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Specific Heat and Susceptibility in Chromium Methylammonium Alum above the Critical Temperature

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The specific heat and susceptibility of chromium methylammonium alum is calculated above the critical temperature. The method is based on a high-temperature expansion of the partition function in the presence of a crystal field, using a Laplace transform. The results are worked out in first (for the susceptibility) and second (for the specific heat) order in the coupling Hamiltonian. The summation over the four different sublattices is worked out for the two different crystallographic phases which seem to occur above and below 170 K. The lack of rotation symmetry of the crystal field in its local reference system, which was found by paramagnetic resonance, is taken into account. The result for the susceptibility is given explicitly in Eq. (4.18a) as a function of a reduced temperature.

I. SHORT DESCRIPTION OF PREVIOUS WORK

The first application of the statistical mechanics of a magnetic system to the chrome alums was described by Van Vleck[1] and applied by Hebb and Purcell.[2] The first studies of the methylamine homologue of this series were done by De Klerk and Hudson[3] and subsequently by Gardner and Kurti[4] who found a Néel temperature at 0.020 K. In all this work powders were used. The general magnetic behavior was studied in single crystals by various authors[5] and a careful temperature-scale investigation on single crystals was done by Ambler and Hudson.[6] They found that the Néel temperature was $T_N = 0.016$ K. In order to explain this behavior, O'Brien[7] calculated the critical temperature for a four-sublattice system. In her paper she also calculated the entropy and susceptibility above the critical point, although she simplified the crystal field (CF) term and dropped, in the last steps, the exchange contribution. This was augmented by Durieux[8] who incorporated this term.

The goal of this paper is to provide experimental physicists, in their search for more accurate temperature scales, with the susceptibility and specific heats as predicted on the basis of the best available experimental parameters. The display of the formalisms used is quite explicit in order to provide a framework for future work on different compounds.

It is a peculiar habit in magnetic thermometry to add all correction terms in the denominator. Although this is not wrong, since we are dealing with a small correction that can be written either way, it gives the false impression that the Curie-Weiss constant is basically correct and only needs small changes. The Curie-Weiss constant may have meaning below T_c, but above the critical temperature the constant is the consequence of the influence of the second term in the $1/kT$ series. This term is subsequently followed by a third-order term. It would therefore be more logical to present data in the same fashion. The denominator habit is even used for powdered specimens, where the constants have little meaning.

Unfortunately, we do not quite practice what we preach since in this paper we shall use a hybrid expansion. Each coefficient in $1/kT$ is itself a function of the temperature. However, this function is determined by the CF parameters only, which are known to a high degree of accuracy.

This paper takes into account the complete CF Hamiltonian. It is shown that the presence of Baker's[9] E term has a small influence of the order of 1% near T_c. It also sets up the calculation in such a way that subsequent terms can be calculated directly. This is done by the resolvent technique using the Laplace transform of the partition function.

II. INTRODUCTION TO THE METHOD

In previous papers[10,11] a high-temperature expansion for a system with dipole-dipole forces was worked out. So far only cases without CF were considered. The presence of a CF will introduce a temperature dependence in the coefficients of the high-temperature series. To determine these functions of the temperature we use a Laplace transform of the partition function which leads to an expression in which the Stevens operators[12] appear in the denominator. A general method, a method of partial summation, is described elsewhere[13] by which one can obtain an expression linear in the operators. The inverse Laplace transform can be calculated independently of the trace operation. Finally, one has to, as before, compute the lattice sums.

The general method of calculating the exponential of a Hamiltonian with several noncommuting pieces is to use the time-ordered expansion (see, for instance, Ref. 14):

$$e^{\beta\mathcal{H}_0}\, e^{-\beta(\mathcal{H}_0+\mathcal{H}_1)} = \sum \frac{(-1)^n}{n!} \int_0^{\beta} \cdots \int_0^{\beta_1} T_0[\mathcal{H}_1(\beta_n)\cdots \times \mathcal{H}_1(\beta_1)]\, d\beta_1 \cdots d\beta_n , \qquad (2.1)$$

where $\beta = 1/kT$ and T_0 is the time-ordering operator. The author tried to use this in an earlier article[15] to calculate the second-order dipole correction to a spin system in a CF, but this method is not very well suited for explicit calculations. In most field-theoretical work the commutator is a c number which simplifies the method.

If we break up the Hamiltonian in two parts, the on-site part $\mathcal{H}_0$ and the intersite part $\mathcal{H}_1$, then

$$\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_c ,$$
$$\mathcal{H}_1 = \mathcal{H}_D + \mathcal{H}_{ex} , \qquad (2.2)$$

where $\mathcal{H}_z$ is the Zeeman term, $\mathcal{H}_c$ is the crystal field term, $\mathcal{H}_D$ is the dipole-dipole interaction, and $\mathcal{H}_{ex}$ is the exchange interaction. The spin dependence of the second part of the Hamiltonian is given by

$$\mathcal{H}_1 = \sum_{ij} \sum_{\alpha,\beta} S_i^{\alpha} P_{ij}^{\alpha\beta} S_j^{\beta} ,$$

where P_{ij} is the tensor shorthand for the dipole-dipole and the exchange interaction. The superscripts α and β are summed over x, y, and z. If we replace the density operator ρ, where $\rho(\beta) = e^{-\beta\mathcal{H}}$, by its Laplace transform (also called the resolvent operator)

$$R(t) = \int_0^{\infty} \rho(\beta)\, e^{t\beta}\, d\beta = 1/(t - \mathcal{H}) , \qquad (2.3)$$

where t is the variable conjugate to β, then the denominator can be expanded in terms of $\mathcal{H}_1$ using the tautology

$$\frac{1}{t-\mathcal{H}_0-\mathcal{H}_1} = \frac{1}{t-\mathcal{H}_0}\left(1+\mathcal{H}_1\, \frac{1}{t-\mathcal{H}_0-\mathcal{H}_1}\right). \qquad (2.4)$$

This leads to a sequence of terms each containing the factor $(t-\mathcal{H}_0)^{-1}$. To evaluate this factor we used a partial summation, explained elsewhere.[13] To illustrate this we assume that $\mathcal{H}_0 = \mathcal{H}_c = B_{20}\, O_{20}$, where O_{20} is the Stevens operator[12] and B_{20} is an energy parameter, and write

$$\frac{1}{t-\mathcal{H}_c} = \frac{1}{t}\,(1 + t^{-1}\mathcal{H}_c + t^{-2}\mathcal{H}_c^2 + t^{-3}\mathcal{H}_c^3 + \cdots) . \qquad (2.5a)$$

Since $\mathcal{H}_c^2$ is proportional to the unit matrix for $S = \frac{3}{2}$, it is useful to write the series as

$$\frac{t}{t-\mathcal{H}_c} = 1 + t^{-1}\mathcal{H}_c + t^{-2}\mathcal{H}_c^2\, \frac{t}{t-\mathcal{H}_c} ; \qquad (2.6)$$

hence,

$$1/(t-\mathcal{H}_c) = (t+\mathcal{H}_c)/(t^2 - \mathcal{H}_c^2) , \qquad (2.5b)$$

where $\mathcal{H}_c^2 = 9B_{20}^2$. In the presence of the E term, which introduces a Stevens operator O_{22}, one has to go up to the fourth power in $\mathcal{H}_c$.

The thermodynamic properties of the system can be calculated from the partition function Z which is an expansion (in T^{-1}) in the interionic coupling and exact in the crystal field interaction according to

$$\begin{aligned} Z &= \mathrm{Tr}\rho = \mathrm{Tr}\mathcal{L}^{-1}(R) = \mathcal{L}^{-1}[\mathrm{Tr}R] \\ &= \mathcal{L}^{-1}[\mathrm{Tr}(R_0 + R_1 + R_2 + \cdots)] \\ &= \mathcal{L}^{-1}(\mathcal{J}_0 + \mathcal{J}_1 + \mathcal{J}_2 + \cdots) , \end{aligned} \qquad (2.7)$$

where $\mathcal{L}^{-1}$ signifies the inverse of the Laplace transform, R_n is the resolvent of order n in the coupling, and $\mathcal{J}_n$ signifies the trace of R_n.

III. EXPERIMENTAL DATA ON CHROMIUM METHYLAMMONIUM ALUM

The lattice constant of chromium methylammonium alum (CMA) was measured by Haussühl[16] at room temperature. The edge of the unit cell is 12.2 Å (compare Table IV of Ref. 16). To reduce this value to the lower helium temperatures, where they are unknown, one could use the reduction of parameters observed in cerium magnesium nitrate by Schiferl[17] which amount to about 1% from room temperature to 4 K. Unfortunately there is an uncertainty in this estimate, since Baker[9] observed in his paramagnetic-resonance work a transition at 160 K from cubic to tetragonal.

From this latter work we take the following constants in the spin Hamiltonian: $D = -958$, $E = -92$, $\Delta = (D^2 + 3E^2)^{1/2} = 971$, all in 10^{-4} cm^{-1}. The g factor is 1.976 and isotropic. The CF is oriented in four different directions corresponding to the four body diagonals of the cube used to describe the fcc lattice. Hence it is easier to use a simple-cubic magnetic unit cell, four times larger than the fcc unit cell. The Baker E parameter means that there is a slight tetragonal distortion, i.e., the x and y directions in the local coordinate system are not quite equivalent. The x (or y) axis points along a face diagonal of the main cube.

The exchange is small and has not been measured directly. The conclusion that the exchange is small has been drawn from the fact that calculations with dipolar interactions alone give good agreement with the observed critical temperature. Owing to the fact that predicting the critical parameters from the fundamental constants of a magnetic substance is far from perfect, particularly in the presence of dipolar forces, the precise value for the exchange constant v thus obtained is open to debate. It is far more satisfactory to determine v from the deviations from either the Curie law, or from the ideal heat capacity, above T_c. In order to establish how much of the heat capacity is due to crystal field interaction, how much to dipolar interaction, and how much to exchange, it is of utmost importance that the CF effect be taken into account without any approximation, that is, without dropping the E term.

IV. CALCULATIONS: ZERO FIELD

First we consider the Boltzmann factor of the CF term only. The Laplace transform of this factor is

$$\frac{1}{t-\mathcal{H}_c}=\frac{1}{t-BO_{20}-\frac{1}{2}E(O_{22}+O_{2-2})}=\frac{t+BO_{20}+\frac{1}{2}E(O_{22}+O_{2-2})}{t^2-9B^2-3E^2}\,, \tag{4.1}$$

where $B=B_{20}=\frac{1}{3}D$ and $E=B_{22}$ using Stevens's[12] notation. This formula is restricted to $S=\frac{3}{2}$ only. For a general evaluation of the inverse of operator polynomials see Ref. 13.

For the lowest-order term $\mathcal{J}_0$, which gives the zero-field heat capacity in zeroth order, i.e., without interaction between the spins, we find

$$\mathcal{J}_0=\mathrm{Tr}\left(\frac{1}{t-\mathcal{H}_c}\right)=2\left(\frac{1}{t+\Delta}+\frac{1}{t-\Delta}\right)\,, \qquad \Delta^2=D^2+3E^2\,. \tag{4.2}$$

If one takes the inverse transform, the result for the zero-field partition function is the same as in[7]

$$Z=2(e^{\beta\Delta}+e^{-\beta\Delta})\,, \tag{4.3}$$

with the only difference that Δ is replacing $D=3B$. (Note that the δ used in Ref. 7 is equal to $-2D$.) Hence the partition function for $H=0$ and no interaction undergoes only a trivial change if Baker's E term is introduced. (The first-order term $\mathcal{J}_1$ is zero; see Appendix A.)

More interesting is the calculation of the second-order term in the interaction. This term contributes

$$\mathcal{J}_2=2\,\mathrm{Tr}[(t-\mathcal{H}_c)_i^{-1}\vec{S}_i P_{ij}\vec{S}_j(t-\mathcal{H}_c)_j^{-1}\vec{S}_j P_{ji}\vec{S}_i(t-\mathcal{H}_c)^{-1}] \tag{4.4}$$

as obtained by iteration of the process used in Eq. (2.4). The factor of 2 stems from the fact that each pair of spins in the Zeeman term of the Hamiltonian can be matched in two ways to the spin appearing in the coupling terms. This term has to be summed over all site labels i and j. The quantities P are tensors and incorporate both the exchange and the dipole interaction. The notation implies summation over the tensor and vector components, such that each factor $S^{(\alpha)}P^{(\alpha\beta)}S^{(\beta)}$ is a scalar in configuration space. One can cycle and regroup the terms and introduce two new tensors Q_1 and Q_2 given by

$$Q_1^{(\alpha\beta)}=\mathrm{Tr}[S_j^{(\alpha)}(t-\mathcal{H}_c^{(\Gamma)})_j^{-1}S_j^{(\beta)}]\,, \tag{4.5a}$$

$$Q_2^{(\alpha\beta)}=\mathrm{Tr}[(t-\mathcal{H}_c^{(\Gamma)})_i^{-2}S_i^{(\beta)}S_i^{(\alpha)}]\,. \tag{4.5b}$$

The values of the elements of the first tensor are independent of j and the values of the elements of the second tensor are independent of i. This is the consequence of the homogeneity of the substance, and is violated only if we either use a space-dependent external field or deal with a nonuniform spontaneous magnetization. The fact that the sites are not magnetically equivalent is taken into account by using the above formulas for each sublattice separately. This is the reason for the superscript Γ (= I, II, III, IV) on the crystal field Hamiltonian. In order to evaluate the resolvents on one common system of axes we have to perform a rotation from each of the CF axes (unprimed) to the axes coinciding with the edges of the cube (primed). The transformation is explained in Fig. 1 for the case where the symmetry axes of the (cylindrical) crystal field is along the [111] direction (label I). The three other orientations are indicated as the corollary to the next Eq. (4.6). The transformation is given by

$$\begin{aligned} S_x&=\tfrac{1}{6}(-\epsilon_x S_{x'}-\epsilon_y S_{y'}+2\epsilon_z S_{z'})\,,\\ S_y&=(\epsilon_x/\sqrt{2})S_{x'}-(\epsilon_y/\sqrt{2})S_{y'}\,,\\ S_z&=(1/\sqrt{3})(\epsilon_x S_{x'}+\epsilon_y S_{y'}+\epsilon_z S_{z'})\,,\\ \epsilon_x,\ \epsilon_y,\ \epsilon_z&=1,\ 1,\ 1 \text{ in case I}\\ &=1,\ -1,\ -1 \text{ in case II} \end{aligned} \tag{4.6}$$

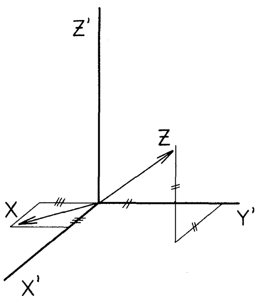

FIG. 1. New z axis is the body diagonal; the new x axis is along the face diagonal perpendicular to the z axis. The cube is not drawn. Compare Ref. 9.

$$= -1,\ 1,\ -1 \text{ in case III}$$

$$= -1,\ -1,\ 1 \text{ in case IV} .$$

We transform $\mathcal{H}_c$, or actually R_c [see Eq. (2.3)], to the primed coordinates. The denominator in Eq. (4.1) remains the same, and we obtain

$$t + BO_{20} + \tfrac{1}{2}E(O_{22} + O_{2,-2})$$

$$\to t + B_{20}^{(\Gamma)} O_{20} + (B_{21}^{(\Gamma)} O_{21} + B_{22}^{(\Gamma)} O_{22} + B_{2,-1}^{(\Gamma)} O_{2,-1} + B_{2,-2}^{(\Gamma)} O_{2,-2}) , \qquad (4.7)$$

where $B_{20}^{(\Gamma)} = \frac{1}{9}E$ and the other $B^{(\Gamma)}$'s are given by

Γ	B_{21}	B_{22}
I	$(1-i)B + \frac{1}{3}(-1+i)E$	$-\frac{1}{2}iB - \frac{1}{3}iE$
II	$-(1+i)B + \frac{1}{3}(1+i)E$	$\frac{1}{2}iB + \frac{1}{3}iE$
III	$(1+i)B - \frac{1}{3}(1+i)E$	$\frac{1}{2}iB + \frac{1}{3}iE$
IV	$-(1-i)B + \frac{1}{3}(1-i)E$	$-\frac{1}{2}iB - \frac{1}{3}iE$

and $B_{2,-n}^{(\Gamma)} = (B_{2,n}^{(\Gamma)})^*$.

We now have to evaluate the tensor Q_1. Its components are

$$\begin{aligned}
Q_1^{xx} &= (5t - 6B_{20} + 6B_{22} + 6B_{22}^*)(t^2 - \Delta^2)^{-1} ,\\
Q_1^{yy} &= (5t - 6B_{20} - 6B_{22} - 6B_{22}^*)(t^2 - \Delta^2)^{-1} ,\\
Q_1^{zz} &= (5t + 12B_{20})(t^2 - \Delta^2)^{-1} ,\\
Q_1^{xy} &= Q_1^{yx} = 6i(B_{22}^* - B_{22})(t^2 - \Delta^2)^{-1} ,\\
Q_1^{xz} &= Q_1^{zx} = \mathrm{Re}(B_{21})(t^2 - \Delta^2)^{-1} ,\\
Q_1^{yz} &= Q_1^{zy} = \mathrm{Im}(B_{21})(t^2 - \Delta^2)^{-1} ,
\end{aligned} \qquad (4.8)$$

for each value of Γ in turn. In order to evaluate the other tensor, Q_2, we first compute the product of two resolvent operators R, and then substitute in Eq. (4.5b):

$$q_2 = Q_2^{(\alpha\alpha)} = 15[3(B_{20}^{(\Gamma)} - t)^2 + B_{21}^{(\Gamma)} B_{21}^{(\Gamma)*} + 4B_{22}^{(\Gamma)} B_{22}^{(\Gamma)*}](t^2 - \Delta^2)^{-2} , \qquad (4.9)$$

$$Q_2^{(\alpha\beta)} = 0 .$$

Hence the matrix Q_2 is diagonal and proportional to unit matrix. This result is simple, because we are dealing with a rather low spin value. In general, it will contain operators such as O_{40}, etc., which are excluded here on the basis of the triangular rule.

The next step is to insert these tensors in Eq. (4.4):

$$\mathcal{J}_2 = 2 \sum_{\alpha\beta\gamma\delta} Q_1^{\alpha\beta} P^{\beta\gamma} Q_2^{\gamma\delta} P^{\delta\alpha} = 6q_2 \sum_{\alpha\beta\gamma} Q_1^{\alpha\beta} P^{\beta\gamma} P^{\gamma\alpha} . \qquad (4.10)$$

Now we discuss separately the two cases $\alpha = \beta$ and $\alpha \neq \beta$. In the first case we obtain, if the two sites are located on the same sublattice,

$$\mathcal{J}_2' = 2 \textstyle\sum_\Gamma \{3q_2[Q_1^{xx} \sum_\gamma (P^{x\gamma})^2 + Q_1^{yy} \sum_\gamma (P^{y\gamma})^2 + Q_1^{zz} \sum_\gamma (P^{z\gamma})^2]\} . \qquad (4.11)$$

Since each sublattice is simple cubic, we have

$$\sum (P^{x\gamma})^2 = \sum (P^{y\gamma})^2 = \sum (P^{z\gamma})^2 ,$$

and the diagonal elements of Q_1 can be summed, with the result

$$Q_1^{xx} + Q_1^{yy} + Q_1^{zz} = 15t(t^2 - \Delta^2)^{-1} . \qquad (4.12)$$

Note that this expression does not contain $B^{(\Gamma)}$ and hence is independent of the sublattice. The tensor Q_2 depends on the absolute value of the B's only and they are all the same, hence the sum over all sublattices simply introduces a factor of 4.

If the two sites are not located on the same sublattice, we have

$$\mathcal{J}_2'' = \sum_{\Gamma\Gamma'} 3q_2^{(\Gamma)} \sum_\alpha Q_1^{(\Gamma'\alpha\alpha)} \sum_\gamma (P_{\Gamma\Gamma'}^{\alpha\gamma})^2 , \qquad (4.13)$$

where the dipole sums have to be taken between each point on Γ and the points on Γ'. A rotation of the x, y, z axes will induce a cyclic permutation of the three sublattices, with respect to a fourth. Hence, the nine terms created by the Γ' and α summations will be equal in sets of three. In each set we choose the z direction:

$$\mathcal{J}_2'' = 4(3q_2)\, 3 \sum_{\Gamma'} Q_1^{\Gamma' zz} \sum_\gamma (P_{\Gamma\Gamma'}^{z\gamma})^2 , \qquad (4.14)$$

where the factor of 4 is from the sum over Γ. The sum over Γ' introduces a factor 3 since the B_{20} component is the same for each sublattice, and

$$\mathcal{J}_2'' = 36q_2 \frac{3(5t + 12B_{20})}{t^2 - \Delta^2} \sum_\gamma (P_{\Gamma\Gamma'}^{z\gamma})^2 . \qquad (4.15)$$

To evaluate the case where $\alpha \neq \beta$ we notice that at least one of the $P^{\alpha\gamma}$ becomes odd in either x, y, or z. This will lead to a cancellation of the lattice sum both on the same sublattice as well as on two different sublattices.

To collect the results, we obtained two contributions to the second-order Laplace transform; one containing the lattice sum between points of the same sublattice,

$$\mathcal{J}_2' = 12(15)^2 t\{3(B_{20} - t)^2 + B_{21}B_{21}^* + 4B_{22}B_{22}^*\} \times [\sum (P^{z\gamma})^2](t^2 - \Delta^2)^{-3} , \qquad (4.16)$$

where the quantity in curly brackets is given by

$$\{\cdot\cdot\cdot\} = 3(\tfrac{1}{3}E - t)^2 + 3B^2 + \tfrac{2}{3}E^2 ,$$

and another part that contains the lattice sum $(\sum P^{z\gamma})_{\mathrm{dif}}^2$ taken with respect to different sublattices:

$$\mathcal{J}_2'' = 9(5t + 4E)\{\cdot\cdot\cdot\}(\sum P^{z\gamma})_{\mathrm{dif}}^2 (t^2 - \Delta^2)^{-3} . \qquad (4.17)$$

To obtain the contribution to the partition function we have to take the inverse Laplace transform. This is done by using the formulas given in Appendix B.

The result for the same sublattice is

$$Z^{1}_{(2)} = 3(\tfrac{1}{2}225)\,(\sinh(\Delta\beta)\{-\beta/3\Delta - 2E[(\Delta\beta)^2-1]/\Delta^3 + 9\beta/\Delta\} + \cosh(\Delta\beta)\,(\beta/3\Delta - 2E\,\beta/\Delta^2 + 3\beta^2/\Delta^2))\,[\textstyle\sum(P^{z\gamma})^2]$$

and for two different sublattices, it is

$$Z''_{(2)} = 9(\sinh(\Delta\beta)\{4E[3+(\Delta\beta)^2]/3\Delta^3 + 3(E^2-5B^2)\beta/\Delta^3 + 2E[(\Delta\beta)^2-1]/\Delta^3 + 45\beta/\Delta\} + \cosh(\Delta\beta)\,[4E\beta/\Delta^2 - 3(E^2-5B^2)\,\beta^2/\Delta^2 + 2E\beta/\Delta^2 + 15\beta^2])\,\textstyle\sum(P^{z\gamma})^2_{\rm dif}\,.$$

V. CALCULATIONS: SMALL FIELD

We return to a system of axes referenced to the CF, z being the symmetry axis, and consider one set of ions. Let us first consider the field to be in the z direction. The resultant resolvent is given by the following matrix:

$$(t - \mathcal{H}_c - \mathcal{H}_z)^{-1} = \begin{pmatrix} (t+D-\frac{1}{2}H)/\delta_+ & 0 & E\sqrt{3}/\delta_+ & 0 \\ 0 & (t-D-\frac{3}{2}H) & 0 & E\sqrt{3}/\delta_- \\ E\sqrt{3}/\delta_+ & 0 & (t-D+\frac{3}{2}H)\,\delta_+ & 0 \\ 0 & E\sqrt{3}/\delta_- & 0 & (t+D+\frac{1}{2}H)/\delta_- \end{pmatrix}, \qquad (5.1)$$

where $\delta_\pm = t^2 - \frac{3}{4}H^2 - \Delta^2 \pm (2B+t)H$.

For the sake of elegance we could also express this in Stevens operators. One needs new operator polynomials:

$$O_{30} = 5J_z^3 - J_z(3J^2 + 3J - 1) \qquad (5.2)$$

and

$$O_{32} = \tfrac{1}{2}(J_z J^{+2} + J^{+2} J_z)\,. \qquad (5.3)$$

The coefficients are determined by the need to be orthogonal to the lower-order polynomials.[18] (Contrary to the tensor operators, which are all properly normalized, the Stevens operators seem to have a rather arbitrary proportionality factor.) The resolvent expressed in these operator polynomials is

$$(t - \mathcal{H}_c - \mathcal{H}_z)^{-1} = \{[t + BO_{20} + H(\tfrac{3}{2}O_{10} + \tfrac{4}{15}O_{30})] \times [t^2 - \tfrac{3}{4}H^2 - \Delta^2 + (O_{10} - \tfrac{3}{2}O_{30})(t+2B)H] + \tfrac{1}{2}E(O_{32} + O_{3-2})\}/ \times [t^2 - (\tfrac{3}{4}H^2 - \Delta^2) - (t+2D)^2H^2]\,. \qquad (5.4)$$

This is a complicated expression for handling by the method used heretofore. In the susceptibility calculation, however, we need only the terms up to the second order in the magnetic field; hence, we prefer to use perturbation theory in the parameter H.

The general expression for the energy eigenvalues of a spin Hamiltonian as a function of the powers of H is

$$E = E^{(0)} + E^{(1)}H + E^{(2)}H : H + \cdots\,.$$

The second term gives rise to the $1/T$ term in the susceptibility, and the third to the so-called temperature-independent paramagnetism of Van Vleck. In the case considered by O'Brien[7] this contribution is absent if the field is in the z direction: Now, with the incorporation of Baker's E term, there *will* be such a contribution. The roots of the eigenvalue equation are

$$\begin{aligned} \lambda_1 &= \Delta + (\tfrac{1}{2} + D/\Delta)H + (3E^2/2\Delta^3)H^2\,, \\ \lambda_2 &= -\Delta + (\tfrac{1}{2} - D/\Delta)H - (3E^2/2\Delta^3)H^2\,, \\ \lambda_3 &= \Delta - (\tfrac{1}{2} + D/\Delta)H + (3E^2/2\Delta^3)H^2\,, \\ \lambda_4 &= -\Delta - (\tfrac{1}{2} - D/\Delta)H - (3E^2/2\Delta^3)H^2\,. \end{aligned} \qquad (5.5)$$

The resulting susceptibilities are, for the temperature-dependent part,

$$\chi_1 = \beta[\tfrac{1}{4} + (D/\Delta)^2 - (D/\Delta)\tanh(\beta\Delta)]\,, \qquad (5.6)$$

and for the so-called temperature-independent part,

$$\chi_2 = -3(E^2/\Delta^3)\tanh(\beta\Delta)\,. \qquad (5.7)$$

Since they represent the magnetization in the z direction produced in response to a field in the z direction, these quantities are actually the zz component of the susceptibility tensor.

In order to obtain the xx component, we assume the field to be in the x direction and evaluate [see Eq. (5.1)] the secular equation:

$$[(\lambda^2 - D^2) - \tfrac{3}{4}H^2]^2 - (D-\lambda)^2H^2 + \tfrac{1}{2}EH^2(D - \lambda - \tfrac{3}{2}E) - 3E^2(D-\lambda)^2 + 9E^4 = 0\,. \qquad (5.8)$$

Rather than to search for the roots of this equation, we note that the matrix

$$BO_{20} + \tfrac{1}{2}E\,(O_{22} + O_{2-2}) + S_x H_x$$

can be used for perturbation theory provided we first diagonalize the center part. This is necessary on account of the degeneracy of these two diagonal elements. We obtain, after interchanging the second and third rows and columns,

$$\begin{pmatrix} D-\lambda & E\sqrt{3} & \frac{1}{2}\sqrt{3}\,H_x & 0 \\ E\sqrt{3} & -D-\lambda & H_x & \frac{1}{2}\sqrt{3}\,H_x \\ \frac{1}{2}\sqrt{3}\,H_x & H_x & -D-\lambda & E\sqrt{3} \\ 0 & \frac{1}{2}\sqrt{3}\,H_x & E\sqrt{3} & D-\lambda \end{pmatrix} = 0 \,.$$

The matrix is now in such a form that we can first diagonalize each "diagonal block" and subsequently look for the influence of the magnetic field in the x direction. If we do that and apply the same unitary transformations to the matrix as a whole, we find

$$\begin{pmatrix} \Delta & 0 & x & y \\ 0 & -\Delta & z & x \\ x & z & -\Delta & 0 \\ y & x & 0 & \Delta \end{pmatrix} \,,$$

where

$$x = \sqrt{3}\,(D+E)\,H_x/\,2\Delta \;,$$

$$y = 3E(D+\Delta+E)\,H_x/\,2\Delta(D+\Delta) \;,$$

and

$$z = (D+\Delta-3E)H_x/\,2\Delta \;,$$

and Δ is defined by Eq. (4.2), as before. This matrix, however, can be completely solved by rewriting it using half the sum and half the difference of the first and fourth, and of the second and third rows and columns, respectively, which breaks it up into two 2×2 matrices. The resulting eigenvalues are

$$\lambda_\pm = \pm\tfrac{1}{2}\,(y+z) + \epsilon[\tfrac{1}{2}\,(2\Delta \pm y + z)^2 + x^2]^{1/2} \,, \qquad (5.9)$$

with $\epsilon = +1$. The other two roots are given by the same equation with $\epsilon = -1$. For small values of H_x, these reduce to

$$\begin{aligned} \lambda_{1,2} &= \Delta \pm y - x^2/2\Delta \;, \\ \lambda_{3,4} &= -\Delta \pm z + x^2/2\Delta \;, \end{aligned} \qquad (5.10)$$

and with this result we can calculate the susceptibilities

$$\chi_1^{xx} = \tfrac{1}{2}\,\beta\left[\left(1-\frac{3DE}{\Delta^2}\right)+\left(\frac{D}{\Delta}-3\,\frac{DE}{\Delta^2}\right)\tanh(\beta\Delta)\right] \,, \qquad (5.11)$$

$$\chi_2^{xx} = \tfrac{3}{4}\,[(D+E)^2/\Delta^3]\tanh(\beta\Delta) \;. \qquad (5.12)$$

In order to determine χ^{yy} one can use a simple transformation by which the crystal field parameter E goes into $-E$. Since there are no off-diagonal elements of the susceptibility tensor in the CF system of reference, this completes the calculation of the site susceptibility.

To obtain the net susceptibility, a rotation from the CF system to the simple-cubic system of the magnetic cell is needed. If we indicate the transformations used in Eq. (4.6) by U_L^{-1}, we find for the magnetic-moment matrix in the single cubic system

$$\chi_\Gamma = U_\Gamma^{-1}\chi_{\mathrm{CF}}\,U_\Gamma \,, \qquad (5.13)$$

where χ_{CF} is the (diagonal) magnetic-moment matrix in the CF system. The three nonzero elements of χ_{CF} are the components calculated above. We introduce $\chi_\perp = \frac{1}{2}(\chi_x+\chi_y)$ and $\Delta\chi = \chi_x - \chi_y$ to obtain equations similar to Durieux's. His $P = kT\chi_z$, his $Q = kT\chi_\perp$ and $\Delta\chi$ is absent in his case, since he did not introduce the E term.

For the case $\Gamma = \mathrm{I}$, we find

$$\frac{1}{6}\begin{pmatrix} 4\chi_\perp+2\chi_z-\Delta\chi & -2(\chi_\perp-\chi_z-\Delta\chi) & -2\chi_\perp+2\chi_z-\Delta\chi \\ -2(\chi_\perp-\chi_z-\Delta\chi) & 4\chi_\perp+2\chi_z-\Delta\chi & 2\chi_\perp+2\chi_z-\Delta\chi \\ -2(\chi_\perp+2\chi_z-\Delta\chi) & -2\chi_\perp+2\chi_z-\Delta\chi & 4\chi_\perp+2\chi_z+2\Delta\chi \end{pmatrix}. \qquad (5.14)$$

The result for the other three orientations [as defined below (4.6)] is found by multiplying each row and column by the corresponding ϵ; the diagonal elements do not change sign, of course. The off-diagonal elements occur with plus and minus signs twice. The zeroth-order susceptibility has a zz component equal to

$$\chi^{zz} = \tfrac{2}{3}\,\chi_\perp + \tfrac{1}{3}(\chi_z + \Delta\chi) \;. \qquad (5.15)$$

The xx and yy components are different. This means that the total symmetry, i.e., averaged over the four sublattices, may be noncubic. If that symmetry were cubic, and we shall see that below a certain temperature this is no longer the case, we should have to modify the rotations I, II, III, IV. The rotations of the axes in (4.6) can be described by Eulerian angles:

$$\psi_{\mathrm{I}} = \psi_{\mathrm{II}} = -\psi_{\mathrm{III}} = -\psi_{\mathrm{IV}} = \tfrac{1}{4}\pi \,,$$

$$\theta_{\mathrm{I}} = -\theta_{\mathrm{II}} = \theta_{\mathrm{III}} = -\theta_{\mathrm{IV}} = \cos^{-1}(1/\sqrt{3}) \approx 55^\circ \;,$$

$$\Phi_{\mathrm{I}} = \Phi_{\mathrm{II}} = \Phi_{\mathrm{III}} = \Phi_{\mathrm{IV}} = 0 \;.$$

We can obtain cubic symmetry by taking $\Phi_{\mathrm{II}} = \Phi_{\mathrm{III}} = \frac{1}{2}\pi$ instead of zero. This means that in these two cases the x and y axes are transformed into y and $-x$ and such a rotation over the third Euler angle will make $\chi_{xx} = \chi_{yy} = \chi_{zz}$. It is not clear from the existing information[7,8] whether this rotation corresponds to the actual situation in CMA. In the articles quoted, only the zz components were calculated, hence the author does not know what these authors considered for the orientation of the x and y axes and moreover their results did not depend on such a choice. The author considers it more satisfactory, from general considerations of symmetry, to make another choice for the angles Φ, viz., $\Phi = \frac{1}{4}\pi + n(\frac{1}{2}\pi)$ with $n = 1, 2, 3, 4$. There is no easy way to distinguish between the two cases. From Baker's[9] work it became evident that below 170 K the crystal does not have cubic symmetry any more but becomes slightly tetragonal, and that the angle between the CF axis (which he calls the rhombic axis) and the tetragonal axis is not exactly

55° but seems to be closer to 60°. We shall sidestep this point for the moment by introducing an unspecified angle θ. Again we raise the question about the orientation of the z and y axes of the CF. We analyzed Baker's results (Appendix C) and came to the conclusion that the four angles Φ are definitely not equal, and were close to 0, 0 and $\frac{1}{2}\pi$, $\frac{1}{2}\pi$. If these are the exact values of the angles, we have to modify the results obtained by O'Brien and Durieux for the susceptibility in the first order of the interaction.

To calculate this susceptibilitity contribution, we distinguish, as before, between two cases. If both spins of a pair are on the same sublattice, the dipolar contribution is now only approximately zero since each sublattice is near cubic rather than cubic. However, the deviation is so small that the corresponding dipole sum almost vanishes and we shall continue to take it as zero. There is also a contribution from the exchange interaction between atoms of the same sublattice. Since this is a next-nearest-neighbor contribution, we discount it (in the absence of information).

If the spins are on different sublattices, we have to evaluate the interaction between six pairs. We consider a pair where the x and y axes are parallel (or antiparallel) to each other. We introduce the matrix $\chi(\theta, \epsilon)$ which has the elements

$$\begin{aligned} \chi_{11} &= \chi_{22} = \tfrac{1}{2}(\cos^2\theta + 1)\, Q + \tfrac{1}{2}(\sin^2\theta)\, P + \tfrac{1}{4}(\cos^2\theta - 1)\, R, \\ \chi_{33} &= (\sin^2\theta)\, Q + (\cos^2\theta)\, P + \tfrac{1}{2}(\sin^2\theta)\, R\ , \qquad (5.16) \\ \chi_{12} &= \tfrac{1}{2}\epsilon(\cos^2\theta - 1)\, Q + \tfrac{1}{2}(\cos^2\theta + 1)\, R + \tfrac{1}{2}(\sin^2\theta)\, P\ , \\ \chi_{13} &= \epsilon\chi_{23} = -\tfrac{1}{2}(\sin\theta\cos\theta)\,(Q - P - \tfrac{1}{2}R)\ , \end{aligned}$$

where $P = \chi_z$, $Q = \frac{1}{2}(\chi_x + \chi_y)$, and $R = \chi_x - \chi_y$ $(\epsilon = \pm 1)$. (That is, P and Q are Durieux's constants multiplied by β.) The angle θ depends on the temperature range: Above the transition, $\cos\theta = 1/\sqrt{3}$, as was used in Refs. 7 and 8, and below the transition one has to use $\cos\theta = \frac{1}{2}$.

We have introduced the interaction matrix $P_{ij}^{\alpha\beta}$ ($\alpha\beta = x, y, z$) between the sites i and j. The exchange part we consider diagonal and independent of x, y, and z and zero for all sites j not nearest neighbors of i. For this type of lattice, assuming it is nearly fcc, the dipolar part has zero off-diagonal elements after summation over j and its diagonal elements between sublattices I and IV have the property that

$$\sum_{ij} P_{ij}^{xx} = \sum_{ij} P_{ij}^{yy} = -\tfrac{1}{2}\sum_{ij} P_{ij}^{zz}\ .$$

The same relation holds between sublattices II and III. The other two pairs have similar equalities: I-II and III-IV with the factor $-\frac{1}{2}$ in front of the xx component rather than in front of the zz component and I-III and II-IV with the factor in front of the yy component. We shall use these relations in the final calculation and express all sums in $\sum P^{zz}$ between I and IV.

To obtain the contribution to the susceptibility of the set of pairs mentioned above, we matrix multiply $\chi(\theta, \epsilon)$, P and $\chi(-\theta, \epsilon)$. The two other sets are found by multiplying $\chi(\theta, \epsilon)$ and $\chi(\theta, -\epsilon)$ on one hand, and $\chi(\theta, \epsilon)$, P, and $\chi(-\theta, -\epsilon)$ on the other hand. This gives three pairs, and the other three give the same total result. Hence, if we sum over all six pairs we find a matrix $\chi_{(1)}$ whose zz component is

$$\begin{aligned} \chi_{(1)}^{zz} = 2\{3\,(\textstyle\sum v_{ij})\,[(Q + \tfrac{1}{2}R)\sin^2\theta + P\cos^2\theta]^2 \\ -(\textstyle\sum v_{ij} + \sum P_{ij}^{zz})\sin^2\theta\cos^2\theta\,(Q + \tfrac{1}{2}R - P)^2\}\ . \end{aligned} \qquad (5.17)$$

In the above expression we have broken up the interaction tensor in two parts: P_{ij}, the dipole interaction proper, and v_{ij}, the exchange interaction. The factor of 2 arises from the same considerations as mentioned before [compare Eq. (4.4)]. The zeroth-order term has to be described in the same way:

$$\chi_{(0)}^{zz} = (Q + \tfrac{1}{2}R)\sin^2\theta + P\cos^2\theta\ . \qquad (5.16\text{a})$$

The susceptibility in the z direction is given by the sum of Eqs. (5.16a) and (5.17). The quantity P is given by the sum of (5.6) and (5.7) and the quantities Q and R are determined by the sum of (5.11) and (5.12) with $\pm E$ inserted. We find, introducing the factor $\mu_B^2 g^2$ which we left out so far for convenience,

$$\begin{aligned} \chi^{zz} = (\tfrac{1}{2}g\mu_B)^2(3Q + P - \tfrac{3}{2}R) + 6\,(\tfrac{1}{2}g\mu_B)^4 \\ \times[(\textstyle\sum v_{ij})\,(3Q + \tfrac{1}{2}R + P)^2 \\ -(\textstyle\sum v_{ij} + \sum P_{ij})\,(Q + \tfrac{1}{2}R - P)^2] \end{aligned} \qquad (5.18)$$

for temperatures below the crystallographic transition (170 K). The summations are over one sublattice only. For CMA $\sum_j v_{ij} = 2v$.

In order to be able to make a direct comparison with experiments we inserted the expressions for P, Q, and R, using Baker's parameters, in this equation. The result is

$$\begin{aligned} \chi^{zz} = 0.6079\times 10^{-24}\,[A + 7.2947\times 10^{-24}\,v(B^2 - C^2) \\ + 1.7857\times 10^{-2}\,C^2], \\ A = 24.9646\Delta\beta - 0.2576\Delta\beta\tanh\Delta\beta + 13.4525\tanh\Delta\beta\ , \\ (5.18\text{a}) \\ B = 20.1532\Delta\beta - 5.0550\Delta\beta\tanh\Delta\beta + 18.2628\tanh\Delta\beta\ , \\ C = -6.8476\Delta\beta - 12.7996\Delta\beta\tanh\Delta\beta + 56.7729\tanh\Delta\beta, \end{aligned}$$

where $\Delta\beta$ is a temperature scale using the reduction factor 0.1273 K.

For temperatures above the transition temperature,

$$\chi^{zz} = \tfrac{1}{3}\,(g\mu_B)^2(2Q + R + P) + \tfrac{2}{3}\,(g\mu_B)^4\,(\textstyle\sum v_{ij})$$

$$\times(2Q+R+P)^2$$

$$-\tfrac{4}{9}\,(g\mu_B)^4\,(\textstyle\sum v_{ij}+\sum P)\,(Q+\tfrac{1}{2}R-P)^2\,. \qquad (5.19)$$

The exchange part of this formula corresponds to Durieux's equation if one takes $R=0$.

APPENDIX A: SPECIFIC-HEAT CONTRIBUTIONS LINEAR IN THE DIPOLE INTERACTION

If the CF is absent there is no contribution linear in $\mathcal{H}_D$, the dipolar part of the Hamiltonian, nor is there one linear in the exchange, since the trace of each spin matrix is zero. In the presence of the crystal field this remains true since the field contains no linear (or, more generally, odd) terms in the spin operators. The trace over an odd number of spin operators is either zero or pure imaginary. In the last case there is always a term in the sum that gives the opposite, i.e., complex-conjugate, value, since the Hamiltonian and its powers are Hermitian operators. Hence, the sum of all terms will again have a zero trace.

There is also a general reason why the term linear in the dipole interaction should be zero. If it were not, then the dipolar sum, which converges only conditionally, would introduce a shape-dependent specific heat. This is not possible on thermodynamic grounds, at least not for zero external field.

APPENDIX B

The necessary inverse Laplace transforms can be evaluated using the expression[19]

$$f(t)=\frac{\Gamma(k)}{(t^2-a^2)^K}\rightarrow F(\beta)=\pi^{1/2}\left(\frac{\beta}{2a}\right)^{k-1/2} I_{k-1/2}(a\beta)\,, \qquad \text{(B1)}$$

where t is the variable used in the Laplace transform and a is a constant. The right-hand side contains the new variable β and I is the Bessel function of imaginary argument. The first three are[20] $(z=a\beta)$

$$(t^2-a^2)^{-1}\rightarrow a^{-1}\sinh z\,, \qquad \text{(B2)}$$

$$(t^2-a^2)^{-2}\rightarrow \tfrac{1}{2}a^{-3}\,(-\sinh z+z\cosh z)\,, \qquad \text{(B3)}$$

$$(t^2-a^2)^{-3}\rightarrow \tfrac{1}{8}a^{-5}\,[(3+z^2)\sinh z-3z\cosh z]\,. \qquad \text{(B4)}$$

To find the expression with t in the numerator we use $tf(t)-F(0)\rightarrow F'(\beta)$. All functions have the property that $F(0)=0$, hence we can use simple differentiation, again using $z=a\beta$:

$$t/(t^2-a^2)^2\rightarrow \tfrac{1}{2}a^{-2}\,(z\sinh z)\,, \qquad \text{(B5)}$$

$$t^2/(t^2-a^2)^2\rightarrow \tfrac{1}{2}a^{-1}\,(\sinh z+z\cosh z)\,, \qquad \text{(B6)}$$

$$t/(t^2-a^2)^3\rightarrow \tfrac{1}{8}a^{-4}\,(-z\sinh z+z^2\cosh z)\,, \qquad \text{(B7)}$$

$$t^2/(t^2-a^2)^3\rightarrow \tfrac{1}{8}a^{-3}\,(z^2-1)\,(\sinh z+z\cosh z), \qquad \text{(B8)}$$

$$t^3/(t^2-a^2)^3\rightarrow \tfrac{1}{8}a^{-2}\,(3z\sinh z+z^2\cosh z)\,. \qquad \text{(B9)}$$

APPENDIX C

In this appendix we evaluate the formulas necessary to analyze a part of Baker's data in order to determine the positions of the CF x-y axes in the sublattices relative to each other. Our main concern is to determine the "third" Euler angle Φ for each system. By the third angle we mean the angle of rotation after the rotation around the node line has taken place, i.e., the rotation around the "new" z axis.

The formula needed to describe an arbitrary rotation in S^+, S^-, S^0 space is given by the following matrix R:

$$R=\begin{pmatrix} \tfrac{1}{2}(1+\cos\theta)\,e^{i(\Phi+\psi)} & -\sin\theta\,e^{-i\Phi} & \tfrac{1}{2}(\cos\theta-1)\,e^{i(\psi-\Phi)} \\ \tfrac{1}{2}\sin\theta\,e^{-i\psi} & \cos\theta & \tfrac{1}{2}\sin\theta\,e^{i\psi} \\ \tfrac{1}{2}(\cos\theta-1)\,e^{i(\Phi-\psi)} & -\sin\theta\,e^{i\Phi} & \tfrac{1}{2}(\cos\theta+1)\,e^{i(\psi+\Phi)} \end{pmatrix},$$

where ψ is the angle of rotation around the original z axis and θ is the angle around the node line or "new" y axis. Note that this expression is not unitary since the operators S^+ and S^- are not normalized. It would be far handier to normalize these operators, but we refrain from doing so on account of the possible confusion with the rest of the literature.

We select one of the four CF z axes as the z axis of our reference system, that is, we take our z axis along one of the four body diagonals. The orientation of the x-y axis can be ignored for the time being. In this system the other three body diagonals are oriented as follows: They make equal angles with the z axis and the angle θ_{dd} is given by $\cos\theta_{dd}=\frac{1}{3}$. Their projections on the x-y plane, which is a $\{1, 1, 1\}$ plane in the cubic lattice, make angles of 120° with each other. The orientation of one of the projections may be taken to be the x axis. Our first task is to transform the Hamiltonian that describes the CF of our reference system, which is given by

$$\mathcal{H}=BO_{20}+\tfrac{1}{2}E\,[(S^+)^2e^{i\Phi_1}+(S^-)^2e^{-i\Phi_1}]\,,$$

where Φ_1 is the angle that determines the orientation with respect to that x axis into the Hamiltonians that describe the other three crystal fields. This is done by a rotation ψ_i $(i=2, 3, 4)$ which puts the node line perpendicular to the plane of projection, followed by the actual projection, which is a rotation of $\cos^{-1}(\frac{1}{3})$ around the node line, and finally by a rotation of Φ_i around each of the new z axes. It is this last angle that we want to determine from the spin-resonance experimental data. The resulting Hamiltonians for the three CF systems are

$$\mathcal{H}_i=(-\tfrac{1}{3}B+\tfrac{4}{9}E\cos 2\Phi_i)O_{20}$$

$$+\sqrt{2}\,(\tfrac{1}{3}B-\tfrac{2}{9}\,E\,e^{-2i\Phi_i}+\tfrac{1}{18}\,E\,e^{2i\Phi_i})\,O_{21}\,e^{-i\psi_i}$$

$$+(2B+\tfrac{2}{9}E\,e^{-2i\Phi_i}+\tfrac{1}{18}E\,e^{2i\Phi_i})\,O_{22}\,e^{-2i\psi_i}+\text{c.c.}$$

$$(i = 2, 3, 4) \; .$$

In the experiment the field was rotated in the x-y plane, hence we would have to solve these Hamiltonians, as well as the Hamiltonian referring to the $i=1$ system, after adding the appropriate Zeeman term. Since this introduces large off-diagonal elements it is much easier to make use of the fact that the magnetic field energy was much larger than the CF energy in the experiment and to exert a 90° rotation in each of the Hamiltonians, using again matrix R. In this rotation we take $\psi = 0$; $\theta = \frac{1}{2}\pi$, and the third angle is called Φ_H since it represents the angular dependence of the resonance field. The result of this transformation is

$$\mathcal{H} = \mathcal{H}_z + [\tfrac{1}{6} B - \tfrac{2}{9} E \cos(2\Phi_i)] - \cos(2\Phi_H)(2B + \tfrac{2}{9} E\, e^{-2i\Phi_i} + \tfrac{1}{8} E\, e^{2i\Phi_i} + \text{c.c.})\, O_{20}$$

$$+ \text{off-diagonal elements} \; .$$

All curves in the experimental data [Baker's Fig. 1(a)] have a periodicity of 180° but they all have different phase angles and different base lines, except for a few coincidences. From the figure we determined the positions of the base lines of the different curves. The numerical values can be compared with the coefficient $\frac{1}{6}B - \frac{2}{9}E\cos 2\Phi_i$ in the previous equation. From this we conclude that the angles Φ_i are not zero, and that two are equal and one is different. We estimate that one is zero and the two others are 90°. This choice is partially suggested by the high-temperature cubic symmetry.

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