

### Piezoresistivity of Bismuth

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The temperature dependences of the longitudinal and transverse piezoresistivities have been measured over the range 70–300°K for five pure bismuth crystals of different crystallographic orientation. An oscillatory stress collinear with a direct current in the sample was employed. The data were analyzed by a least-squares technique, and the temperature dependences of the piezoresistivity coefficients  $\pi_{11}$ ,  $\pi_{33}$ ,  $\pi_{14}$ ,  $\pi_{41}$ ,  $(\pi_{13} + \pi_{44})$ , and  $(\pi_{31} + \pi_{44})$  were obtained. These results are compared with published data on the change in resistivity under hydrostatic pressure to obtain estimates of all eight piezoresistivity coefficients at room temperature and seven of the coefficients at liquid-nitrogen temperature. The relative magnitudes of the coefficients are compared with a theory based on the electron-transfer model.

#### INTRODUCTION

THE importance of piezoresistivity data in elucidating the band structures of semiconductors and semimetals has been recognized for many years,<sup>1</sup> but the data available for bismuth are relatively incomplete.<sup>2</sup> The present work provides sufficient data to warrant detailed analysis. Bismuth is characterized by the point-group symmetry  $\bar{3}m$ . The form of the piezoresistivity tensor for this group has been given by Smith,<sup>3</sup> and is reproduced in Fig. 1. The representation of the fourth-rank piezoresistivity tensor as a 6×6 matrix and the notation used throughout this paper are explained in Ref. 3. There are eight independent nonvanishing piezoresistivity coefficients, seven of which can be determined using an experimental configuration in which uniaxial stress is applied parallel to the direction of the current. The eighth coefficient  $\pi_{12}$  cannot be determined in this way, but can be found by comparison with data on the change in resistivity with hydrostatic stress.

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & 0 & \pi_{14} & \pi_{11} - \pi_{12} \end{bmatrix}$$

FIG. 1. Piezoresistivity tensor for  $\bar{3}m$  point-group symmetry.

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<sup>1</sup> R. W. Keyes, Phys. Rev. 104, 665 (1956). References to earlier work are given in this paper.

<sup>2</sup> M. Allen, Phys. Rev. 42, 848 (1932); 49, 248 (1936).

<sup>3</sup> C. S. Smith, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 175.

#### EXPERIMENTAL PROCEDURE

The most satisfactory geometrical arrangement for piezoresistance measurements employs a sample in the shape of a rectangular parallelepiped having a large ratio of length to lateral dimensions (see Fig. 2). The current and stress are introduced at the ends, so that the current (which is held constant) and stress are parallel to the long axis of the sample over most of its length. For an arbitrary orientation of the crystal axes, the change in electric field under stress can be resolved into three components, one parallel to the long axis of the sample and two perpendicular to it. These components can be found by measurement of the three voltages indicated in Fig. 2. It will be shown subsequently that seven of the piezoresistance coefficients can be determined in this way, but at least three different sample orientations are required. In this work five different crystallographic orientations have been employed, and the resulting redundancy has been used as a check on the consistency of the measurements.

Figure 3 shows the systems of coordinates which were used to describe the sample orientations. A system of laboratory coordinates 0-x'y'z' is initially set up coincident with the orthogonal set of crystal axes commonly employed (binary-x, bisectrix-y, trigonal-z). The positive direction of the bisectrix axis is determined from x-ray diffraction patterns according to the con-

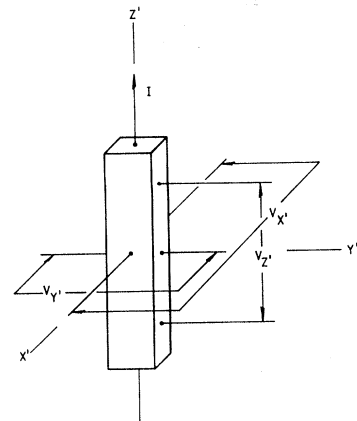


FIG. 2. Simplified sample arrangement.

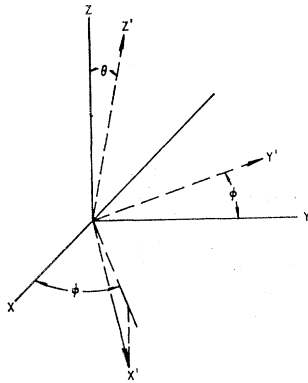


FIG. 3. Definition of coordinate system.

vention given by Boyle and Smith.<sup>4</sup> Two successive rotations of the primed coordinate system are then carried out. An initial positive rotation by  $\varphi$  about the  $z'$  (or  $z$ ) axis is followed by a positive rotation through an angle  $\theta$  about the  $y'$  axis. The  $z'$  axis is then coincident with the long axis of the sample, the positive direction of current being the positive  $z'$  direction. The stress is also applied along the  $z'$  axis and is defined to be positive when compressive. The sample is cut so that its two smaller dimensions are parallel to the  $x'$  and  $y'$  axes, respectively, in the rotated coordinate system.

The components of the matrix of direction cosines characterizing these rotations are<sup>3</sup>

$$\begin{aligned} a_{11} &= \cos\theta \cos\varphi, \\ a_{12} &= \cos\theta \sin\varphi, \\ a_{13} &= -\sin\theta, \\ a_{21} &= -\sin\varphi, \\ a_{22} &= \cos\varphi, \\ a_{23} &= 0, \\ a_{31} &= \sin\theta \cos\varphi, \\ a_{32} &= \sin\theta \sin\varphi, \\ a_{33} &= \cos\theta. \end{aligned} \tag{1}$$

Following Smith's procedure<sup>3</sup> for transformation of the piezoresistance tensor, the following result is obtained for the three piezoresistance coefficients (in the lab-

TABLE I. Summary of sample orientations.

Sample No.	$\theta$	$\varphi$	$\pi_{ij}' \neq 0$
1	0°	0°	$\pi_{33}'$
2	90°	90°	$\pi_{33}', \pi_{53}'$
3	45°	90°	$\pi_{33}', \pi_{53}'$
4	135°	15°	$\pi_{33}', \pi_{43}', \pi_{53}'$
5	112.5°	90°	$\pi_{33}', \pi_{53}'$

<sup>4</sup> W. S. Boyle and G. E. Smith, in *Progress in Semiconductors*, edited by A. F. Gibson (Heywood and Company Ltd., London, 1963), Vol. 7, p. 1.

oratory coordinate system) which are measured

$$\begin{aligned} \pi_{33}' &= \pi_{11} \sin^4\theta + \pi_{33} \cos^4\theta + (\pi_{13} + \pi_{31} + 2\pi_{44}) \sin^2\theta \cos^2\theta \\ &\quad + (\pi_{14} + 2\pi_{41}) \sin^3\theta \cos\theta \sin 3\varphi, \\ \pi_{43}' &= (\pi_{14} + \pi_{41}) \sin^2\theta \cos\theta \cos 3\varphi, \\ \pi_{53}' &= (\pi_{11} - \pi_{31}) \sin^3\theta \cos\theta + (\pi_{13} - \pi_{33}) \sin\theta \cos^3\theta \\ &\quad + (\pi_{14} + \pi_{41}) \cos^2\theta \sin^2\theta \sin 3\varphi - \pi_{41} \sin^4\theta \sin 3\varphi \\ &\quad + \left(\frac{1}{4}\right)\pi_{44} \sin 4\theta. \end{aligned} \tag{2}$$

These coefficients are defined by the relations

$$\begin{aligned} \delta E_{z'} &= \pi_{33}' j_{z'} \kappa_{z'}, \\ \delta E_{y'} &= \pi_{43}' j_{z'} \kappa_{z'}, \\ \delta E_{x'} &= \pi_{53}' j_{z'} \kappa_{z'}, \end{aligned} \tag{3}$$

where  $\delta E$  is the change in electric field induced by the application of a compressive stress,  $\kappa$ , and  $j_{z'}$  is the current density. Since  $\pi_{12}$  does not appear in Eq. (2), only seven piezoresistivity coefficients can be determined by applying Eq. (2) to piezoresistivity data on at least three appropriately oriented samples. If the orientations are chosen so that none of the  $\pi_{ij}'$  vanish, nine equations are obtained for the seven  $\pi_{ij}$ . However, care must be taken to choose the orientations such that at least seven *independent* equations are obtained.

Five different orientations, which are listed in Table I, were used in this experiment. For all but one of the samples, at least one of the transverse piezoresistivities vanished identically because of the special symmetry, so that only ten nonvanishing coefficients were measured. From these values, the angles given in Table I, and the set of Eq. (2), ten equations for the seven  $\pi_{ij}$  are obtained. Of course, not every subset of seven equations taken from these ten is determinant. In fact, inspection of the first of Eq. (2) reveals that only four

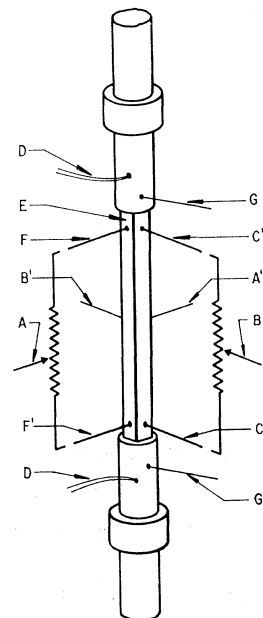


FIG. 4. Actual sample arrangement.

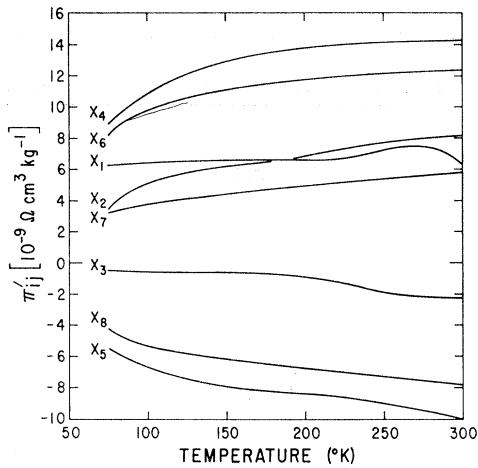


FIG. 5. Temperature dependence of  $\pi'_{ij}$ .  $X_1 = \pi'_{33}$  (sample 1);  $X_2 = \pi'_{33}$  (sample 2);  $X_3 = \pi'_{53}$  (sample 2);  $X_4 = \pi'_{33}$  (sample 3);  $X_5 = \pi'_{53}$  (sample 3);  $X_6 = \pi'_{33}$  (sample 4);  $X_7 = \pi'_{43}$  (sample 4);  $X_8 = \pi'_{53}$  (sample 4).

independent equations can be obtained by measurement of  $\pi'_{33}$  no matter what orientations are employed. Hence any subset of seven equations containing all of the five equations for  $\pi'_{33}$  will be indeterminate.

The lead arrangement shown in Fig. 2 is adequate in principle, but it is in fact difficult to align the transverse probes precisely enough to eliminate a contribution from the longitudinal piezoresistance. The configuration shown in Fig. 4 was therefore adopted. The voltage dividers connected between  $F$  and  $F'$  and between  $C$  and  $C'$  have a resistance ( $2 \Omega$ ) large compared with the sample resistance ( $< 4 \times 10^{-3} \Omega$ ). With a known direct current  $I_{dc}$  through the current leads  $G$  and  $G'$ , the sliding contacts  $A$  and  $B$  are adjusted so that the voltages between  $A'$  and  $A$  and between  $B'$  and  $B$  satisfy the following conditions:

$$\begin{aligned} V_{A'A} &= V_{x'} = I_{dc} [(\rho_{11} - \rho_{33}) / 2W_{y'}] \sin 2\theta, \\ V_{B'B} &= V_{y'} = 0, \end{aligned} \quad (4)$$

where  $\rho_{11}$  and  $\rho_{33}$  are the two principal components of resistivity, and  $W_{y'}$  is the dimension of the sample in the  $y'$  direction. The transverse piezoresistive voltages are then measured between  $A$  and  $A'$  and between  $B$  and  $B'$  in Fig. 4.

The apparatus employed for piezoresistivity measurements has been described elsewhere.<sup>5</sup> The sample chamber normally contained helium gas at atmospheric pressure to minimize temperature gradients. This chamber was separated from the external liquid-nitrogen bath by an evacuable sleeve. Temperatures above  $77^\circ\text{K}$  were obtained by evacuating this sleeve and supplying power to a heater inside the sample chamber which surrounds the sample. Temperatures below  $77^\circ\text{K}$  were obtained by allowing air to condense

<sup>5</sup> W. E. Drobish, R. T. Bate, and N. G. Einspruch, Rev. Sci. Instr. 37, 470 (1966).

in the sample chamber and then pumping the air from the chamber with the sleeve evacuated.

Because this measurement technique employs a direct current in the sample, it is subject to error if a temperature gradient due to Peltier heat transport is allowed to build up. This gradient is always such that the Seebeck effect increases the potential drop along the sample.<sup>6</sup> If the Seebeck coefficient is a function of stress, this gradient will also introduce an error in the piezoresistance even when the frequency of the alternating applied stress is high. The magnitude of this effect has been checked by making measurements with the sample directly immersed in liquid nitrogen and in an ice water bath. Within the experimental error, determined by the reproducibility of successive measurements made under the same conditions, there was no difference between the resistivity or piezoresistance measured with the sample directly immersed in a bath or in helium gas.

## RESULTS

The measured piezoresistivity coefficients  $\pi'_{ij}$  calculated from Eq. (3) are plotted as functions of temperature in Fig. 5. After correction for sample strain (see Appendix A) the coefficients  $\pi_{ij}$  were extracted from these data by a least-squares technique using a digital computer. It was found that the combinations  $(\pi_{13} + \pi_{44})$  and  $(\pi_{31} + \pi_{44})$  could be fairly precisely determined from the data, but  $\pi_{44}$  could not be reliably determined. These results are plotted as functions of temperature in Fig. 6. The probable errors in the coefficients can be estimated from the appropriate entries in Table II.

## DISCUSSION

Jain and Jaggi have previously shown<sup>7</sup> that piezocalvanomagnetic effects in bismuth for stresses applied

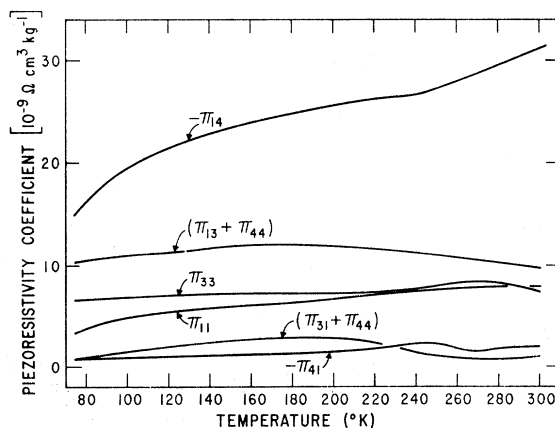


FIG. 6. Temperature dependence of  $\pi_{ij}$ .

<sup>6</sup> W. C. Myers and R. T. Bate, Rev. Sci. Instr. 31, 464 (1960).

<sup>7</sup> A. L. Jain and R. Jaggi, Phys. Rev. 135, A708 (1964).

TABLE II. Comparison with earlier results.

Coefficient ( $10^{-9} \Omega \text{ cm}^2/\text{kg}$ )	Present work	Allen <sup>a</sup>	Bridgman <sup>b</sup>	Jain and Jaggi <sup>c</sup>	Derived
$\pi_{11}$ (295°K)	$7.88 \pm 0.64$	$7.2 \pm 0.16$			
(77°K)	$3.51 \pm 0.21$				
$\pi_{33}$ (295°K)	$7.65 \pm 0.67$	$6.2 \pm 0.41$		$4.76 \pm 0.42$	
(77°K)	$6.47 \pm 0.21$			$5.28 \pm 0.47$	
$\pi_{13} + \pi_{44}$ (295°K)	$9.96 \pm 2.08$				
(77°K)	$10.36 \pm 0.69$				
$\pi_{31} + \pi_{44}$ (295°K)	$0.84 \pm 1.58$				
(77°K)	$0.68 \pm 0.52$				
$\pi_{14}$ (295°K)	$-30.38 \pm 1.90$				
(77°K)	$-15.49 \pm 0.63$				
$\pi_{41}$ (295°K)	$-1.85 \pm 0.66$				
(77°K)	$-0.67 \pm 0.22$				
$2\pi_{31} + \pi_{33}$ (295°K)			3.3	$4.22 \pm 0.68$	
(77°K)				$1.15 \pm 0.31$	
$\pi_{11} + \pi_{12} + \pi_{13}$ (295°K)			8.4		$9.0 \pm 2.6$
$\pi_{13} + \pi_{31} + 2\pi_{44}$ (295°K)	$10.8 \pm 1.9$	$7.1 \pm 0.99$			$7.61 \pm 0.90$
$\pi_{14} + 2\pi_{41}$ (295°K)	$-33.6 \pm 2.2$	$-27.0 \pm 0.54$			$-0.17 \pm 0.40$
$\pi_{13}$ (295°K)					$-2.06 \pm 0.28$
(77°K)					$1.0 \pm 1.6$
$\pi_{31}$ (295°K)					$2.74 \pm 0.59$
(77°K)					$-8.5 \pm 2.7$
$\pi_{44}$ (295°K)					
(77°K)					
$\pi_{12}$ (295°K)					

<sup>a</sup> M. Allen, Phys. Rev. **49**, 248 (1936).

<sup>b</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).

<sup>c</sup> A. L. Jain and R. Jaggi, Phys. Rev. **135**, A708 (1964).

<sup>d</sup> The probable errors resulting from the least-squares fit indicate that the number of significant figures stated is excessive for many of the coefficients. The results are expressed in this way only to indicate precisely the range of values within which the true value probably lies.

along the trigonal axis at 80 and 300°K cannot be interpreted simply in terms of interband and/or inter-valley transfer of carriers among bands which contribute to conduction at very low temperatures.<sup>8</sup> These workers, as well as Hall and Koenig,<sup>9</sup> suggest that this behavior is the result of thermal excitation of electrons from a valence band lying below the Fermi energy.

In the case of the piezogalvanomagnetic data, the relative values of one piezo-Hall coefficient and one piezoresistivity coefficient were found to be inconsistent with the simple band model. This model also predicts four relations among the piezoresistivity coefficients. These are

$$\pi_{13}/\rho_1 = \pi_{33}/\rho_3, \quad (5a)$$

$$(\pi_{11} + \pi_{12})/2\rho_1 = \pi_{31}/\rho_3, \quad (5b)$$

$$\pi_{14}/\pi_{44} = [(\mu_1 - \mu_2)/2\mu_4](\rho_1/\rho_3), \quad (5c)$$

$$\pi_{11}/\rho_1 - \pi_{31}/\rho_3 = \pi_{41}\pi_{14}/\rho_1\pi_{44}. \quad (5d)$$

Equations (5a) and (5b) are in fact valid for any band model if the mobility anisotropy of each band is assumed independent of strain. Since Eq. (5d) involves no band parameters, one might anticipate that it also has more general validity. On the other hand, Eq. (5c) is specific to the model. The present results cannot be compared directly with Eqs. (5) over the entire temperature range covered because of the inability to obtain  $\pi_{12}$  and  $\pi_{44}$  in the present experiment, but it is

possible to do so at temperatures where the pressure coefficients of these quantities have been measured. The changes in the resistivity components per unit hydrostatic pressure are

$$\Delta_1 = \delta\rho_{11}/\delta p = \pi_{11} + \pi_{12} + \pi_{13},$$

$$\Delta_3 = \delta\rho_{33}/\delta p = 2\pi_{31} + \pi_{33}.$$

Thus  $\pi_{44}$  can be obtained by combining the present values of  $(\pi_{31} + \pi_{44})$  and  $\pi_{33}$  with the published values of  $\Delta_3$ . Then  $\pi_{12}$  can be found if the derived value of  $\pi_{44}$  is compared with  $\Delta_1$ ,  $\pi_{11}$ , and  $(\pi_{13} + \pi_{44})$ . Although  $\Delta_3$  has been measured at three fixed temperatures,  $\Delta_1$  has been measured only at room temperature. Thus  $\pi_{12}$  can be estimated only at room temperature. A summary of the present results at 295 and 77°K and a comparison with earlier work is given in Table II. The values of  $\pi_{13}$ ,  $\pi_{31}$ ,  $\pi_{44}$ , and  $\pi_{12}$  derived by comparison of the present data with the pressure coefficients

TABLE III. Test of relations between coefficients. (Units are  $10^{-5} \text{ cm}^2/\text{kg}$ ).

$\pi_{13}/\rho_1$ (295°K)	$= 8.0 \pm 2.3$
$\pi_{33}/\rho_3$ (295°K)	$= 5.7 \pm 0.5$
$\pi_{13}/\rho_1$ (77°K)	$= 26.7 \pm 3.2$
$\pi_{33}/\rho_3$ (77°K)	$= 21.6 \pm 0.7$
$(\pi_{11} + \pi_{12})/2\rho_1$ (295°K)	$= -0.27 \pm 1.16$
$\pi_{31}/\rho_3$ (295°K)	$= -0.13 \pm 0.30$
$(\pi_{11}/\rho_1 - \pi_{31}/\rho_3)$ (77°K)	$= 18.8 \pm 1.2$
$(\pi_{41}/\rho_1)(\pi_{14}/\pi_{44})$ (77°K)	$= 13.1 \pm 4.8$
$\pi_{14}/\pi_{44}$ (77°K)	$= -5.65 \pm 1.2$ (dimensionless)

<sup>8</sup> A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962).

<sup>9</sup> J. J. Hall and S. H. Koenig, IBM J. Res. Develop. **8**, 241 (1964).

are also given. In Table III, these coefficients are used to test the relations between the coefficients derived earlier.

Inspection of Table III reveals that relations (5a), (5b), and (5d) are satisfied within the errors of the estimates, but  $\pi_{14}/\pi_{44}$  is negative, while Eq. (5c) predicts a positive value. Further analysis of these data, taking into account the possible influence of other bands above and below the Fermi level, may explain this discrepancy.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: CORRECTIONS FOR STRAIN

The measured piezoresistivity coefficients were corrected for strain according to the following formulas:

$$\begin{aligned}\pi_{33}'(\text{true}) &= \pi_{33}'(\text{measured}) - \rho_3'(S_{13}' + S_{23}' - S_{33}'), \\ \pi_{43}'(\text{true}) &= \pi_{43}'(\text{measured}) - \rho_4'S_{13}', \\ \pi_{53}'(\text{true}) &= \pi_{53}'(\text{measured}) - \rho_5'S_{23}',\end{aligned}$$

where  $\rho_i'$  and  $S_{jk}'$  are, respectively, the resistivity tensor components and the elastic compliance tensor components in the laboratory (primed) coordinate system. The convention used here (and throughout this paper) is that  $\pi_{13}$  is positive when a *compressive* stress along axis 3' increases  $\rho_i'$ . The corrections to  $\pi_{33}'$  were about 10% and were always positive. The corrections to  $\pi_{43}'$  and  $\pi_{53}'$  were negligible.

### Re-Evaluation of Some Thermodynamic Properties of Gadolinium Metal\*

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The heat capacity of Gd metal has previously been measured over the temperature range 15 to 355°K by M. Griffel *et al.* In this note, the  $\gamma$  coefficient ( $16 \times 10^{-4}$  cal/g atom deg<sup>2</sup> in the original work) used in calculating the electronic specific heat of Gd has been replaced by the more recent value of  $22 \times 10^{-4}$  cal/g atom deg<sup>2</sup>. This leads to a slightly higher calculated Debye temperature and a subsequent readjustment of the lattice-specific-heat term. In addition, an error was discovered in the evaluation of the thermodynamic functions, particularly the ( $S_T^0$ ) term. A Simpson's-rule integration procedure was applied to the original heat-capacity data and the thermodynamic functions were re-evaluated. These changes lead to a magnetic-entropy calculation considerably closer to the complete spin-order entropy,  $R \ln 8$ , than was reported in the original work.

#### HEAT CAPACITY

THE total measured heat capacity at constant pressure is commonly split into the following terms:

$$C_p = C_q + C_e + C_m + \delta C.$$

In this equation  $C_q$ ,  $C_e$ , and  $C_m$  are respectively the lattice, electronic and magnetic contributions to the total  $C_p$ . The quantity  $\delta C$  is the dilatation term, which is the difference between the heat capacity at constant pressure and that at constant volume. In the original work<sup>1</sup> this contribution to the total  $C_p$  was found to be 0.034 cal/g atom deg at 25°C.

In evaluating the lattice heat capacity of Gd we assume, as in the original work, that it may be repre-

sented by a single Debye curve. To obtain a suitable value of  $\Theta_D$ , the electronic heat capacity was evaluated at low temperatures ( $T < 20^\circ\text{K}$ , where  $C_m = 0$ ) and subtracted from the corresponding value of  $C_p$ . From the difference a low-temperature  $\Theta_D$  of 153.7 was obtained with the use of Beattie's tables.<sup>2</sup> In making the electronic-heat-capacity calculation, a  $\gamma$  coefficient of  $22 \times 10^{-4}$  was used<sup>3</sup> instead of the La  $\gamma$  coefficient of  $16 \times 10^{-4}$  cal/g atom deg.<sup>2</sup>

Adopting the value 153.7 as the Debye temperature and utilizing Beattie's tables once again, we evaluated the lattice heat capacity ( $C_q$ ) as a function of temperature. These results are shown in Table I along with the original smooth-curve  $C_p$  results.

#### MAGNETIC ENTROPY

An error discovered in the publication of the thermodynamic functions of Gd<sup>1</sup> lead to a recalculation of

\* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1872.

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<sup>1</sup> M. Griffel, R. E. Skochdopole, and F. H. Spedding, *Phys. Rev.* **93**, 657 (1954).

<sup>2</sup> J. A. Beattie, *J. Math. Phys.* **6**, 1 (1926).

<sup>3</sup> K. A. Gschneidner, Jr., in *Rare Earth Research III*, edited by Leroy Eyring (Gordon and Breach, Science Publishers, Inc., New York, to be published).