Galvanomagnetic Properties of Gallium at Low Temperatures*

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The galvanomagnetic properties of gallium single crystals in a transverse magnetic field have been investigated at helium temperatures, 77°K and 290°K. At 290°K and 77°K the galvanomagnetic properties are described according to a set of phenomenological equations, these properties then being specified by the tensors in the equations. This formalism breaks down at helium temperatures, where an apparent reduction in crystal symmetry occurs; the number of coefficients specifying the magnetoresistivity tensor according to crystal symmetry considerations is insufficient for a description of the observed galvanomagnetic properties. The results at helium temperatures can be qualitatively understood in terms of the recent fundamental theory of galvanomagnetic effects of Lifshitz, Azbel', and Kaganov which is based on considerations involving the topology of the Fermi surface. The anomaly of a marked displacement of the maximum in the Hall rotation curve at 77°K and 290°K is accounted for in detail according to the phenomenological formalism, on the basis of the anisotropy of the Hall coefficients at those temperatures combined with a small displacement of crystallographic axes from specimen axes. Well-defined oscillations in the magnetoresistance and Hall effects, superposed on the monotonic variation of the effects, have been observed for every crystal orientation studied. The general characteristics of these oscillations are the same as those in the diamagnetic susceptibility (the de Haas-van Alphen effect).

INTRODUCTION

TO a large extent galvanomagnetic measurements have been superseded by other techniques in investigating the band structure of solids.[1] Cyclotron resonance, for example, has proved particularly fruitful in investigating the band structure of semiconductors (principally germanium and silicon). However, when such techniques are inapplicable, galvanomagnetic measurements remain a significant method of investigation; a method which has been largely neglected in the case of metals.

Where the de Haas-van Alphen effect is observable, galvanomagnetic measurements at low temperatures are of further interest in establishing the relation between the various oscillatory phenomena.[2] The periods of the de Haas-van Alphen effect and the oscillatory transport phenomena have been found to be equal in the few cases investigated in detail,[3] as might be expected from the simplest theory,[4] but there have been no quantitative experimental studies of the relative amplitudes and no theoretical investigation until the recent work of Lifshitz and Kosevich[2] which directly relates the amplitudes of the components of the oscillatory magnetoconductivity tensor to the de Haas-van Alphen amplitudes.

An investigation of the galvanomagnetic properties of gallium in particular appeared of interest as there is no published data for the Hall effect[5] in single crystals and the data on the magnetoresistance seem to be inconsistent.[6] Further, gallium exhibits the de Haas-van Alphen effect[7] and the large anisotropy in resistivity might also be expected to show up in the components of the oscillatory part of the magnetoresistivity tensor. In the present work both the monotonic and the oscillatory field dependence of the magnetoresistivity tensor were investigated.

Casimir has shown,[8] on the basis of the Onsager principle of microscopic reversibility in time, that one may write a phenomenological equation describing the galvanomagnetic effects in the form

$$E_i=\rho_{ij}(B)I_j+\epsilon_{ijk}I_jA_k(B), \qquad (1)$$

where $\rho_{ij}(B)$ is an even function of B (the magnetic field), $A_k(B)$ is an odd function of B, and

$\epsilon_{ijk}=0$, when $i=j$ or $j=k$ or $i=k$,
$\epsilon_{ijk}=1$, when all numbers are different and in cyclic order,
$\epsilon_{ijk}=-1$, when all numbers are different and not in cyclic order.

One may then expand the functions ρ_{ij} and A_k in terms of even and odd powers of the magnetic field, respectively, according to the procedure of Mason *et al.*[9] The constant coefficients in the expansion are the components of the magnetoresistivity tensor. It was found

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‡ Assisted by a National Science Foundation Research Grant.

[1] B. Lax, Revs. Modern Phys. **30**, 122 (1958).

[2] E. M. Lifshitz and A. M. Kosevich, J. Phys. Chem. Solids **4**, 1 (1958).

[3] R. A. Connell and J. A. Marcus, Phys. Rev. **107**, 940 (1957).

[4] R. Peierls, Z. Physik **81**, 186 (1933).

[5] The only published data on the Hall effect in gallium is that of I. Fakidov and B. C. Lazarev, [Physik Z Sowjetunion **7**, 677 (1935)] who measured the Hall coefficient at room temperature using a thin circular plate of gallium. No attempt at obtaining a single crystal was made.

[6] It is difficult to evaluate the work of Blom [J. W. Blom, *Magnetoresistance for Crystals of Gallium* (Martinus Nijhof, The Hague, 1950)] since he failed to observe any anisotropy in zero-field resistivity though he was presumably using single crystals.

[7] D. Shoenberg, Trans. Roy. Soc. (London) **A245**, 1 (1952).

[8] H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).

[9] Mason, Hewitt, and Wick, J. Appl. Phys. **24**, 166 (1953).

that this phenomenological formalism describes the galvanomagnetic effects at 77°K and at 290°K, but at 4.2°K it does not provide an adequate description of the phenomena.

Superposed on the monotonic variation of the galvanomagnetic properties, small oscillations, periodic in reciprocal magnetic field, were observed. A preliminary report of this work has already appeared.[10] These oscillations are due to the fact that in the presence of a magnetic field the orbital motion of the electrons is quantized, giving rise to a quasiperiodic dependence of the energy as a function of the density of states. Consequently any physical quantity dependent on the energy of the electrons will show oscillations as a function of magnetic field (under the appropriate experimental conditions of low temperatures and high magnetic fields). In particular, the electrical transport phenomena will show oscillations, as is known to be the case experimentally.[3]

EXPERIMENTAL DETAILS

I. Designation of Crystals

A crystal is designated by two letters, e.g., *ab*, the first letter referring to the crystallographic axis parallel to the current and the second to the crystallographic axis perpendicular to the plane of the Hall probes and the current. The following crystals were investigated in the range 0–10 kilogauss: *ab*, *ac*, *ba*, *bc*, *ca*, *cb*, *ac*-1, and *ab*-1. [The crystals designated by letters and numerals are thin (∼0.07 mm) crystals and the crystals designated by just two letters are thick (∼0.7 mm) crystals.]

II. Method of Measurement

The samples used were in the form of a narrow strip 30 mm long, 3 mm wide, and ∼0.7 mm or ∼0.07 mm thick. The current flows in the direction of the 1-axis, the Hall voltage is measured in the direction of the 2-axis and the magnetoresistance is measured in the direction of the 1-axis using potential probes placed about 5 mm apart. The magnetic field is always in the 2-3 plane.

In the Hall measurements the standard procedure of reversing both the current and magnetic field was used throughout. In that case we have

$$4V_{\text{odd}}=V(I,B)-V(-I,B)-V(I,-B)+V(-I,-B),$$
$$4V_{\text{even}}=V(I,B)-V(-I,B)+V(I,-B)-V(-I,-B),$$

where V_{odd} is and odd function of the magnetic field B and V_{even} is an even function of the field.

V_{odd} is the Hall voltage and V_{even} is the ohmic voltage due to a misplacement of the Hall probes but may also include a transverse quadratic voltage.[10,11] In the magnetoresistance measurements the current alone was reversed and not the magnetic field since it was established at the beginning of every measurement that reversal of the magnetic field left the magnetoresistance unchanged.

III. Preparation of Crystals

All of the crystals were grown from 99.95% purity gallium obtained from the Alcoa Company. Initial measurements[12,13] were made using thin (∼0.07 mm) crystals in order to obtain large enough voltages (∼1 microvolt) for reliable measurements using a current of one ampere and a magnetic field of 10 kgauss. The thin crystals were made using a modification of a method devised by Fultyn.[14] These crystals had to be treated very delicately and were usually somewhat strained due to the way in which they were removed from the mold. Furthermore, a calculation of the ratio of thickness to mean free path showed that this ratio was not large enough at low temperatures to enable us to neglect size effects.[15,16] For these reasons, a method of making thick (∼0.7 mm) crystals was devised and the current through the crystal increased by a factor of five to ten. This method consisted essentially of pressing the molten gallium between two plates of Plexiglas, one of which had a slit milled along its length so that the molten gallium filled the slit completely. The molten metal was then seeded and, after solidification, the Plexiglas was removed from around the gallium crystal by immersing mold and metal in an acetone bath. The crystals made by this method were not as strained as the thin crystals (compare residual resistance ratios in Table I).

IV. Determination of Orientation

A General Electric x-ray diffractometer was used to determine the position of the crystallographic axes relative to the specimen axes by observing the position of the crystal for sharp reflections from the planes perpendicular to the crystallographic axes.[17] The crystals were analyzed along their whole length to assure the fact that they were single crystals, and this turned out to be the case for almost every crystal grown.

The Bragg angle for reflection is almost identical for the *a*-planes and for the *b*-planes, since the separation of these planes is 4.5258 A and 4.5198 A, respectively,[18]

[10] J. Yahia and J. A. Marcus, Bull. Am. Phys. Soc. Ser. II, 3 17 (1958).
[11] See "Experimental Results and Discussion," Sec. IV.
[12] J. Yahia and J. A. Marcus, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957* edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958).
[13] J. Yahia and J. A. Marcus, Bull. Am. Phys. Soc. Ser. II, **2**, 184 (1957).
[14] R. V. Fultyn, M. S. thesis, Northwestern University, Evanston, Illinois, 1955 (unpublished).
[15] T. G. Berlincourt, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958).
[16] E. H. Sondheimer, Phys. Rev. **80**, 401 (1950).
[17] B. D. Cullity, *Elements of x-ray Diffraction* (Addison Wesley Press, Cambridge, 1956).
[18] A. J. Bradley, Z. Krist. **91**, 302 (1935).

TABLE I. The temperature variation of the Hall coefficient for single crystals of gallium.[a]

Crystal	Thickness (10^{-2} cm)	ρ at 20°C (10^{-6} ohm-cm)	ρ at 20°C[b] (10^{-6} ohm-cm)	$\frac{\rho_{4.2°K}}{\rho_{290°K}}\times 10^4$	A (4.2°K) (10^{-3} emu)	A (77°K) (10^{-3} emu)	A (279°K) (10^{-3} emu)
ba	7.5	7.8	7.85	3.5	−12.0	−6.2	−4.3
ca	6.6	54	55.53	1.40	−12.0	−7.4	−5.1
ab	7.8	17.8	17.27	1.29	−10.9	−6.6	−5.0
cb	8.0	61	55.53	3.3	−11.8	−5.9	
ac	8.0	17.4	17.27	4.2	−12.4	−0.54	−0.68
bc	6.2	8.1	7.85	1.05	−9.3	−0.50	−0.57
ab-1	0.66	17.8	17.27	7.8	−8.2	−4.7	−4.6
ac-1	0.86	16.6	17.27	10	−10.6	−1.1	−1.2

[a] Note that for crystals *ab*-1 and *ac*-1 the crystallographic axes deviate from the specimen (or measuring) axes by about 10°, but for crystals *ba*, *ca*, *ab*, *cb*, *ac*, and *bc* this alignment is within 2°.
[b] See reference 19.

and this means that a simple x-ray analysis cannot distinguish between reflections from these two sets of planes. However, since there exists a marked anisotropy in zero-field resistivity (the ratio of the room temperature resistivities being given by[19] $\rho_c:\rho_a:\rho_b=55.53:17.27:7.85$), the *a*-axis and the *b*-axis were distinguished one from the other using the results of resistivity measurements. The resistivity measurements together with the x-ray measurements identified the axial directions in the seed crystals and in the crystals used in this investigation.

V. Potential and Current Leads

The current leads consisted of thin copper ribbon soldered to each end of the crystal. The end of the copper ribbon was tinned with gallium before soldering and a small quantity of HCl was used as a flux. A connection of this type was found to be extremely sturdy and did not break after repeated heating and cooling.

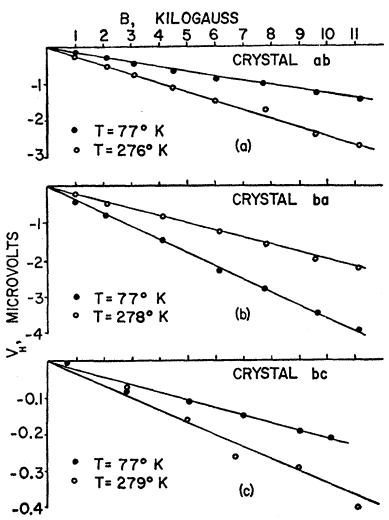

FIG. 1. Hall voltage field dependence for gallium single crystals at 77°K and 290°K; (a) $J\|a$-axis, $B\|b$-axis, (b) $J\|b$-axis, $B\|a$-axis, (c) $J\|b$-axis, $B\|c$-axis.

[19] R. W. Powell, Proc. Roy. Soc. (London) **A209**, 525 (1951).

The potential leads were spotwelded to the crystal and here, also, the end of a small-diameter (~3 mil) clean copper wire was tinned with gallium before spotwelding. A small spotwelder operated in the range 20 to 40 volts was used. It was found that a connection of this type was quite satisfactory for low-temperature work, where, in most cases, it stayed intact through repeated heating and cooling, that is, throughout a whole course of measurements.

The crystal-mount details, the positioning of the crystal in the magnetic field, the cryogenic techniques employed, as well as more details on Secs. I–V are given in the Ph. D. thesis of one of the authors.[20]

EXPERIMENTAL RESULTS AND DISCUSSION

I. The Monotonic Galvanomagnetic Effects at 77°K and Room Temperature

For all crystals at these temperatures, the magnetoresistance was negligible (less than 3% at 77°K and too small for measurement at room temperature), the Hall voltage was a linear function of B (Fig. 1) and the Hall rotation curves were sinusoidal (Fig. 2). Further, since the transverse magnetoresistance is small at these temperatures, one expects the longitudinal magnetoresistance to be small also, and, indeed, a measurement of the longitudinal effects for one orientation (ac) showed this magnetoresistance to be of the order of a 1.5% effect in a field of 5 kgauss.

Thus, Eq. (2′), Appendix A, simplifies to

$$\begin{aligned} E_a&=I_a\rho_a+I_bA_{cc}B_c-I_cA_{bb}B_b,\\ E_b&=-I_aA_{cc}B_c+I_b\rho_b+I_cA_{aa}B_a,\\ E_c&=I_aA_{bb}B_b-I_bA_{aa}B_a+I_c\rho_c. \end{aligned} \tag{2}$$

(a, b, and c are the crystallographic axes in the orthorhombic crystal.)

The resistivity tensor is specified by the numbers ρ_a, ρ_b, ρ_c, A_{aa}, A_{bb}, A_{cc}, which are given in Table II.

[20] J. Yahia, Ph. D. thesis, Northwestern University, Evanston, Illinois, 1958 (unpublished).

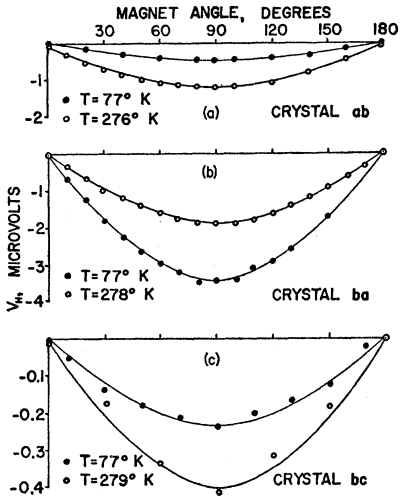

FIG. 2. Hall voltage rotation curves for gallium single crystals at 77°K and 290°K; (a) $J\|a$-axis, B in bc plane, (b) $J\|b$-axis, B in ac plane, (c) $J\|b$-axis, B in ac plane. All of the rotation curves are for a field of 9.6 kgauss.

The Hall effect is specified by three independent coefficients rather than six as in the formalism of Kohler.[21] This is because the Onsager principle is added to the symmetry arguments of Kohler. To see this, consider, following Kohler,[21] a specification of the linear Hall effect by the relation:

$$E_i(\text{Hall})=A_{ijk}I_jB_k. \tag{3}$$

For an orthorhombic crystal, the independent nonzero terms in the tensor A_{ijk} are[21] A_{123}, A_{132}, A_{231}, A_{213}, A_{312}, A_{321}. This means that using crystal symmetry principles alone the linear Hall effect is specified by 6 constants.

Now, it has been shown, under quite general conditions, that the following relation holds between coefficients specifying phenomenologically an effect where a magnetic field is present[22]:

$$L_{ij}(\mathbf{B})=L_{ji}(-\mathbf{B}). \tag{4}$$

If we define $L_{ij}(\mathbf{B})=A_{ijk}B_k$ [i.e., $L_{ij}(\mathbf{B})$ is a linear function of $\mathbf{B}$], then, according to Eq. (4),

$$A_{ijk}B_k=A_{jik}(-B_k),$$

or

$$A_{ijk}=-A_{jik}.$$

Thus the coefficients specifying the Hall effect depend only on the direction of the magnetic field but not on the direction of the current (since i and j may be interchanged without affecting the value of the coefficient). Thus, $A_{123}=-A_{213}$, $A_{132}=-A_{312}$, and $A_{231}=-A_{321}$, and there are only three coefficients specifying the linear Hall effect when one applies *both* the symmetry relations and the Onsager reciprocal relations. By starting out with Eq. (1) and applying the symmetry conditions to the components of the tensors appearing in the expansion of this equation, we have applied both relations [since Eq. (1) embodies the Onsager relations], and thus we arrive at the conclusion that the linear Hall effect in gallium is specified by 3 constants.

This conclusion is susceptible to a direct experimental test. In Table I, the crystal orientations that should have the same coefficients according to the above arguments are grouped together in pairs. The value of the Hall coefficient for crystals *ba*, *ca*, *ab*, *cb* is quite close for any fixed temperature and also, the temperature variation of the Hall coefficient for these crystals is about the same, so that a separation experimentally of these four crystals into two pairs of crystals, each pair having the same coefficient, is arbitrary. The significant experimental point in support of the conclusion regarding the application of the Onsager reciprocal relations to the linear Hall effect is that the crystals *ac* and *bc* exhibit the same striking temperature variation of the Hall coefficient and also the Hall coefficients are approximately the same for this pair of crystals at a fixed temperature (Table I). The similarity of the temperature variation of the Hall coefficient for these two crystals is shown in Table III. This temperature variation is markedly different from the temperature variation of the crystals *ba*, *ca*; *ab*, *cb* (see Table I).

TABLE II. The components of the magnetoresistivity tensor for gallium at 77°K and 290°K.

	Resistivity (10^{-6} ohm cm)	Hall coefficient (10^{-3} emu)
$T=77$°K	$\rho_a=3.13$	$A_{aa}=-6.8$
	$\rho_b=1.44$	$A_{bb}=-6.3$
	$\rho_c=9.4$	$A_{cc}=-0.52$
$T=290$°K	$\rho_a=17.6$	$A_{aa}=-4.7$
	$\rho_b=8.0$	$A_{bb}=-5.0$
	$\rho_c=54$	$A_{cc}=-0.63$

TABLE III. The temperature variation of the Hall coefficient for crystals *ac* and *bc*.

Crystal	A(4.2°K)/A(77°K)	A(4.2°K)/A(279°K)
ac	23	18
bc	19	16

A further confirmation of the correctness of the application of the Onsager reciprocal relations to the phenomenon of the linear Hall effect is the observation by Connell and Marcus[3] that in Bi, at room temperature and 77°K, the Hall coefficient depends on the orientation of the magnetic field and not of the current. At helium temperatures any orientation dependence such as that observed at the higher temperatures was obscured by the increased sensitivity to impurities.

[21] M. Kohler, Ann. Physik **20**, 878 (1934).
[22] S. R. de Groot, *The Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam; Interscience Publishers, New York, 1951).

II. The Influence of a Small Deviation of Crystallographic Axes from Specimen Axes on the Hall Rotation Diagram at 77°K and Room Temperature

At these temperatures for crystals *ac* and *ac*-1 the Hall rotation curves were sinusoidal but had a displaced maximum, i.e., the maximum in the Hall voltage did not occur for B perpendicular to the face of the crystal (Fig. 3), as was the case for all other orientations (Fig. 2). This apparent anomaly was previously observed by Fultyn[14] in his measurements at room temperature and can be understood on the basis of the anisotropy in the Hall coefficients and a small deviation of crystallographic axes from specimen axes.

From the term in B on the right-hand side of Eq. (5′), Appendix B, one may derive a condition for a maximum in the Hall field as a function of the magnet azimuthal angle for the case where the specimen axes

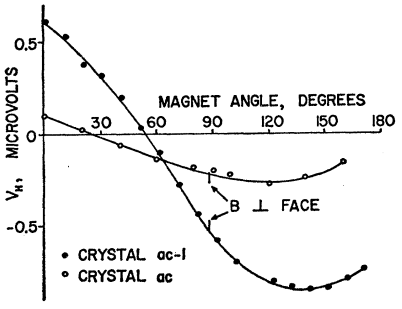

FIG. 3. Shift in the maximum of the Hall rotation curve for crystals *ac* and *ac*-1 at 77°K. Here $J\|a$-axis and $B(=9.6$ kgauss) is in the *bc* plane. (Crystal *ac*-1 has a larger misorientation of crystallographic axes from specimen axes than crystal *ac* with a correspondingly larger shift, see Text.)

do not coincide with the crystallographic axes:

$$\tan\psi=\frac{A_{33}n_3n_2+A_{22}m_3m_2+A_{11}l_3l_2}{A_{33}n_3^2+A_{22}m_3^2+A_{11}l_3^2}, \tag{5}$$

where $B_2'=|\mathbf{B}'|\sin\psi$ and $B_3'=|\mathbf{B}'|\cos\psi$, $|\mathbf{B}'|=$magnitude of magnetic field, and the l, m, and n are the direction cosines of the transformation from the crystallographic axes to the specimen axes.

For the simple case where the misorientation is due to a rotation of the specimen axes by the angle δ about the 1-axis in the crystallographic system, we have[23]

$$l_2=0,\quad m_2=\cos\delta,\quad n_2=\sin\delta,$$
$$l_3=0,\quad m_3=-\sin\delta,\quad n_3=\cos\delta,$$

and Eq. (5) reduces to

$$\tan\psi=\frac{\cos\delta\sin\delta(A_{33}-A_{22})}{A_{33}\cos^2\delta+A_{22}\sin^2\delta}. \tag{6}$$

[23] See definition of l, m, n in Appendix B.

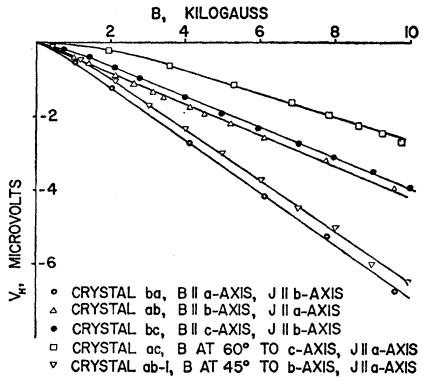

FIG. 4. Hall voltage field dependence for gallium single crystals at 4.2°K. Note that the dependence is linear above 3 kgauss but that below this field a nonlinear dependence seems indicated.

X-ray analysis of crystal *ac* showed that the deviation of specimen axes from crystallographic axes was due to a rotation of 2° about the axis of the length (the *a*-axis). For this crystal (taking into account that the *a*-axis corresponds to the 1-axis, the *b*-axis corresponds to the 2-axis and the *c*-axis corresponds to the 3-axis), we have

$$\tan\psi=\frac{\cos2^\circ\sin2^\circ(A_{cc}-A_{bb})}{A_{cc}\cos^2 2^\circ+A_{bb}\sin^2 2^\circ}.$$

Since $A_{bb}\cong A_{aa}\cong 10A_{cc}$ (Table I), $\psi=15°$.

Crystal *ac*-1 had a misorientation due to a rotation about the *a*-axis of $\sim 10°$. The shift in the maximum for this crystal turns out to be appreciable, namely, 50°, and checks quite well with the observed shift (Fig. 3).

III. The Monotonic Galvanomagnetic Effects at 4.2°K

At this temperature, as for the higher temperatures, the field dependence of the Hall effect is linear (Fig. 4)

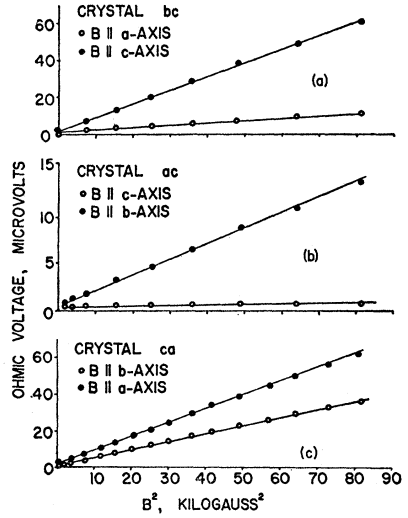

FIG. 5. Field dependence of magnetoresistance for gallium single crystals at 4.2°K; (a) $J\|b$-axis, (b) $J\|a$-axis, (c) $J\|c$-axis.

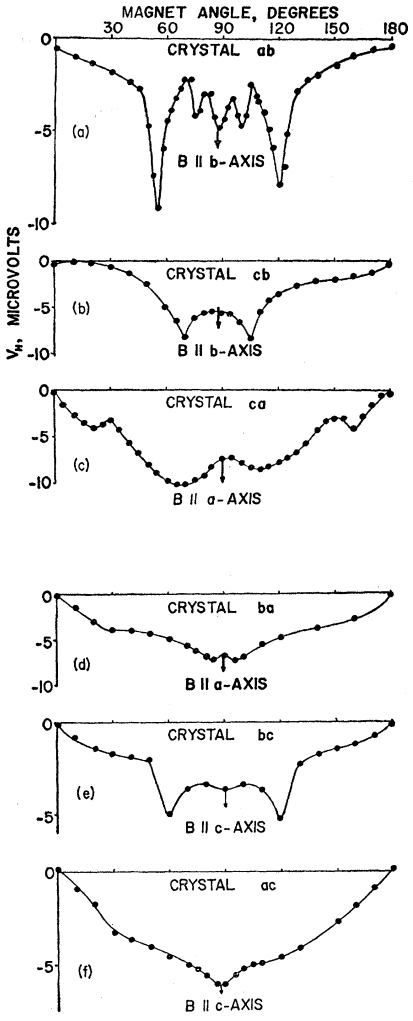

FIG. 6. Hall voltage rotation curves for gallium single crystals at 4.2°K; (a) $J\|a$-axis, B in bc plane, (b) $J\|c$-axis, B in ab plane, (c) $J\|c$-axis, B in ab plane, (d) $J\|b$-axis, B in ac plane, (e) $J\|b$-axis, B in ac plane, and (f) $J\|a$-axis, B in bc plane. All of the rotation curves are for a field of 9.6 kgauss.

and for the magnetoresistance effect it is quadratic (Fig. 5) so that, according to Equation (1′) of Appendix A, the rotation curves for these phenomena should be simple sine curves. However, the rotation diagrams for the Hall effect (Fig. 6) and for the magnetoresistance effect (Fig. 7) are complicated functions of azimuthal angle, exhibiting many maxima and minima. Thus, the phenomenological formalism for the galvanomagnetic properties breaks down at 4.2°K, in contrast to the situation at 77°K and room temperature.

Where complicated rotation curves of this sort have been observed for other metals, e.g., Bi and Zn,[24,25] the field dependence has been complicated, and it has been assumed that the complex rotation data could be accounted for on the basis of the inclusion of higher order terms in B in a phenomenological equation of the same form as Eq. (1). However, Justi and Sheffers[26] have observed that in the magnetoresistance of single crystals of gold at 20.4°K the rotation diagram was complicated but the field dependence was linear.

Lifshitz *et al.*[27] have recently published a paper on the fundamental theory of galvanomagnetic effects which can qualitatively account for data of the type observed by us in terms of complex Fermi surfaces. Thus it seems that a phenomenological description, consistent with crystal symmetry principles and the Onsager principle of microscopic reversibility in time, is *not* a general framework into which the results of any electron theory must fit, as has been generally assumed to be the case.[28] At all temperatures the galvanomagnetic properties must depend on the details of the Fermi surface; at high temperatures these details are smeared out so that the symmetry requirements on the galvanomagnetic properties are the same as the macroscopic symmetry requirements and thus the galvanomagnetic properties may be described by a phenomenological equation such as Eq. (1′), and indeed, this has been found to be the case in the present investigation.[29] At low temperatures the details of the Fermi surface are sharp, and the galvanomagnetic properties will reflect this structure and may show less symmetry than

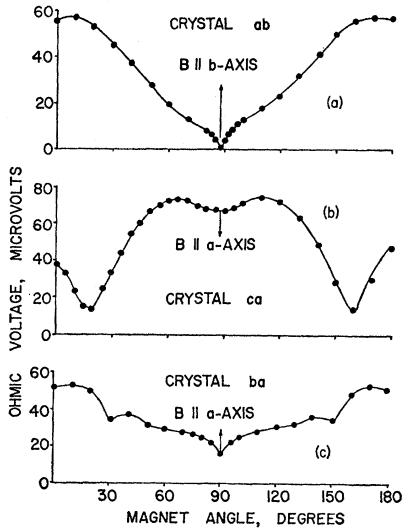

FIG. 7. Magnetoresistance rotation curves for gallium single crystals at 4.2°K; (a) $J\|a$-axis, B in bc plane, (b) $J\|c$-axis, B in ab plane, (c) $J\|b$-axis, B in ac plane. All of the rotation curves are for a field of 9.6 kgauss.

[24] P. B. Alers and R. T. Webber, Phys. Rev. **91**, 1060 (1953).
[25] A. Borovik, J. Exptl. Theoret. Phys. U.S.S.R. **30**, 262 (1956) [translation: Soviet Phys. JETP **3**, 243 (1956)].
[26] E. Justi and H. Sheffers, Physik. Z. **37**, 475 (1936).
[27] Lifshitz, Azbel', and Kaganov, J. Exptl. Theoret. Phys. U.S.S.R. **31**, 63 (1956) [translation: Soviet Phys. JETP **4**, 41 (1957)].
[28] For instance, Kohler (reference 21) concludes that a phenomenological description consistent with crystal symmetry principles *alone* is the general framework into which any electron theory of the galvanomagnetic effects must fit.
[29] See Experimental Results and Discussion I.

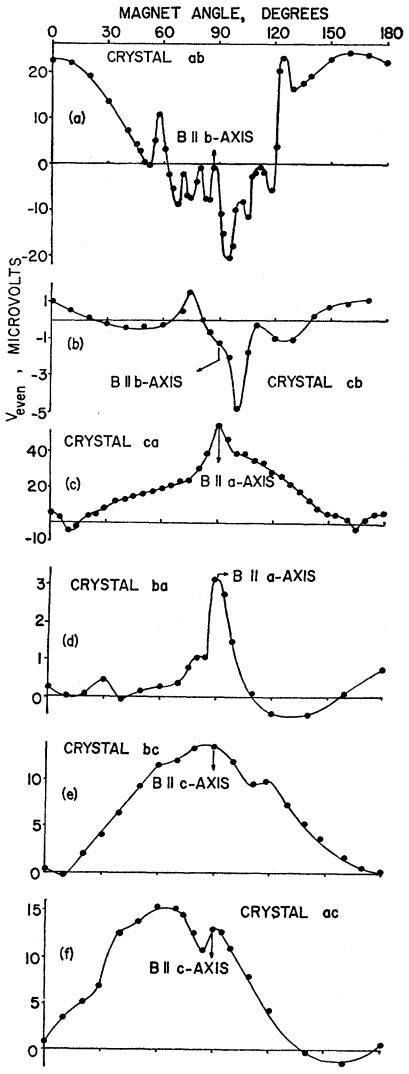

FIG. 8. Rotation curves of quadratic transverse effect at 4.2°K; (a) $J\|a$-axis, B in bc plane, (b) $J\|c$-axis, B in ab plane, (c) $J\|c$-axis, B in ab plane, (d) $J\|b$-axis, B in ac plane, (e) $J\|b$-axis, B in ac plane, (f) $J\|a$-axis, B in bc plane. All of the rotation curves are for a field of 9.6 kgauss. The ordinate is the sum of the pure transverse quadratic voltage in B and the even voltage due to a resistive component associated with a longitudinal misalignment of the Hall probes. The alignment of crystallographic axes and specimen axes for all of these crystals is within 2°.

the gross crystal symmetry. Thus, more complete measurements should lead to a quantitative specification of the complex Fermi surface in gallium.

IV. Transverse Quadratic Field Effect at 4.2°K

It is a difficult experimental problem to place the Hall probes along an equipotential. Thus, when current is flowing in the crystal, the voltage measured across the Hall probes (in zero magnetic field) is unequal to zero due to the small longitudinal misplacement of the probes which gives rise to a resistive voltage so that magnetoresistance data may be obtained from these probes and should agree with the magnetoresistance data obtained from the longitudinal probes. However, the rotation diagrams of the even voltage obtained from the Hall probes (Fig. 8) are markedly different from the rotation diagrams of the voltage obtained from the longitudinal probes (Fig. 7) and it is clear that the voltage obtained from the Hall probes contains other terms besides the resistive component. In some measurements,[12] the resistive component was eliminated by using three Hall probes and a slidewire in the potentiometer circuit and a measuring technique similar to that of Logan and Marcus,[30] and the even transverse voltage was found to be quadratic in B and to persist to low fields.[12]

The quadratic transverse effect was at first ascribed to the anisotropy in the magnetoresistance coefficients combined with a deviation of crystallographic axes from specimen axes,[12] [see the term in B^2 on the right-hand side of Eq. (5′), Appendix B]. However, if this is the only origin of the effect, then, as the alignment of crystallographic axes and specimen axes gets better the quadratic transverse voltage should tend to vanish, and this is not observed to be the case. In fact, a comparison of the rotation curve for a crystal where the misalignment is $\sim 10°$ (crystal ab-1, Fig. 9) shows less complexity than a rotation curve for a crystal where the misalignment is $\sim 2°$ (crystal ab, Fig. 8) and the quadratic transverse field does not tend to vanish as the alignment gets better.

According to the theory of galvanomagnetic effects of Lifshitz *et al.*,[27] a quadratic transverse field of this sort is predicted on the basis of considerations involving the topology of the Fermi surface. This additional[31]

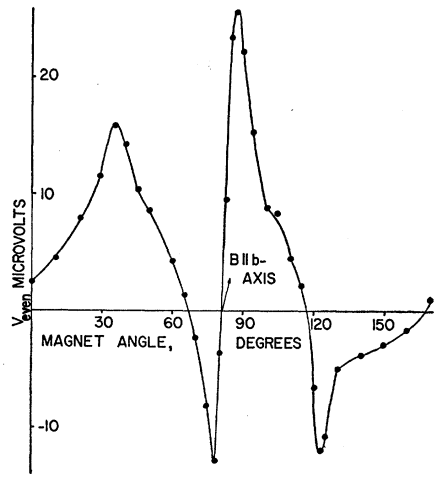

FIG. 9. Rotation curve of quadractic transverse effect for crystal ab-1 at 1.4°K, $J\|a$-axis and $B(=11.2$ kgauss) is in the bc plane. The ordinate is the sum of the pure quadratic voltage in B and the even voltage due to a resistive component associated with a longitudinal misalignment of the Hall probes. For this crystal, the crystallographic axes and specimen axes are misaligned by about 10°.

[30] J. K. Logan and J. A. Marcus, Phys. Rev. 88, 1234 (1952).
[31] See "Experimental Results and Discussion," Sec. III.

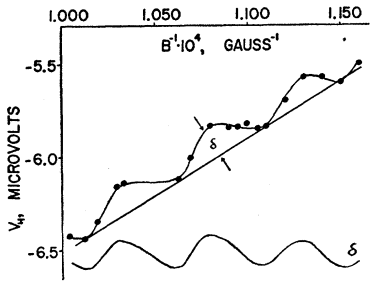

FIG. 10. Oscillations in Hall voltage for crystal *ac*, $J\|a$-axis, $B\|c$-axis, $T=1.4°K$.

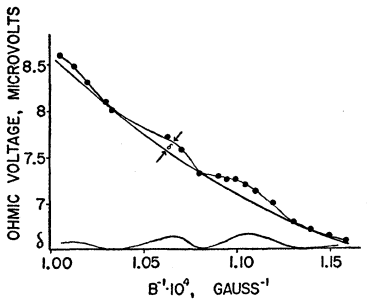

FIG. 11. Oscillations in magnetoresistance for crystal *ac*, $J\|a$-axis, $B\|c$-axis, $T=1.4°K$.

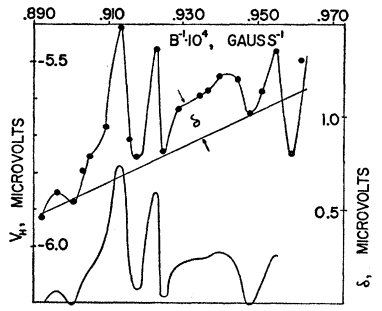

FIG. 12. Oscillations in Hall voltage for crystal *ba*, $J\|b$-axis, $B\|a$-axis, $T=1.4°K$.

qualitative agreement of the observed galvanomagnetic properties with the predictions of this theory indicates that the approach adopted in it may be an appropriate one for interpreting future data on gallium.

V. Oscillatory Component of the Hall and Magnetoresistance Effects

A detailed investigation of the oscillations in magnetoresistance and Hall effect was not attempted. The main purpose of the measurements was to determine whether these were observable (in the extensive work of Blom[7] on the magnetoresistance of gallium crystals none were reported, probably because the data was not obtained at sufficiently close intervals of field), and, if so, to see if their general characteristics were the same as for those in the de Haas-van Alphen effect (see Introduction). Oscillations in the galvanomagnetic properties were observed for all orientations and their characteristics are shown in Figs. 10–14. Figure 10 shows the oscillations in the Hall voltage when the period is fairly pure, and Fig. 11 shows those in the magnetoresistance for a similar case. Figure 12 shows the oscillations in the Hall voltage where the period is complex. Figures 13 and 14 show the temperature variation of the oscillations in Hall voltage and magnetoresistance, respectively, and it may be seen that the amplitude decreases with an increase in temperature but the period is independent of temperature. There is a marked dependence on field of the amplitude of the magnetoresistance oscillations in the range 13–17 kgauss (Fig. 14); it gets bigger with increasing field, but the period (in reciprocal field) is independent of the field. In the lower ranges of field (8.5–10 kgauss, Figs. 10–13) the amplitude of both magnetoresistance and Hall effect oscillations changes little with field, and also the period (in reciprocal field) is independent of the field strength. From Table IV (where a few of the salient features of the oscillatory component of the galvanomagnetic properties are summarized) it is seen that these periods are comparable to the periods of the de Haas-van Alphen effect, the agreement being especially close where the magnetic field is parallel to the *c*-axis, i.e., where the period is pure and comparatively large. For this orientation the period is independent of the current direction, but for $B\|b$-axis, the period depends strongly on current direction (Table IV). For most of the crystals, the magnetoresistance and Hall effect oscillations were found to be equal and out of phase by

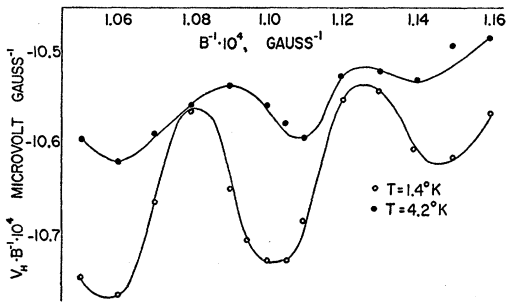

FIG. 13. Temperature variation of the oscillatory component of the Hall effect for crystal *ac*-1, $J\|a$-axis, $B\|c$-axis.

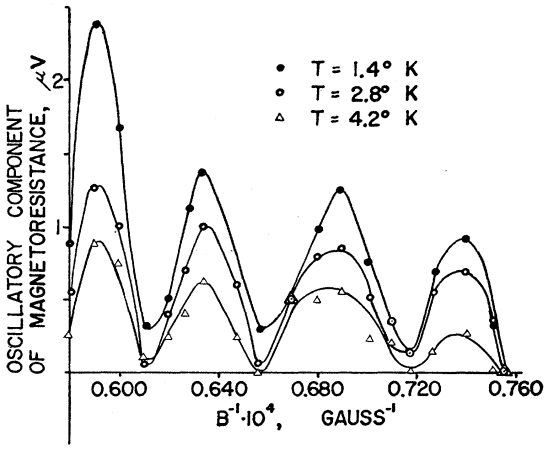

FIG. 14. Temperature variation of the oscillatory component of the magnetoresistance for crystal *ac*, $J\|a$-axis, $B\|c$-axis.

TABLE IV. A summary of the data on the oscillatory galvanomagnetic effects for different orientations of gallium single crystals.

Crystal[a]	Period, B^{-1}, in Hall voltage (10^{-7} gauss^{-1})	Period, B^{-1}, in magnetoresistance (10^{-7} gauss^{-1})	Period, B^{-1}, in diamagnetic susceptibility[b] (10^{-7} gauss^{-1})	Phase difference between Hall and magnetoresistance oscillations
ba	complex	complex	42.0, 11 (B makes an angle 0.5° with a-axis)	
ca	complex	complex	42.0, 11 (B makes an angle 0.5° with a-axis)	
ab	27	26	30.2 (B makes an angle 11.7° with b-axis)	π
cb	48	43	30.2 (B makes an angle 11.7° with b-axis)	π
bc	53	55	51.3, 47.4 (B makes an angle 5.2° with c-axis)	π
ac	46	48	51.3, 47.4 (B makes an angle 5.2° with c-axis)	π
ac-1	50	50	same as for crystal *ac* above	π
ab-1	35	too small for measurement	same as for crystal *ab* above	

[a] Note that the first letter refers to the crystallographic axis parallel to the direction of the current, the second letter to the crystallographic axis parallel to the magnetic field.
[b] See reference 18.

π (see for instance Figs. 10 and 11) and this agrees with the result concerning the relative phases derived by Zil'berman[32] using a strong-field two-band model for the galvanomagnetic effects.

These results show the general characteristics of the oscillatory component of the galvanomagnetic effects to be the same as for the oscillatory diamagnetism, and it would thus appear as a result of this exploratory investigation that gallium is a good metal for a detailed study of the relation of the amplitudes of the first phenomenon to those of the second one.[2]

ACKNOWLEDGMENT

We would like to thank Dr. M. H. Bailyn for stimulating and helpful discussions and the Metallurgy Department of Northwestern Technological Institute for use of its x-ray equipment.

APPENDIX A. PHENOMENOLOGICAL EQUATION FOR THE GALVANOMAGNETIC EFFECTS TO THIRD ORDER IN B

Starting from Eq. (1) of the Introduction, one may expand $\rho_{ij}(B)$ and $A_k(B)$ in terms of a Maclaurin series in B as follows:

$$\rho_{ij}(B)=\rho_{ij}(0)+\alpha_{ijkl}B_kB_l+\cdots,$$

$$A_k(B)=A_{km}+\gamma_{kmno}B_mB_nB_o+\cdots,$$

where

$$\alpha_{ijkl}=\frac{1}{2!}\frac{\partial^2\rho_{ij}(B)}{\partial B_k\partial B_l},$$

$$A_{km}=\frac{\partial A_k(B)}{\partial B_m},$$

$$\gamma_{kmno}=\frac{1}{3!}\frac{\partial^3 A_k(B)}{\partial B_m\partial B_n\partial B_o}.$$

[32] G. E. Zil'berman, J. Exptl. Theoret. Phys. U.S.S.R. **29**, 762 (1955) [translation: Soviet Phys. JETP **2**, 650 (1956)].

Substituting these expansions for $\rho_{ij}(B)$ and $A_k(B)$ in Eq. (1) of the Introduction, we obtain the following equation specifying the galvanomagnetic effects to third order in B:

$$E_i=[\rho_{ij}(0)+\alpha_{ijkl}B_kB_l]I_j+\epsilon_{ijk}I_j(A_{km}B_m+\gamma_{kmno}B_mB_nB_o). \quad (1')$$

It is now necessary to evaluate the tensors ρ_{ij}, α_{ijkl}, A_{km}, γ_{kmno}. By application of the symmetry properties for the orthorhombic crystal, one can find the independent nonzero terms in these tensors. The procedure consists of seeing how the components of the tensors transform under a symmetry operation, i.e., if the symmetry operation leaves the sign of the component unchanged, this component is unequal to zero; however, if the operation changes the sign of the tensor component then this component must be zero. To do this in detail, one writes down the transformation equation for a second rank tensor and for a fourth rank tensor [which are $D_{i'j'}=(\partial x_i'/\partial x_i)(\partial x_j'/\partial x_j)D_{ij}$ and $P_{i'j'k'l'}=(\partial x_i'/\partial x_i)(\partial x_j'/\partial x_j)(\partial x_k'/\partial x_k)(\partial x_l'/\partial x_l)P_{ijkl}$, respectively] and applies the symmetry conditions to these equations. The symmetry conditions for an orthorhombic crystal are that a rotation by π about each of three mutually perpendicular axes[33] does not change the physical situation.

After determining the independent terms unequal to zero (as described above) in the tensors specifying the magnetoresistivity one may rewrite Eq. (1') as:

[33] The rotations are specified as follows:

Rotation about z-axis:
$$\begin{cases}\partial x_1'/\partial x_1=-1, & \partial x_1'/\partial x_2=0, & \partial x_1'/\partial x_3=0,\\ \partial x_2'/\partial x_1=0, & \partial x_2'/\partial x_2=-1, & \partial x_2'/\partial x_3=0,\\ \partial x_3'/\partial x_1=0, & \partial x_3'/\partial x_2=0, & \partial x_3'/\partial x_3=1.\end{cases}$$

Rotation about y-axis:
$$\begin{cases}1, & 0, & 0;\\ 0, & -1, & 0;\\ 0, & 0, & -1.\end{cases}$$

Rotation about x-axis:
$$\begin{cases}1, & 0, & 0;\\ 0, & -1, & 0;\\ 0, & 0, & -1.\end{cases}$$

$$
\begin{aligned}
E_1 &= I_1(\rho_{11}+\alpha_{1111}B_1^2+\alpha_{1122}B_2^2+\alpha_{1133}B_3^2)\\
&\quad +I_2(2\alpha_{1221}B_2B_1+A_{33}B_3+3\gamma_{3113}B_1^2B_3\\
&\quad +3\gamma_{3223}B_2^2B_3+\gamma_{3333}B_3^3)+I_3(2\alpha_{1331}B_1B_3-A_{22}B_2\\
&\quad -3\gamma_{2112}B_1^2B_2-3\gamma_{2233}B_3^2B_2-\gamma_{2222}B_2^3),\\
E_2 &= I_1(2\alpha_{1221}B_1B_2-A_{33}B_3-3\gamma_{3113}B_1^2B_3\\
&\quad -3\gamma_{3223}B_2^2B_3-\gamma_{3333}B_3^3)+I_2(\rho_{22}+\alpha_{2211}B_1^2\\
&\quad +\alpha_{2222}B_2^2+\alpha_{2233}B_3^2)+I_3(2\alpha_{2332}B_3B_2+A_{11}B_1\\
&\quad +\gamma_{1111}B_1^3+3\gamma_{1122}B_1B_2^2+3\gamma_{1133}B_1B_3^2),\\
E_3 &= I_1(2\alpha_{1331}B_1B_3+A_{22}B_2+\gamma_{2222}B_2^3+3\gamma_{2112}B_2B_1^2\\
&\quad +3\gamma_{2233}B_3^2B_2)+I_2(2\alpha_{2332}B_3B_2-A_{11}B_1\\
&\quad -\gamma_{1111}B_1^3-3\gamma_{1122}B_2^2B_1-3\gamma_{1133}B_3^2B_1)\\
&\quad +I_3(\rho_{33}+\alpha_{3333}B_3^2+\alpha_{3311}B_1^2+\alpha_{3322}B_2^2).
\end{aligned}
\tag{2'}
$$

APPENDIX B. EFFECT OF A MISALIGNMENT OF CRYSTALLOGRAPHIC AXES FROM SPECIMEN AXES ON THE TRANSVERSE FIELD

Assume a measuring coordinate system x_1', x_2', x_3', with $I_1'\|x_1'$, $B_3'\|x_3'$, $B_2'\|x_2'$. Assume that x_1, x_2, x_3 are the coordinate axes of the crystallographic system. Then a transformation from the unprimed (or crystallographic) system to the primed (or measuring) system is defined by the equations:

$$
B_1=l_3B_3'+l_2B_2', \quad B_2=m_3B_3'+m_2B_2', \quad B_3=n_3B_3'+n_2B_2', \tag{3'}
$$

$$
I_1=l_1I_1', \quad I_2=m_1I_1', \quad I_3=n_1I_1', \quad E_2'=l_2E_1+m_2E_2+n_2E_3, \tag{4'}
$$

where

$$
\begin{aligned}
&\partial x_1'/\partial x_1=l_1, \quad \partial x_1'/\partial x_2=m_1, \quad \partial x_1'/\partial x_3=n_1,\\
&\partial x_2'/\partial x_1=l_2, \quad \partial x_2'/\partial x_2=m_2, \quad \partial x_2'/\partial x_3=n_2,\\
&\partial x_3'/\partial x_1=l_3, \quad \partial x_3'/\partial x_2=m_3, \quad \partial x_3'/\partial x_3=n_3.
\end{aligned}
$$

If we employ Eq. (2') in conjunction with Eqs. (3') and (4') above, we obtain the following expression for the transverse field:

$$
\begin{aligned}
E_2' &= I_1'(l_2l_1\rho_{11}+m_2m_1\rho_{22}+n_2n_1\rho_{33})\\
&\quad +I_1'\{A_{33}(n_3B_3'+n_2B_2')(-n_3)+A_{22}(m_3B_3'\\
&\quad +m_2B_2')(-m_3)+A_{11}(l_3B_3'+l_2B_2')(-l_3)\}\\
&\quad +I_1'\{(l_3B_3'+l_2B_2')^2(\alpha_{1111}l_2l_1+\alpha_{2211}m_2m_1\\
&\quad +\alpha_{3311}n_2n_1)+(m_3B_3'+m_2B_2')^2(\alpha_{1122}l_2l_1\\
&\quad +\alpha_{2222}m_2m_1+\alpha_{3322}n_2n_1)+(n_3B_3'+n_2B_2')^2\\
&\quad \times(\alpha_{1133}l_2l_1+\alpha_{2233}m_2m_1+\alpha_{3333}n_2n_1)\\
&\quad +(m_3B_3'+m_2B_2')(l_3B_3'+l_2B_2')(2\alpha_{1221})\\
&\quad \times(l_2m_1+l_1m_2)+(l_3B_3'+l_2B_2')(n_3B_3'+n_2B_2')\\
&\quad \times(2\alpha_{1331})(l_2n_1+l_1n_2)+(n_3B_3'+n_2B_2')\\
&\quad \times(m_3B_3'+m_2B_2')(2\alpha_{2332})(m_2n_1+m_1n_2)\}\\
&\quad +I_1'\{(l_3B_3'+l_2B_2')^3(-l_3\gamma_{1111})+(m_3B_3'\\
&\quad +m_2B_2')^3(-m_3\gamma_{2222})+(n_3B_3'+n_2B_2')^3\\
&\quad \times(-n_3\gamma_{3333})+(l_3B_3'+l_2B_2')^2(m_3B_3'+m_2B_2')\\
&\quad \times(-3\gamma_{2112}m_3)+(l_3B_3'+l_2B_2')(m_3B_3'+m_2B_2')^2\\
&\quad \times(-3\gamma_{1122}l_3)+(l_3B_3'+l_2B_2')(n_3B_3'+n_2B_2')^2\\
&\quad \times(-3\gamma_{1133}l_3)+(l_3B_3'+l_2B_2')^2(n_3B_3'+n_2B_2')\\
&\quad \times(-3\gamma_{3113}n_3)+(n_3B_3'+n_2B_2')^2(m_3B_3'+m_2B_2')\\
&\quad \times(-3\gamma_{2233}m_3)+(m_3B_3'+m_2B_2')^2(n_3B_3'+n_2B_2')\\
&\quad \times(-3\gamma_{3223}n_3)\}.
\end{aligned}
\tag{5'}
$$