Inversion of Cubic de Haas–van Alphen Data, with an Application to Palladium*

F. M. MUELLER AND M. G. PRIESTLEY
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
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We have constructed to high order ($l=30$) all the linear combinations of spherical harmonics which transform as the identity representation of the full cubic group O_h. These are used with Mueller's inversion scheme to obtain the radius vectors of the palladium s-band surface from the de Haas–van Alphen areas. The accuracy of this inversion is limited by the ambiguities inherent in data restricted to the symmetry planes. The limits to which such data define the anisotropy uniquely are calculated explicitly in an analysis which applies to any anisotropic quantity in a cubic system. The practical importance of this point is emphasized. We find that the electron surface in Pd contains 0.364 ± 0.004 electrons/atom.

I. INTRODUCTION

IN nearly all comparisons of de Haas–van Alphen (dHvA) data with the results of band structure calculations there is an unnecessary error associated with the fact that the dHvA effect measures extremal areas of the Fermi surface, whereas what is really needed for a comparison is the Fermi surface radius. Lifshitz and Pogorelov[1] have shown that a unique solution to this inversion problem exists if the surface is closed, centrosymmetric, and has a single-valued radius vector from that center. A solution in terms of the expansion of the data in the appropriate spherical harmonics has recently been discussed by Mueller.[2] In this paper we apply the expansion technique to the dHvA data[3,4] for the palladium s-band electron surface centered at Γ.

In the special case of the full cubic symmetry, i.e., the identity representation of the group O_h, we have derived to arbitrary order the appropriate linear combinations of spherical harmonics. Using these we invert the Pd s-band dHvA data to the highest coefficients which can be fitted uniquely from the present data. The question of how much information is contained within the data is considered in detail in Sec. 3, where it is shown that the usual method of taking data only along symmetry lines in an anisotropic cubic system determines only a limited number of expansion coefficients. To avoid either unnecessary ambiguity or excessive redundancy this point must be carefully considered if data can be obtained accurately. The analysis in this section applies to any anisotropic quantity which is being studied experimentally in a cubic system.

II. INVERSION

The Pd dHvA data (taken from Refs. 3 and 4) are shown in Figs. 1(a) and 1(b). Note that the data were taken only along the basic symmetry lines of the cubic system, i.e., in the (100) and (110) planes. We use atomic units ($\hbar=m=e=1$) throughout the calculation. Using a standard matrix inversion technique,[5] we make least-squares fit of the area $A(\theta,\varphi)$ to the finite expansion

$$A(\theta,\varphi)=\sum_{il} {}_i\beta_l\, {}_iK_l, \tag{1}$$

where the cubic harmonics

$${}_iK_l=\sum_m {}_ia_{lm}C_{lm} \tag{2}$$

are linear combinations of spherical harmonics with the appropriate cubic symmetry, and the ${}_ia_{lm}$ are the symmetry coefficients calculated in the Appendix and listed in Table I. Here the indices l and m are the usual indices for spherical harmonics and the index i labels independent irreducible representations for a given l. The spherical harmonics C_{lm} are real functions related to the usual complex spherical harmonics by the relations

$$\begin{aligned} C_{lm}&=2^{-1/2}(Y_{lm}+Y_{l,-m}),\\ C_{l0}&=Y_{l0}. \end{aligned} \tag{3}$$

The φ variation of C_{lm} is thus $\cos m\varphi$. The functions C_{lm} so defined form an orthonormal set over the unit sphere, and so do the ${}_iK_l$.

The least-squares fit determines a set of coefficients ${}_i\beta_l$. The number of these coefficients that may be fitted uniquely depends on the number of planes in which data is taken and is discussed in detail in Sec. 3. It is enough at this point to remark that data taken only in symmetry planes do not contain complete information, in practice as well as in principle. For the data discussed in this paper we cannot make a complete expansion beyond $l=18$. In fact we can fit just the first 11 coefficients ${}_i\beta_l$ with data in the (100) and (110) planes, although our present computer program will handle 27 of these coefficients without modification. It is shown in Sec. 3 that the only further coefficients that we can fit are those of the form ${}_1\beta_l$. It is doubtful whether it is worthwhile to include these while omitting

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[1] I. M. Lifshitz and A. V. Pogorelov, Dokl. Akad. Nauk SSSR **96**, 1143 (1954).

[2] F. M. Mueller, Bull. Am. Phys. Soc. **10**, 1089 (1965); and the preceding paper, Phys. Rev. **148**, 636 (1966).

[3] J. J. Vuillemin and M. G. Priestley, Phys. Rev. Letters **14**, 307 (1965).

[4] J. J. Vuillemin, Phys. Rev. **144**, 396 (1966).

[5] C. Lanczos, *Applied Analysis* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1961), p. 230.

TABLE I. The coefficients $_ia_{lm}$ of symmetrized spherical harmonics which transform as the identity representation Γ_1 of the group O_h. These are commonly referred to as cubic harmonics. These coefficients were calculated in double precision and are accurate to one digit in the last place.

		m							
i	l	0	4	8	12	16	20	24	28
1	0	1.00000000	0	0	0	0	0	0	0
1	4	0.76376261	0.64549722	0	0	0	0	0	0
1	6	0.35355338	−0.93541434	0	0	0	0	0	0
1	8	0.71807033	0.38188130	0.58184332	0	0	0	0	0
1	10	0.41142537	−0.58630197	−0.69783892	0	0	0	0	0
1	12	0.69550265	0.31412555	0.34844954	0.54422797	0	0	0	0
2	12	0	0.55897937	−0.80626751	0.19358400	0	0	0	0
1	14	0.44009645	−0.45768183	−0.49113230	−0.59634848	0	0	0	0
1	16	0.68136168	0.27586801	0.29048987	0.32756975	0.51764542	0	0	0
2	16	0	0.63704821	−0.32999033	−0.64798073	0.25572816	0	0	0
1	18	0.45791513	−0.38645598	−0.40209462	−0.43746593	−0.53657149	0	0	0
2	18	0	0.14872751	−0.63774601	0.72334167	−0.21894515	0	0	0
1	20	0.67141495	0.24982619	0.25782846	0.27469333	0.31248919	0.49719956	0	0
2	20	0	0.66299538	−0.11295259	−0.42738441	−0.52810433	0.29347435	0	0
1	22	0.47032747	−0.33986007	−0.34871252	−0.36650299	−0.40183160	−0.49587665	0	0
2	22	0	0.21497472	−0.67045552	0.15126929	0.62745985	−0.29611988	0	0
1	24	0.66391779	0.23043627	0.23542093	0.24510494	0.26292776	0.30074488	0.48066030	0
2	24	0	0.67270178	−0.00361069	−0.24496919	−0.44669340	−0.43171389	0.31864943	0
3	24	0	0	0.26563038	−0.68036113	0.63424215	−0.25204068	0.02759743	0
1	26	0.47959634	−0.30642626	−0.31202488	−0.32263184	−0.34116419	−0.37590092	−0.46577346	0
2	26	0	0.26049909	−0.63956244	−0.11681329	0.36798485	0.50757374	−0.34119025	0
1	28	0.65799998	0.21519893	0.21856660	0.22482529	0.23535695	0.25360376	0.29116473	0.46682221
2	28	0	0.67603415	0.05632341	−0.12515216	−0.31376506	−0.43318803	−0.35350399	0.33626918
3	28	0	0	0.37778608	−0.63788873	−0.01342908	0.56861801	−0.35289583	0.04830504
1	30	0.48685080	−0.28097712	−0.28478765	−0.29176328	−0.30317406	−0.32189928	−0.35589278	−0.44227251
2	30	0	0.29408104	−0.59701923	−0.24375591	0.13917957	0.42377798	0.40271380	−0.36950003
3	30	0	0	0.06993604	−0.36082391	0.67571677	−0.59060740	0.24146388	−0.03464088

those of the other degenerate sets, and indeed a 14-term fit (i.e., with the addition of $_1\beta_{20}$, $_1\beta_{22}$, $_1\beta_{24}$) yields an only marginally better fit to the observed areas. The 11-term fit to the area is shown in Fig. 1.

For cubic symmetry the inversion relation derived by Mueller[2] yields

$$_i\gamma_l = {}_i\beta_l/\pi P_l(0)\,, \tag{4}$$

where the P_l are Legendre polynomials and the $_i\gamma_l$ are the coefficients of the expansion of the square of the radius vector

$$\rho^2(\theta,\varphi) = \sum_{il} {}_i\gamma_l\, {}_iK_l\,. \tag{5}$$

These equations were then used to find the coefficients $_i\gamma_l$ and the radius vectors. The coefficients $_i\beta_l$ and $_i\gamma_l$ are listed in Table II together with the rms error of the area expansion. For the 11-term fit, this is 0.17% of the average area or 0.75% of the maximum area variation, the latter being probably a fairer estimate of the goodness of fit. The random errors in the data are almost all less than 0.1%. Figure 2 shows the calculated radius vectors in the (100) and (110) planes for both the 11-term fit and the incomplete 14-term fit discussed above. The difference between these gives some estimate

TABLE III. The principal radii of the electron Fermi surface of Pd. As is shown in the text, the radii are accurate to 1%–2%.

Direction	Radius (atomic units) 11-term	14-term
[100] ΓX	0.602	0.605
[111] ΓL	0.558	0.569
[110] ΓK	0.447	0.434

TABLE II. The expansion coefficients found by the least-squares fit.

		11-term fit		14-term fit	
		Area[a]	(Radius)^2 [b]	Area	(Radius)^2
i	l	$_i\beta_l$	$_i\gamma_l$	$_i\beta_l$	$_i\gamma_l$
1	0	2.54322	0.8095	2.54994	0.81168
1	4	0.04127	0.03503	0.03810	0.03234
1	6	−0.1069	0.1089	−0.11400	0.11615
1	8	0.02150	0.02502	0.02407	0.02802
1	10	−0.00377	0.00487	−0.00298	0.03851
1	12	0.00788	0.01112	0.01015	0.01432
2	12	−0.02983	−0.04209	−0.02858	−0.04033
1	14	0.01375	0.02089	0.01343	0.02041
1	16	0.00889	0.01442	0.00326	0.00529
2	16	−0.00403	−0.00654	−0.00645	−0.01049
1	18	−0.00567	0.00973	−0.00739	0.01268
2	18			...	...
1	20			0.00569	0.01027
2	20			...	...
1	22			0.00118	−0.00224
2	22			...	...
1	24			−0.00171	−0.00338
rms error (a.u.)		0.00129		0.00091	

[a] The $_i\beta_l$ are the coefficients of the expansion for the area in Eq. (1). They are independent of the number of terms in the fit only when the least-squares fit is made by projection integrals on the surface of the sphere.
[b] The $_i\gamma_l$ are the corresponding coefficients of the expansion of the square of the radius vector in Eq. (5).

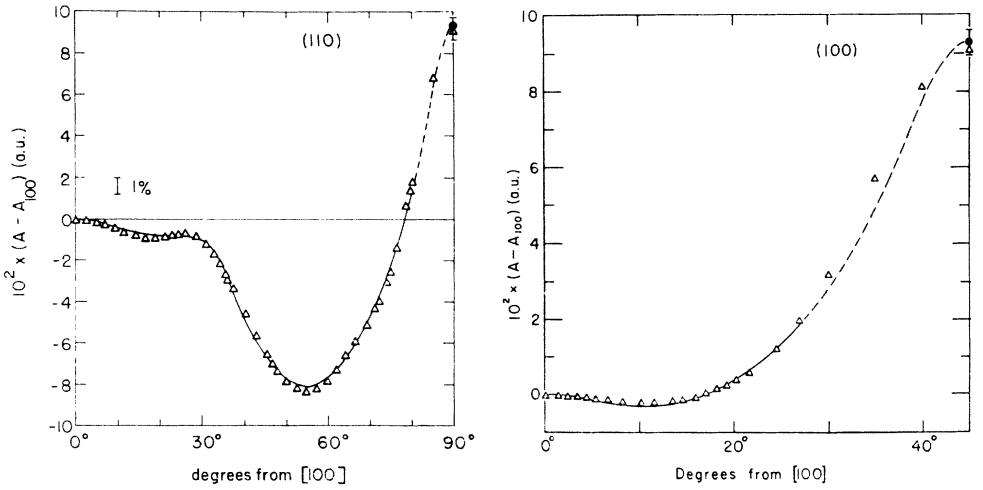

FIG. 1. (a) The solid line and the point at [110] are the Pd data in the (110) plane taken from Ref. 4. Δ—the least-squares fit to the data for 11 coefficients. A_{100} was taken as 0.726 a.u. (b) The corresponding plot for the (100) plane. The symbols are the same.

of the error due to the finite inversion. We conclude that the palladium electron surface has the radii shown in Table III. The discussion below shows that the accuracy of an 11-term fit is of the order of 2% in radius vector, which is to be compared with the 0.17% rms error in the same fit to the observed areas. It is evident that more data, taken away from lines of symmetry, are required to obtain more accurate radius vectors.

The total volume of the electron surface was also computed, with the result that

$$n_e = 0.364 \pm 0.004 \text{ electrons/atom},$$

with an error which is predominantly due to the error in the measured dHvA area for $\mathbf{H} \| [100]$.

The data show that for $\mathbf{H}$ near [111] there are two extremal areas on this surface, and we can use our model to calculate the noncentral extremal for $\mathbf{H} \| [111]$. The calculation of noncentral extremal areas is a complicated problem, but one which has widespread importance in the accurate relation of Fermi surface data to the band structure. It also provides a sensitive check on the accuracy of the inversion, since there are no adjustable parameters. The results of a numerical integration of the area as a function of k_z, where z is the [111] direction, are shown in Fig. 3. Calculations were made for both the 11- and 14-term fits. Both shown noncentral extremal areas, but their magnitudes are not in close agreement with the data. The predicted values differ from the experimental value by 2.4 and 3.0%. Since there are no constraints on the noncentral areas, we use this as our only independent check on the accuracy of the radius vectors. We conclude that these latter are accurate to rather better than 2%. Clearly more terms in the expansion are needed.

The calculations were carried out on the IBM 7094-7040 computer in the University of Chicago Computation Center. It should be remarked that it was necessary to use double-precision techniques to calculate both the symmetrized coefficients ${}_i a_{lm}$ and the spherical harmonics C_{lm}. If this was not done, accumulated rounding errors swamped the correct answers for large values of l.

III. UNIQUENESS OF THE EXPANSION

The question of how many terms in the expansion can be determined from a restricted set of data is of considerable interest, although it appears that the point has not been discussed before. Its relevance is that data on any anisotropic quantity in, for example, a cubic system, are usually taken only along the basic symmetry lines, which in this case are the (100) and (110) planes. It is shown below that this places a severe limitation on the information obtained. Paradoxically enough, in the absence of either noise or systematic errors a given number of data points contain the most information if they are taken at random but accurately known values of θ and φ. Then the maximum number of coefficients ${}_i\beta_l$ that can be fitted is equal to the number of data points.

We wish to analyze in detail the usual case where data for some property (which we shall call T) are taken only in the (100) and (110) planes. We assume again the full cubic symmetry of the Γ_1 representation of the group O_h, and this allows us to construct from these data for the property T the functions $T(\theta,0)$ and $T(\theta,\pi/4)$ for all θ. We assume that the data form a sufficiently fine net to determine T completely in these two planes. It should also be noted that these two functions contain all our information. We wish to expand these data in the symmetrized harmonics ${}_i K_l$ as defined in Eq. (2). Since for cubic harmonics $m = 0 \bmod (4)$, we can express these data as the sum and difference, respectively, of functions T_s and T_a which are symmetric and antisymmetric to a rotation by $\frac{1}{4}\pi$

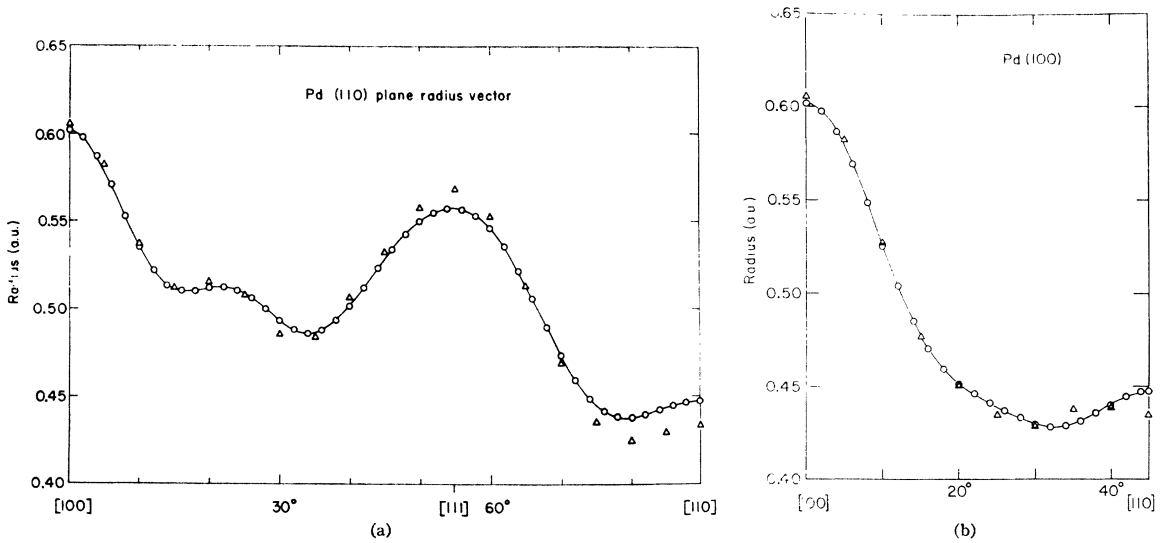

FIG. 2. (a) The calculated radius vectors of the Pd Fermi surface in the (110) plane; ○—the 11-term expansion, △—the incomplete 14-term expansion. The smooth curve is drawn through the 11-term radii. (b) The radius vectors in the (100) plane; the symbols are the same as in (a).

about the polar axis z. Thus we have

$$T_s = \sum_{ilm,\, m=0 \bmod(8)} {}_i\beta_l \, {}_ia_{lm} \, C_{lm},$$

$$T_a = \sum_{ilm,\, m=4 \bmod(8)} {}_i\beta_l \, {}_ia_{lm} \, C_{lm}.$$

We can derive the extent of the uniqueness of the expansion by a projection argument using the basic orthogonality relation for the real spherical harmonics C_{lm}:

$$\int_0^{\pi}\int_0^{2\pi} C_{lm} C_{l'm'} \sin\theta \, d\theta d\varphi = \delta_{ll'}\delta_{mm'}. \qquad (6)$$

The integral

$$\int_0^{\pi}\int_0^{2\pi} T_s(\theta,\varphi) C_{l0} \sin\theta \, d\theta d\varphi$$

will project out from T_s all the coefficients of the form ${}_1\beta_l \, {}_1a_{l0}$ because for $m=0$ the unknown φ variation vanishes and so does not matter, while for $i \neq 1$ we have specifically chosen the degenerate sets such that ${}_{i\neq 1}a_{l0}=0$. Now we can use the relations between the ${}_1a_{lm}$ given in Table I and can determine the ${}_1\beta_l$, i.e., the first degenerate set of the cubic harmonics. It follows that all the coefficients ${}_i\beta_l$ up to $l=12$ can be determined from data in only one plane, since the first doubly degenerate set occurs for $l=12$.

It remains to determine as many as possible of the second and further degenerate sets, and the first few of these are ${}_2\beta_{12}$, ${}_2\beta_{16}$, ${}_2\beta_{18}$ ($i=3$ does not occur until $l=24$). It turns out that a knowledge of T_a enables us to determine only two more of the ${}_2\beta_l$ coefficients. We demonstrate this as follows.

Let F_a be the function obtained from T_a by subtracting off all the terms of the first degenerate sets which are determined once the ${}_1\beta_l$ have been found by the projection from T_s. Thus F_a contains only terms of the following kind:

$$F_a = {}_2\beta_{12}({}_2a_{12,4}C_{12,4} + {}_2a_{12,12}C_{12,12}) + {}_2\beta_{16}({}_2a_{16,4}C_{16,4} + {}_2a_{16,12}C_{16,12})$$

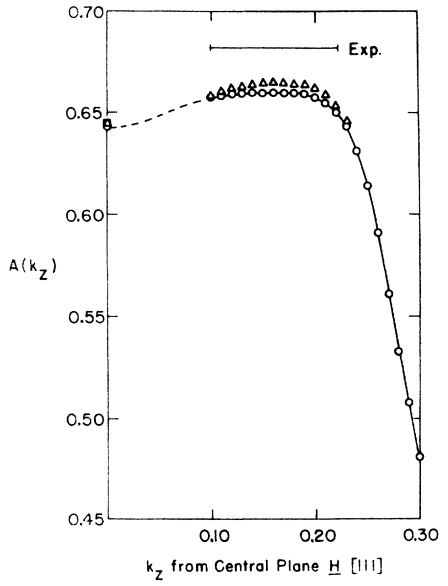

FIG. 3. Noncentral areas of the Fermi surface for H[111]; ○—the 11-term expansion, Δ—the 14-term expansion. The experimental noncentral extremal value is also shown, and □ denotes the experimental value for the central extremal area. k_z is measured in atomic units along the field direction.

plus higher l terms with $i\neq 1$ and $m=4 \bmod(8)$. There are just two useful projection integrals that we can perform. We keep only terms with $l<18$ and form

$$I_1=\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta\, F_a(\cos 4\varphi) \times (C_{12,4}+C_{12,12}+C_{16,4}+C_{16,12}),$$

because the C_{lm} form an orthonormal set over the unit sphere

$$I_1={}_2\beta_{12}\,{}_2a_{12,4}+{}_2\beta_{16}\,{}_2a_{16,4}.$$

We now form I_2:

$$I_2=\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta\, F_a(\cos 12\varphi) \times (C_{12,4}+C_{12,12}+C_{16,4}+C_{16,12})$$

and, similarly, the orthogonality relations give

$$I_2={}_2\beta_{12}\,{}_2a_{12,12}+{}_2\beta_{16}\,{}_2a_{16,12}.$$

Hence we can find the two coefficients ${}_2\beta_{12}$ and ${}_2\beta_{16}$ only if we terminate our finite expansion at ${}_1\beta_{18}$. If we attempt to fit more coefficients ${}_2\beta_l$ of the second degenerate set we cannot do so uniquely. We can, of course, fit higher terms by taking data away from the lines of symmetry, which is easily done once it is realized that it is necessary.

The correctness of the above conclusion was tested empirically by a quite different method in which spherically symmetric data[6] in the same two planes were expanded in a finite number of cubic harmonics by the least-squares technique used in Sec. 2. If the expansion was not unique, an obviously nonspherical expansion resulted which, nevertheless, had a constant area at all the data points. The results agreed with those of the projection approach described above.

APPENDIX: CALCULATION OF THE CUBIC HARMONICS

Altmann and Cracknell[7] have solved the general problem of constructing symmetrized spherical harmonics. They used a general projection approach and dealt only with harmonics up to $l=12$. We need higher values of l, and since we are concerned with just one particular case, the identity representation Γ_1 of the full cubic group O_h, we can use this symmetry explicitly to obtain the linear combinations for arbitrary l in a simpler fashion.

The general rotation operator R can be represented as

$$RY_{lm}=\exp[-i\theta(\hat{n}\cdot L)]Y_{lm}, \qquad \text{(A1)}$$

which describes a rotation by an angle θ about the direction $\hat{n}$. If this rotation is expressed in terms of Euler angles it follows that R is factorized into three successive Euler rotations,

$$R=\exp(-i\alpha L_z)\exp(-i\beta L_y)\exp(-i\gamma L_z). \qquad \text{(A2)}$$

Let $\Phi=\sum_{lm} a_{lm}Y_{lm}$ be a linear combination of spherical harmonics with the required symmetry. This must be invariant to the rotation operators of the group O_h, and since the general rotation operator commutes with $\mathbf{L}\cdot\mathbf{L}$ it does not mix different values of l. Therefore

$$\Phi=\sum_m a_{lm}Y_{lm}. \qquad \text{(A3)}$$

We now note that the group O_h can be generated by three basic operations—the generators of the group. For a one-dimensional representation such as the identity representation these commute, so the full symmetry is satisfied by making Φ invariant to each of the three operations separately. Our choice of these three is a sufficient but not a necessary one. We take one of the fourfold axes as the polar axis z. The other fourfold axes are then x and y. With this choice of axes the operations are:

(1) Inversion, hence l is even. [1(*a*) The mirror plane $y=0$, which follows from (1) and (3) restricts the φ variation to $\cos m\varphi$ only.]

(2) A fourfold rotation about the z axis. This requires $m=0 \bmod(4)$.

(3) A rotation by $\frac{1}{2}\pi$ about the y axis. From Eq. (A2) above, this is described by $R=e^{-(i\pi L_y/2)}$, and our linear combination $\Phi=\sum_m a_{lm}Y_{lm}$ must be invariant to this rotation:

$$R\Phi=R\sum_m a_{lm}Y_{lm}=\sum_{m'} a_{lm'}Y_{lm'}. \qquad \text{(A4)}$$

Multiply through by Y_{ln} and integrate over the sphere. We find

$$\sum_m a_{lm}\langle Y_{ln}|e^{-i\pi L_y/2}|Y_{lm}\rangle=\sum_{m'} a_{lm'}\delta_{nm'}, \qquad \text{(A5)}$$

i.e., a set of linear equations of the form

$$\sum_m a_{lm}d_{m'm}{}^l(\pi/2)=a_{lm'} \qquad \text{(A6)}$$

with the matrix elements $d_{m'm}{}^l(\beta)$ [essentially the Wigner coefficients[8] for integral l] defined by[9]

$$d_{m'm}{}^j(\beta)=\left[\frac{(j-m)!(j+m')!}{(j+m)!(j-m')!}\right]^{1/2} \times\frac{(\cos\tfrac{1}{2}\beta)^{2j+m-m'}(-\sin\tfrac{1}{2}\beta)^{m'-m}}{(m'-m)!} \times{}_2F_1(m'-j,-m-j;m'-m+1;-\tan^2\tfrac{1}{2}\beta), \qquad \text{(A7)}$$

where ${}_2F_1(a,b;c;d)$ is the hypergeometric function, which for our case has a series expansion which terminates.

[6] We are grateful to Dr. L. R. Windmiller for this suggestion.

[7] S. L. Altmann and A. P. Cracknell, Rev. Mod. Phys. **37**, 19 (1965).

[8] E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), Chap. 15.

[9] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1963), p. 53.

We now must solve the linear equations (A6) for the coefficients a_{lm}. Before doing this however we note that the equations can be simplified somewhat. We note that symmetry operation 1(a) has limited us to a real φ variation, i.e., to the real spherical harmonics defined in Sec. 2. Thus by restricting the sum in Eq. (A3) to $m>0$ and using the real harmonics C_{lm} defined in Eq. (3) we can immediately contract the order of the equations by roughly a factor of 2.

Our new matrix elements are thus defined as D_{jk}, where $j=\frac{1}{4}m'+1$ and $k=\frac{1}{4}m+1$.

$$
\begin{aligned}
&D_{11}=d_{00}{}^{l}(\pi/2)\,,\\
&D_{1k}=2^{-1/2}(d_{0m}{}^{l}(\pi/2)+d_{0-m}{}^{l}(\pi/2))\,,\\
&D_{k1}=2^{-1/2}(d_{m'0}{}^{l}(\pi/2)+d_{-m'0}{}^{l}(\pi/2))\,,\\
&D_{jk}=\tfrac{1}{2}(d_{m'm}{}^{l}(\pi/2)+d_{-m'm}{}^{l}(\pi/2)\\
&\qquad\qquad +d_{m'-m}{}^{l}(\pi/2)+d_{-m'-m}{}^{l}(\pi/2))\,.
\end{aligned}
\tag{A8}
$$

The matrix equation is now

$$\sum_k D_{jk}a_{lk}=a_{lj} \tag{A9}$$

or

$$\sum_k (D_{jk}-\delta_{jk})a_{lk}=0\,, \tag{A10}$$

with rank $r=(m_{\max}/4+1)$ instead of $(2m_{\max}/4+1)$.

The matrix equations (A10) cannot be solved directly because the matrix $(\mathbf{D}-\mathbf{1})$ is singular. This is most easily seen from the eigenvalue spectrum of $\mathbf{D}$. The total number p of independent degenerate representations for a given value of l is given in the standard texts on group theory,[10] and the result is quoted in Table I. It follows that $\mathbf{D}$ has p eigenvalues of unity and the remaining $(r-p)$ are necessarily zero. Hence $(\mathbf{D}-\mathbf{1})$ has p eigenvalues of zero and the rest are -1.

We can invert equations (A10), in spite of the zero eigenvalues, by using the following construction. The largest *nonsingular* submatrix of $(\mathbf{D}-\mathbf{1})$ has rank $(r-p)$. We cut out from $(\mathbf{D}-\mathbf{1})$ a codiagonal matrix $\mathbf{Q}$ of rank $(r-p+1)$ such that $Q_{11}=(D-1)_{ii}$, where the subscript i labels the p-independent sets for given l. From the singular matrix $\mathbf{Q}$ we construct the nonsingular codiagonal matrix $\mathbf{P}$ contained within $\mathbf{Q}$ according to the prescription $P_{11}=Q_{22}$, etc. Now form $\mathbf{P}^{-1}$ and then we have

$$A_{ik}=\sum_j P_{jk}{}^{-1}Q_{ij}\,. \tag{A11}$$

The ith row of $\mathbf{A}$ now contains the unnormalized coefficients of the ith representation, except that their position must be adjusted by defining the rectangular matrix $\mathbf{B}$ with the columns displaced according to $B_{i,i+k}=A_{ik}$ and the definitions $B_{ii}=1$, $B_{ij}=0$ if $j<i$ or $j>i+k$. Note that $\mathbf{B}$ has p rows and $(m_{\max}/4+1)$ columns. It now remains to construct an orthonormal set from these vectors (the rows of $\mathbf{B}$). We choose that row with $i=p$ as a basis vector for the degenerate set and normalize it. A row-by-row Schmidt orthogonalization followed by a normalization now results in the desired orthonormal set of row vectors b_{ik}. These are the coefficients shown in Table I as ${}_ia_{lm}$, where ${}_ia_{lm}=b_{ik}$, $m=4(k-1)$.

The choice of basis vector is of course arbitrary but ours corresponds to that used by Altmann and is also very convenient for the discussion of uniqueness in Sec. 3.

[10] M. Hammermesh, *Group Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962), p. 341.