Appendix A).

The series, denoted Y_T, obtained in this manner is

$$\begin{aligned}Y_T=&[2C^{-\frac{3}{2}}+(C+1)^{-\frac{3}{2}}]-[(6/5)B]x\\&+[24B+150(C+1)^{-7/2}+105C^{-7/2}]\frac{x^2}{105}\\&-[-4176B+6000(C+1)^{-7/2}+4440C^{-7/2}\\&-25620(C+1)^{-9/2}+13335C^{-9/2}]\frac{x^3}{15015}\\&+[87072B-127200(C+1)^{-7/2}-90480C^{-7/2}\\&-146160(C+1)^{-9/2}+81900C^{-9/2}+523530(C+1)^{-11/2}\\&+206246.25C^{-11/2}]\frac{x^4}{255255}\cdots, \quad (5)\end{aligned}$$

where $B=C^{-5/2}-(C+1)^{-5/2}$. The first term is the term

TABLE I. Values of Y_R computed by using Eq. (3).

x \ C	0.25	0.50	0.75	1.0
−0.8				5.974
−0.7			21.887	4.614
−0.6			8.916	3.872
−0.5			6.515	3.391
−0.4		15.651	5.332	3.052
−0.3		10.444	4.605	2.802
−0.2	41.231	8.240	4.114	2.613
−0.1	22.508	6.990	3.765	2.466
0	16.716	6.201	3.511	2.354
+0.1	13.968	5.677	3.325	2.267
+0.2	12.461	5.324	3.191	2.203
+0.3	11.608	5.093	3.099	2.158
+0.4	11.128	4.959	3.058	2.131

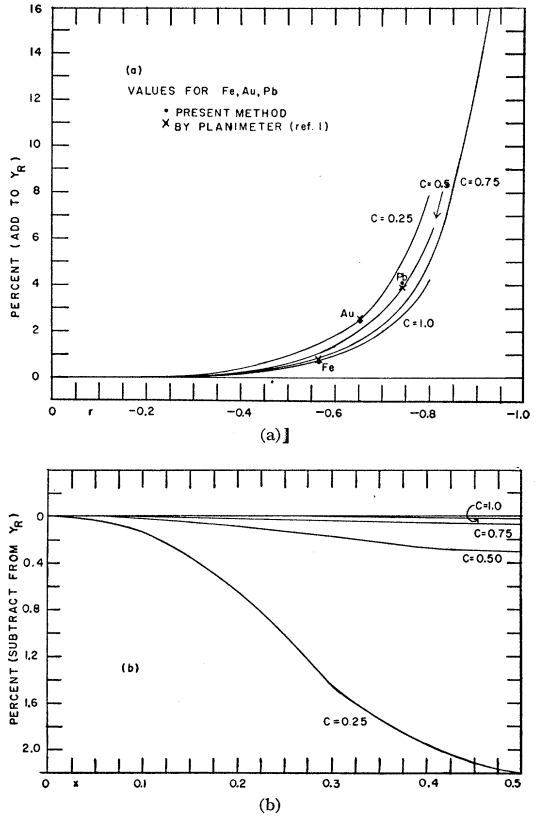

FIG. 1. Correction function E.

for an isotropic body. The second term is that given by Born and v. Kármán.[4,5] The first *three* terms can be obtained from an expansion of Y_R, Eq. (3), since this is the case of $m=2$, $n=5$.

The Taylor's series must diverge for $x\geq|C|$, and converges slowly for $x<|C|$.

Y_T is always less than the true Y for $x<0$ and thus constitutes a lower bound for Y. For $x>0$, the terms of the series alternate in sign so that Y_T alternately bounds above and below as terms are added.

An upper bound for Y can be had for $x<0$ by using $n=5$ and $m=1$ in Eq. (4) and then passing the $[f(z)]_R$ through $z=x$ and $z=1-4x/3$. This $[f(z)]_R$ is then tangent to $f(z)$ at $z=0$ and $z=1$ and lies wholly above $f(z)$ throughout the root ranges. (It can be shown that $[f(z)]_R$ cuts $f(z)$ only at the points chosen.)

ESTIMATE OF CORRECTIONS

The true correction to Y_R is given by

$$E=\sum_i\int_{z_i}\{f(z_i)-[f(z_i)]_R\}\frac{d\Omega}{dz_i}\frac{dz_i}{4\pi}. \quad (6)$$

[4] M. Born, *Atomtheorie des festen Zustandes, Enc. Math. Wiss.* (Teubner, Leipzig), Vol. 3, p. 648.

[5] M. Born and Th. v. Kármán, Physik. Z. **14**, 15 (1913). They appear to have neglected to cancel a factor of 4π. See reference 10, page 18.

The $d\Omega/dz_i$ are not known analytic functions. The shapes of the $d\Omega/dz_i$, however, vary only slightly with x. This is a consequence of the facts, as discussed in reference 1, that the intervals (in z) of the $d\Omega/dz_i$ are all proportional to x, the maxima of the $d\Omega/dz_i$ always remain at the same points in the intervals, and the area under each $d\Omega/dz_i$ is always equal to $4\pi/48$. Thus, if the $d\Omega/dz_i$ are approximated by functions having the same intervals, having areas under them of $4\pi/48$ and having no change in shape with x, then the approximate E computed using these functions varies with x in a way similar to E itself. A first approximation to E, using *constants* in place of the actual $d\Omega/dz_i$ and maintaining the same intervals and area, is denoted by E'. Both E and E' depend on C in nearly the same way, since C enters Eq. (6) only through the known functions $f(z_i)$ and $[f(z_i)]_R$.

E' may be improved as a first approximation to E by dividing E' by the quantities $Q(1+Gx)$ for $x>0$ and $Q(1+Hr)$ for $x<0$, where r is defined as the ratio x/C. These factors are evaluated as follows:

Q is determined by taking the ratio of E' to $(Y-Y_R)$ as $x\rightarrow 0$. This can be computed since $(Y-Y_R)$ may be be replaced by (Y_T-Y_R) as x approaches zero. Both E' and $(Y-Y_R)$ are proportional to the third and higher powers in x. Thus, E'/Q is *identical* with the true E to the order x^3. Values of Q range from $Q=1.4902$ for $C=1.136$ to $Q=1.5298$ for C equal to zero.

Since E and E'/Q have no lower powers of x than x^3, both go through zero with no slope or curvature. Division by Q serves to adjust E' to agree with E in general magnitude. Since E' is computed with a $d\Omega/dz_i$ of substantially different shape than the true $d\Omega/dz_i$, the size of Q is not unexpected.

For $x>0$, the *true value of* Y, and thus E, can be computed at $x=0.5$ (i.e., at $K=0$) since the three roots of the cubic are here simply α^2, β^2 and γ^2. Division of E'/Q by $(1+Gx)$ further adjusts our error estimate so that proper choice of G gives a good fit to the exact errors at $x=0.5$. Thus, the final error curves in Fig. 1(b) are $E'/Q(1+Gx)$. These curves are precise at either end and have the required lack of curvature at $x=0$. Further, as before stated, E and E' should vary with x in a similar manner, so we expect the shape of these curves to be nearly correct. Judging by the size of the adjustment necessary at $x=0.5$ the largest probable error to be expected in the curves shown is about $\pm 0.3\%$ in Y_R.

As a check on the foregoing method of arriving at the error curves in Fig. 1(b), Y has been calculated by the numerical method of Grüneisen and Goens[6] at the point $C=0.25$ and $x=0.3$. This yields $Y=11.409$ requiring a correction for Y_R of -1.71%. This differs from the Fig. 1(b) value of -1.44% by less than 0.3%. The error in the Grüneisen and Goens numerical method should be an order of magnitude less than the change induced in Y by omitting one of the points in their basic triangle. Omission of the worst point increases Y by only 1.9 percent, so it is felt that the $Y=11.409$ above is in error at worst by 0.5%. Thus, use of Eq. (3) and Fig. 1(b) is of comparable accuracy to the Grüneisen and Goens method—and presents much less computational difficulty.

For $x<0$, division of E' by the function $Q(1+Hr)$ gives the curves plotted in Fig. 1(a). The value of H is obtained by choosing it to give the best fit with values computed graphically for Fe, Au, and Pb.[1] The values of C for Fe, Au, and Pb are, respectively, 1.136, 0.3040, and 0.4248. The resultant curves go through $r=0$ with the required lack of curvature and approach infinity at $r=-1.0$ as they must. Also, as before stated, their shapes should be nearly correct since E and E' should vary with x in a like manner. The fact that *one* parameter, H, is sufficient to give good fit at the three different values of r for Fe, Au, and Pb seems to substantiate the accuracy of the shape of these curves (especially since these three metals cover the useful region of the curves where the error is large and important). Judging by the estimated error in the graphically determined values and the fit obtained, it appears that an estimate of 0.3% error in the curves of Fig. 1(a) is reasonable for the range of r from zero to -0.8.

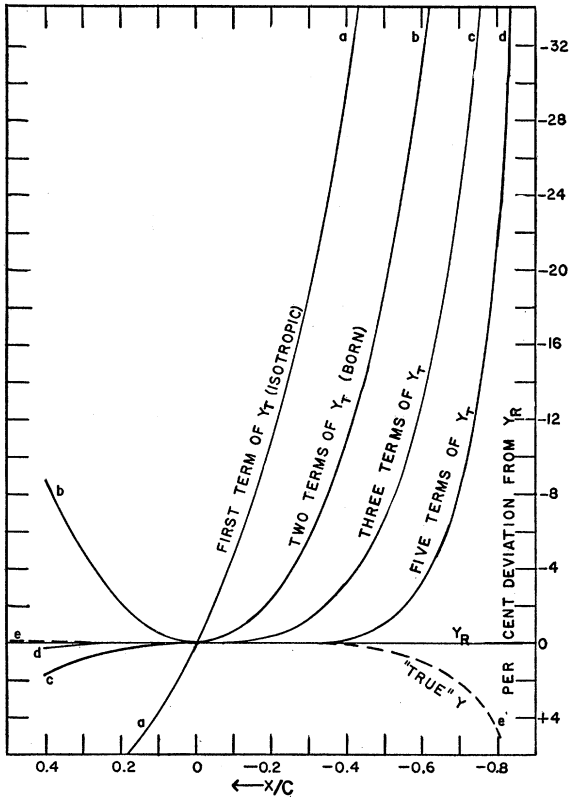

FIG. 2. Comparison of terms of the Taylor series for Y with Y_R, Eq. (3), and the "true" Y. Born's equation is shown to be of low accuracy.

[6] E. Grüneisen and E. Goens, Z. Physik **26**, 255 (1924).

It should be noted that there is good agreement with the Grüneisen and Goens[6] method in this range, too, as mentioned in reference 1. The methods agree to about 0.4% in Y for Au and Ag, *using the same data.* (The trapezoidal averaging method of Grüneisen and Goens can be improved by dividing by the sum of the actual area factors used, rather than using the factor π/n. This raises Y values usually about 0.6%. The need for this improvement is easily demonstrated by applying their method to the isotropic case.)

In summary, it is estimated that the curves of Fig. 1 are accurate to about 0.3%. Interpolation for intermediate C values may double this error. The percent error in the computed Θ_D introduced by the substitution of the corrected Y_R for Y in Eq. (1) is one-third the percent difference between them. Therefore, the use of Eq. (3) and Fig. 1 should result in the mean Θ_D accurate to about 0.1% on a given curve or, when interpolating curves, to about 0.2%. This is about an order of magnitude less than the errors introduced in Θ_D by the present experimental uncertainty in the c_{ij}.

Use of Eq. (3) and Fig. 1 reduces the arrival at an accurate Θ_D to a short operation taking, at most, a few minutes. This makes possible computations of Θ_D for many values of elastic data without being prohibitive in time and effort, and enables the experimenter to compute easily the effect on Θ_D of variation of such parameters as temperature, cold work, radiation damage, or alloy proportion.

COMPARISON OF FORMULAS

Figure 2 compares terms of Y_T to Y_R. The dashed curve is the "true" Y as discussed above. It is apparent that Y_R fits the "true" curve best. For positive r, Y_T to the term in x^4 is nearly as good as Y_R; for negative r, it fails much beyond $r=-0.5$. It appears that Y_T would have to be carried out several further terms in order to compete with Y_R near $r=-0.7$ where many of the metals occur. (As a consequence, Y_T is chiefly of value in computing Q.) Also, the equation given by Born[4,5] is quite inaccurate except close to isotropy, say $r<|0.1|$. (From Hearmon's Table,[3] only tungsten falls in this category.) Figure 2 may be used as a guide to use of Y_T for substances of small x. It is plotted for $C=1$ but the variation of C does not change these curves substantially.

Two papers by Blackman seem to complement the method here described. The first permits calculation of Θ_D for cases where $(c_{12}+c_{44})\ll c_{11}$, i.e., for very positive r.[7] The second applies where $c_{11}-c_{12}$ is small, i.e., $r\doteq -1$.[8] The formulas he proposes are relatively simple but may be in error by several percent.

Bhatia and Tauber[9] give an equation for Y which is also accurate to several percent. This is derived using the first three Kubic Harmonics for the integrand. Their equation contains the same m_i as Eq. (3), but the coefficients are constants.

It is worth noting that the Hopf and Lechner[2] treatment necessarily gives a value of Θ_D which is too high (low Y) for all substances of negative x. The metals are in this category. The Hopf and Lechner representative function intersects $f(z)$ only between $z=0$ and $z=1$ and as a consequence is lower than the true $f(z)$ throughout the root ranges. The wide use of the Hopf and Lechner method may be one reason for the fact that Θ_D from elastic data is frequently high compared to the Θ_D from specific heat data.[10,11] As an example, even for nearly isotropic Al $(r=-0.1561)$[12] the Hopf and Lechner method gives a Y which is 1.7 percent low; for more negative r it worsens rapidly.

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APPENDIX A

Equation (1) may be written

$$Y=\frac{1}{4\pi}\sum_i\int_{z_i} f(z_i)\frac{d\Omega}{dz_i}dz_i, \tag{1A}$$

where $(d\Omega/dz_i)dz_i$ is the solid angle associated with the ith root lying between z_i and z_i+dz_i. The defining equations for y_i are

$$\begin{aligned} z_1&\equiv 1+y_1x,\\ z_2&\equiv y_2x,\\ z_3&\equiv y_3x. \end{aligned} \tag{2A}$$

Then Eq. (1A) becomes

$$Y=\frac{1}{4\pi}\sum_i\int_0^{k_i} f(z_i)\left(x\frac{d\Omega}{dz_i}\right)dy_i, \tag{3A}$$

where the k_i are appropriate *constants* (all ranges of z_i are proportional to x). Also

$$\int_0^{k_i}\left(x\frac{d\Omega}{dz_i}\right)dy_i=\int_{z_i}\frac{d\Omega}{dz_i}dz_i=4\pi. \tag{4A}$$

Taylor's series for $f(z)$ at $z=0$ for z_2 and z_3 and at $z=1$ for z_1 yields ($|k_2|>|k_3|$ and $y_2=y_3=y$)

$$\begin{aligned} Y=\frac{1}{4\pi}\Bigg[&\int_0^{k_1}\left(x\frac{d\Omega}{dz_1}\right)\sum_i x^iy_1^i\frac{f^{(i)}(1)}{j!}dy_1\\ &+\int_0^{k_2}\left[x\frac{d\Omega}{dz_2}+x\frac{d\Omega}{dz_3}\right]\sum_i x^iy^i\frac{f^{(i)}(0)}{j!}dy\Bigg]. \end{aligned} \tag{5A}$$

[7] M. Blackman, Proc. Roy. Soc. (London) **A149**, 126 (1934).
[8] M. Blackman, Phil. Mag. **42**, 1441 (1951).
[9] A. B. Bhatia and G. E. Tauber, Phil. Mag. **45**, 1211 (1954).
[10] M. Blackman, Repts. Progr. Phys. **8**, 19 (1941).
[11] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 111.
[12] P. M. Sutton, Phys. Rev. **91**, 816 (1953), data at 0°K.

On the other hand, use of a representative polynomial

$$[f(z)]_R=\sum_{j=0}^{n} a_j z^j \tag{6A}$$

yields

$$Y=\frac{1}{4\pi}\left[\int_0^{k_1}\left(x\frac{d\Omega}{dz_1}\right)\sum_{i=0}^{n}\left(x^i y_1{}^i\sum_{i=i}^{n}\frac{i!a_i}{(i-j)!j!}\right)dy_1 + \int_0^{k_2}\left(x\frac{d\Omega}{dz_2}+x\frac{d\Omega}{dz_3}\right)\sum_{j=0}^{n}x^i y^i a_j dy\right]. \tag{7A}$$

A jth term in Eq. (5A) or (7A) must be at least of order j in powers of x since it is proportional to

$$\left|x^j\int_0^{k_i}\left(x\frac{d\Omega}{dz_i}\right)y^i dy\right|\leq\left|x^j k_i{}^j\int_0^{k_i}\left(x\frac{d\Omega}{dz_i}\right)dy\right|=|4\pi x^j k_i{}^j|,$$

and the inequality would fail for x sufficiently near zero if the jth term were of order less than j in x.

Therefore, the requirement of Eq. (4) forces Y_R to be *identical* to Y for all powers of x^j where $j\leq m$ as can be seen by comparing Eq. (5A) with Eq. (7A). Equation (4) constitutes $2(m+1)$ conditions on the $(n+1)$ coefficients a_i so that $(n+1)\geq 2(m+1)$. Thus expansion of Y_R in powers of x yields the first $(m+1)$ terms in the Taylor's series for Y in powers of x.

The Y_R needed to give the Y_T of Eq. (5) has $n=9$ and $m=4$. Hopf and Lechner[2] give $\sum_i z_i{}^j$ up to $j=5$ (case of $n=5$). To obtain Y_R for $n>5$, use is made of the recurrence relation

$$\sum_i z_i{}^j=\sum_i z_i{}^{j-1}-K_1\Gamma\sum_i z_i{}^{j-2}+K_2\chi\sum_i z_i{}^{j-3}, \tag{8A}$$

where

$$K_1=(1-K^2),$$
$$K_2=(1-3K^2+2K^3),$$
$$\Gamma=\alpha^2\beta^2+\beta^2\gamma^2+\gamma^2\alpha^2,$$
$$\chi=\alpha^2\beta^2\gamma^2.$$

Equation (8A) is obtained directly from the basic cubic in z. The eleven integrals needed for $n=9$ may then be obtained, and give the following averages over the unit sphere: Γ, 1/5; χ, 1/105; Γ^2, 1/21; $\Gamma\chi$, 1/385; Γ^3, 61/5005; χ^2, 1/5005; $\Gamma^2\chi$, 1/1365; Γ^4, 277/85085; $\Gamma\chi^2$, 5/85085; $\Gamma^3\chi$, 205/969969; χ^3, 5/969969. Hopf and Lechner[2] give the first four of these.

The final equation for Y_R for $n=9$ is[13]

$$\begin{aligned}Y_R=3a_0&+\sum_{j=1}^{9}a_j-\frac{K_1}{5}\sum_{j=2}^{9}ja_j+\frac{K_2}{105}\sum_{j=3}^{9}ja_j\\&+\frac{K_1{}^2}{21}\sum_{j=4}^{9}\frac{j(j-3)}{2}a_j-\frac{K_1K_2}{385}\sum_{j=5}^{9}j(j-4)a_j\\&-\frac{61K_1{}^3}{5005}\sum_{j=6}^{9}\left(\frac{j}{3}\sum_{n=5}^{j}(j-n)\right)a_j+\frac{K_2{}^2}{5005}\sum_{j=6}^{9}\frac{j(j-5)}{2}a_j\\&+\frac{K_1{}^2K_2}{1365}\sum_{j=7}^{9}\left(j\sum_{n=6}^{j}(j-n)\right)a_j+\frac{277K_1{}^4}{85085}(2a_8+9a_9)\\&-\frac{5K_1K_2{}^2}{85085}(8a_8+27a_9)-\frac{205(K_1{}^3K_2)}{969969}(9a_9)\\&+\frac{5K_2{}^3}{969969}(3a_9).\end{aligned} \tag{9A}$$

[13] Terms of Eq. (9A), without a_9, are given by K. Fuchs in powers of K in Proc. Roy. Soc. (London) **A153**, 622 (1936) and **A157**, 444 (1936). An error in the coefficient of a_8 in **A153** is corrected in **A157**.