

# Effect of Pressure on the Mobility of Interstitial Oxygen and Nitrogen in Vanadium\*

G. W. TICHELAAR,† R. V. COLEMAN, AND D. LAZARUS  
*Department of Physics, University of Illinois, Urbana, Illinois*

(Received September 13, 1960)

Measurements of stress relaxation as a function of hydrostatic pressure up to 9000 kg/cm<sup>2</sup> have been made on a vanadium sample containing approximately 0.1 atomic percent dissolved oxygen and 0.2 atomic percent dissolved nitrogen. In the temperature range 83.0° to 98.0°C, the relaxation time due to dissolved oxygen is found to increase exponentially with pressure, the value at 9000 kg/cm<sup>2</sup> being about 1.7 times the value at 1 kg/cm<sup>2</sup>. The pressure dependence of the stress relaxation can be interpreted in terms of an activation volume of 1.7 cm<sup>3</sup>/mole which is about equal to the molar volume of the diffusing oxygen atoms. The relaxation times due to the dissolved nitrogen have been measured at 156.8°C and 163.0°C. The values at 9000 kg/cm<sup>2</sup> are about 1.3 times the values at 1 kg/cm<sup>2</sup>, the activation volume being about 1.1 cm<sup>3</sup>/mole.

## INTRODUCTION

IN a recent paper,<sup>1</sup> results were reported for the effect of pressure on anelastic relaxation in an alpha silver-zinc solid solution. The stress relaxation process in this alloy is generally attributed to diffusion. It is generally assumed that the relaxation phenomenon can be described by a simple rate-theoretic expression relating the observed time to inflection,  $\tau_m$ , with the change in Gibbs free energy of the crystal required for formation ( $\Delta G_m$ ) of vacancies, as

$$\tau_m = \tau_0' \exp(\Delta G_f + \Delta G_m)/RT, \quad (1)$$

where  $\tau_0'$  is a constant independent of pressure and temperature,  $R$  the gas constant, and  $T$  the absolute temperature. One may define an "activation volume"<sup>2</sup> by

$$\Delta V = \Delta V_f + \Delta V_m$$

$$= \left[ \frac{\partial(\Delta G_f + \Delta G_m)}{\partial P} \right]_T = RT \left[ \frac{\partial \ln \tau_m}{\partial P} \right]_T. \quad (2)$$

The term  $\Delta V_f$  can be identified with the molar volume of the defect responsible for diffusion, and the term  $\Delta V_m$  with the expansion of the crystal during a diffusional jump. The experimentally determined value of  $\Delta V$  of 5.36 cm<sup>3</sup>/mole for AgZn was unexpectedly low for the assumed vacancy mechanism, implying that the sum of  $\Delta V_f$  and  $\Delta V_m$  is only of the order of half an atomic volume. If even the highly relaxed vacancy proposed by Tewordt<sup>3</sup> is presumed correct, this result admits only an extremely small dilatation during a diffusional jump, in marked disagreement with usual theoretical models.

It was therefore felt desirable to investigate other materials in which the diffusing defects were not

introduced thermally. In this way, it should be possible to evaluate the dilatational term  $\Delta V_m$  directly. The first systems chosen for this investigation were vanadium-oxygen and vanadium-nitrogen, which have anelastic relaxation peaks in the same temperature range as  $\alpha$ -AgZn, and have been extensively studied at atmospheric pressure by Stanley and Wert,<sup>4</sup> Powers and Doyle,<sup>5</sup> and by Powers.<sup>6</sup>

In body-centered cubic vanadium, the dissolved oxygen and nitrogen atoms presumably occupy random interstitial positions in the lattice. When the crystal is subjected to a uniaxial strain, some interstitial positions become favored, and the applied stress required to maintain a constant strain decreases with time as the oxygen and nitrogen atoms diffuse to the lower energy interstitial sites. These effects occur at temperatures of the order of 100°C in times of about 100 seconds.

The only previous study of the effect of pressure on the mobility of interstitial impurities in a similar lattice is that of Bosman, Brommer, and Rathenau.<sup>7,8</sup> These investigators measured the effect of pressures to 3000 kg/cm<sup>2</sup> on the decay of the magnetic permeability of iron containing either interstitial nitrogen or carbon. They found that the rate of this process, which can be correlated with the rate of diffusion of the nitrogen or carbon atoms, was essentially unaffected by pressure in the range studied. The relaxation times increased by only about one percent in the case of nitrogen and decreased by about the same amount in the case of carbon at the highest pressures. According to their result, the activation volume associated with the motion of interstitial nitrogen in  $\alpha$ -iron is only about 0.04 cm<sup>3</sup>/mole, less than one percent of the molar volume of iron, and about four percent of the molar volume of the diffusing nitrogen atoms. Their results for carbon in  $\alpha$ -iron give a value for  $\Delta V_m$  of  $-0.04$  cm<sup>3</sup>/mole.

\* Supported in part by the U. S. Atomic Energy Commission.

† Present address: Philips Research Laboratories, Eindhoven, The Netherlands.

<sup>1</sup> G. W. Tichelaar and D. Lazarus, *Phys. Rev.* **113**, 438 (1959).

<sup>2</sup> N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, *J. Chem. Phys.* **20**, 1189 (1952); N. H. Nachtrieb and A. W. Lawson, *J. Chem. Phys.* **23**, 1193 (1955).

<sup>3</sup> L. Tewordt, *Phys. Rev.* **109**, 61 (1958).

<sup>4</sup> J. T. Stanley and C. A. Wert, *Acta Met.* **3**, 107 (1955).

<sup>5</sup> R. W. Powers and M. V. Doyle, *Acta Met.* **4**, 233 (1956).

<sup>6</sup> R. W. Powers, *Acta Met.* **2**, 604 (1954).

<sup>7</sup> A. J. Bosman, P. E. Brommer, and G. W. Rathenau, *Physica* **23**, 1001 (1957).

<sup>8</sup> A. J. Bosman, thesis, University of Amsterdam, 1960 (unpublished).

## EXPERIMENTAL PROCEDURE

The apparatus used in the present experiment is identical with that used for the study of anelastic relaxation in AgZn,<sup>1</sup> and so need not be described here. The specimens were made from vanadium wire, initially of 0.030-inch diameter, kindly furnished by Professor C. A. Wert of the Department of Metallurgy at this University. Since difficulty was encountered in reducing the wire size by drawing, the final specimen was prepared by etching the wire in nitric acid to a diameter of 0.015 inch. The etched wire, of length 40 inches, was coiled into a helix of length 0.5 inch and diameter 0.375 inch for use in the high pressure apparatus. The helix, which was extremely hard when formed, was heated in a vacuum of  $10^{-5}$  mm Hg to a temperature of about 900°C for 5 minutes to equilibrate the dissolved oxygen and nitrogen and to remove the cold work.

No attempt was made deliberately to add oxygen or nitrogen to the specimen. A sufficient amount was evidently present as a result of prior heat treatment to provide a sizeable relaxation. The actual amount of dissolved oxygen could be estimated from the observed

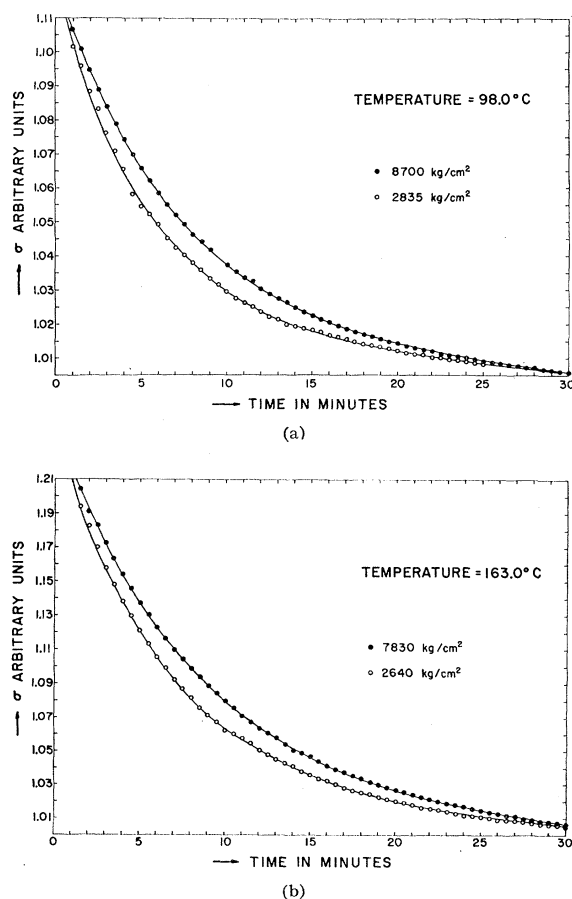


FIG. 1. (a) Experimental curves for oxygen-induced relaxation. (b) Experimental curves for nitrogen-induced relaxation.

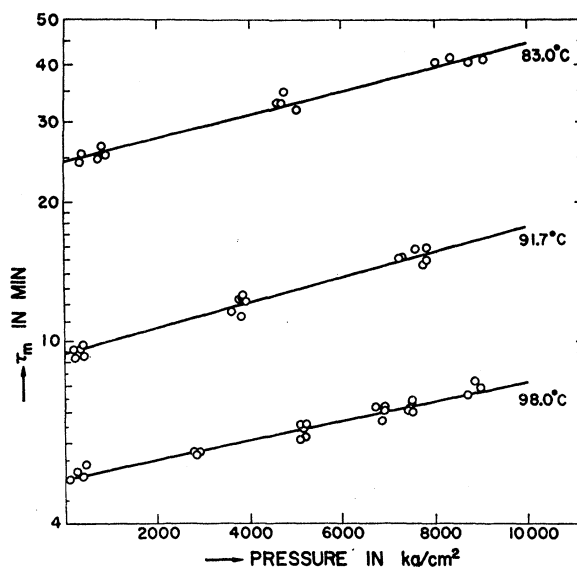


FIG. 2. Isotherms for relaxation time as a function of pressure for oxygen-induced relaxation.

relaxation strength by comparison with the results of Powers and Doyle.<sup>5</sup> In the present case, the oxygen impurity was evidently about 0.1 atomic percent. The amount of nitrogen was considerably more, giving a relaxation strength about twice that of oxygen.

After being placed in the high-pressure apparatus, the specimen was further annealed at a temperature of 170°C for 40 hours before relaxation measurements were begun. Since this temperature is in excess of any used during actual measurements, it is felt that the specimen was presumably equilibrated during all runs. No hysteresis effects were observed following the annealing treatment.

High pressure experiments were carried out using the methods previously described.<sup>1</sup> Pressures were read from a calibrated manganin resistance gauge, and were maintained constant during each run to within  $\pm 5$  kg/cm². The temperature of the specimen was maintained constant by means of an oil bath and a thermistor-bridge controller to within  $\pm 0.01^\circ\text{C}$ .

During each run, the specimen was strained by means of a magnetic solenoid to a total strain of about  $5 \times 10^{-5}$ . The relaxation process was followed by determining the minimum current through the solenoid required to keep the specimen at constant extension as a function of time. Following relaxation, the solenoid current was turned off, and the specimen allowed to relax to its original state during a time much longer than the observed relaxation time.

As in the case of AgZn, the stress relaxation induced by the motion of the interstitial impurities did not follow a simple exponential decay, and the relaxation time,  $\tau_m$ , was taken as the time to inflection in a plot of the logarithm of stress versus time, using the graphical construction described in reference 1.

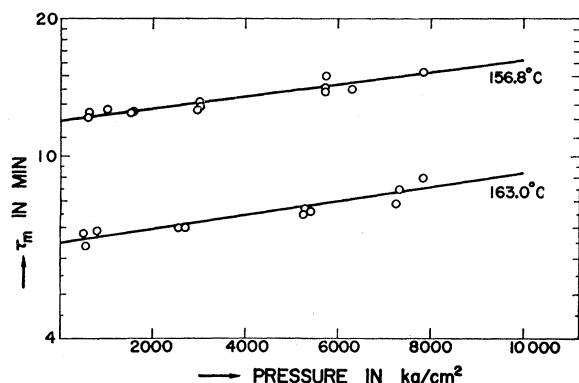


FIG. 3. Isotherms for relaxation time as a function of pressure for nitrogen-induced relaxation.

### RESULTS

The experimental measurements give the decrease with time of the stress,  $\sigma$ , necessary to maintain a constant strain in the vanadium sample. Typical experimental curves for oxygen and nitrogen are shown in Fig. 1. The four curves were taken for the same constant value of strain and show high and low pressure runs for both oxygen and nitrogen, the oxygen data being taken at 98.0°C and the nitrogen data at 163.0°C. Although the stress relaxation process does not obey a simple exponential time dependence of the form,  $\sigma = \sigma_f(1 + \delta e^{-t/\tau_R})$ , all the observations for either the oxygen or nitrogen relaxation can be superimposed in a single simple curve on a reduced time plot. Thus the character of the relaxation process appears to be independent of both temperature and pressure variations.

The measured relaxation times at a variety of temperature and pressures, together with values of  $\Delta V_m$  calculated from Eq. (2), are given in Tables I and II. The data are plotted as a function of pressure in Figs. 2 and 3. The pressure dependence of  $\tau_m$  appears to be exponential; a least-squares analysis leads to the following equations for the oxygen-induced relaxation:

$$83.0^\circ\text{C}: \log \tau_m = (1.390 \pm 0.006) + (2.57 \pm 0.10)10^{-5}P,$$

$$91.7^\circ\text{C}: \log \tau_m = (0.973 \pm 0.006) + (2.77 \pm 0.12)10^{-5}P,$$

$$98.0^\circ\text{C}: \log \tau_m = (0.702 \pm 0.006) + (2.11 \pm 0.09)10^{-5}P.$$

For the nitrogen-induced relaxation:

$$156.8^\circ\text{C}: \log \tau_m = (1.077 \pm 0.007) + (1.31 \pm 0.17)10^{-5}P.$$

$$163.0^\circ\text{C}: \log \tau_m = (0.811 \pm 0.008) + (1.49 \pm 0.17)10^{-5}P.$$

$P$  is in  $\text{kg}/\text{cm}^2$ , and the  $\tau_m$  is in minutes. The indicated limits of error are standard deviations.

The temperature variation of the relaxation time is shown in Figs. 4 and 5 and may be described by a simple Arrhenius equation  $\tau_m = \tau_0 \exp(\Delta H/RT)$ . The following values were found for the constant  $\tau_0$  and the

activation energy  $\Delta H$ . For the oxygen-induced relaxation:

1  $\text{kg}/\text{cm}^2$ :

$$\tau_0 = 10^{-15.7} \text{ min}; \quad \Delta H = 27.9 \pm 0.99 \text{ kcal/mole},$$

9000  $\text{kg}/\text{cm}^2$ :

$$\tau_0 = 10^{-16.3} \text{ min}; \quad \Delta H = 29.2 \pm 2.5 \text{ kcal/mole}.$$

TABLE I. Relaxation times for oxygen-induced relaxation.

Pressure in $\text{kg}/\text{cm}^2$	Temperature in $^\circ\text{C}$	$\tau_m$ in min	$\Delta V$ in $\text{cm}^3/\text{mole}$
103	98.0	5.0	$1.47 \pm 0.06$
264		5.2	
379		5.1	
436		5.4	
2835		5.7	
2835		5.7	
5080		6.1	
5080		6.6	
5190		6.2	
5160		6.4	
5160		6.4	
5160		6.4	
5190		6.6	
6916		7.1	
6916		7.2	
6859		6.7	
6721		7.2	
7470		7.3	
7470		7.0	
7470		7.4	
7440	91.7	7.2	$1.89 \pm 0.08$
7440		7.1	
8700		7.6	
8850		8.2	
8970		7.9	
195		9.6	
229		9.2	
367		9.6	
390		9.8	
413		9.3	
3613		11.6	
3773		12.4	
3820		12.4	
3820		11.3	
3842		12.5	
3923		12.2	
7272		15.2	
7318		15.2	
7582		15.8	
7765	83.0	14.7	$1.72 \pm 0.07$
7788		14.8	
7834		15.9	
344		24.7	
401		25.6	
746		25.1	
814		26.5	
895		25.5	
4623		33.2	
4683		33.1	
4737		35.0	
5024		32.0	
8018		40.6	
8339		41.5	
8740		40.5	
9061		41.0	

TABLE II. Relaxation times for nitrogen-induced relaxation.

Pressure in kg/cm <sup>2</sup>	Temperature in °C	$\tau_m$ in min	$\Delta V$ in cm <sup>3</sup> /mole
510	163.0	6.8	$1.22 \pm 0.13$
550		6.4	
800		6.9	
2620		7.0	
2640		7.0	
5280		7.6	
5280		7.7	
5300		7.6	
7230		7.9	
7320		8.5	
7830		9.0	
590	156.8	12.5	$1.03 \pm 0.13$
600		12.2	
1020		12.7	
1525		12.4	
1680		12.5	
2970		12.7	
3000		12.8	
3000		13.1	
5730		15.0	
5730		13.9	
5730		14.0	
6300		14.0	
7830		15.2	

For the nitrogen induced relaxation:

1 kg/cm<sup>2</sup>:

$$\tau_0 = 10^{-17.2} \text{ min}; \quad \Delta H = 36.7 \pm 2.1 \text{ kcal/mole},$$

9000 kg/cm<sup>2</sup>:

$$\tau_0 = 10^{-16.3} \text{ min}; \quad \Delta H = 34.6 \pm 2.1 \text{ kcal/mole}.$$

The limits of error are calculated using the standard deviations in the least-squares plot of  $\log \tau_m$  as a function

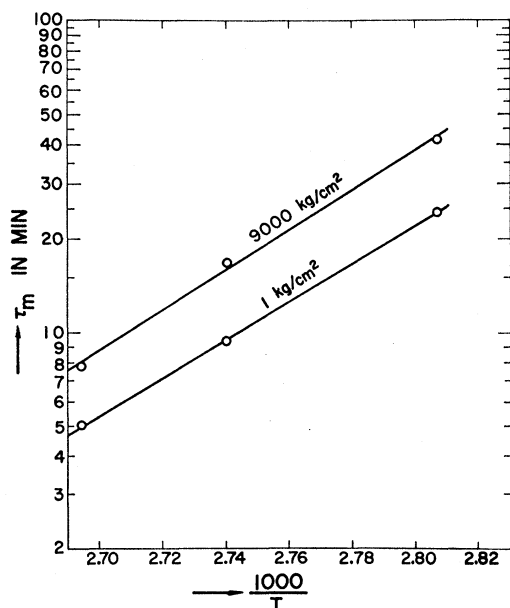


FIG. 4. Temperature dependence of relaxation time due to oxygen-induced relaxation at high and low pressure.

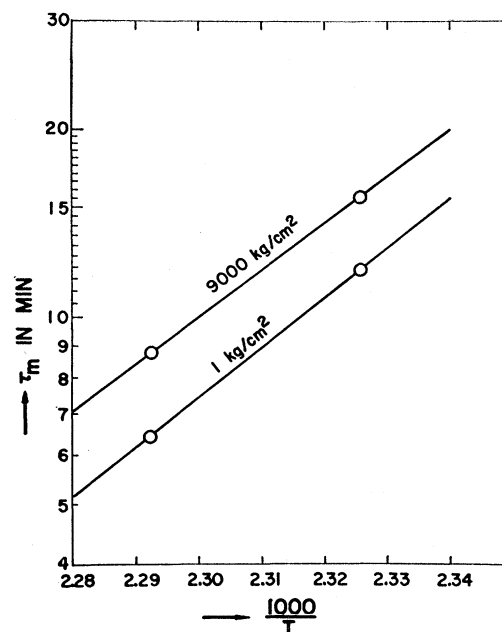


FIG. 5. Temperature dependence of relaxation time due to nitrogen-induced relaxation at high and low pressure.

of pressure. For the nitrogen-induced relaxation, the maximum possible error obtained in  $\Delta H$  by allowing a  $\frac{1}{2}$ -min uncertainty in each measured value of  $\tau_m$  would be about  $\pm 4.8$  kcal/mole. The fact that  $\Delta H$  appears to decrease with increase of pressure is, therefore, probably not significant; more accurate data would be needed to determine directly the change in  $\Delta H$  with pressure.

## DISCUSSION

The present values for the activation energies at 1 kg/cm<sup>2</sup> of  $27.9 \pm 0.9$  kcal/mole for the oxygen-induced relaxation and  $36.7 \pm 2.1$  kcal/mole for the nitrogen-induced relaxation agree reasonably well with the previous values of  $29.3 \pm 0.3$  kcal/mole (Powers and Doyle<sup>5</sup>) and 34.1 kcal/mole (Powers<sup>6</sup>) obtained over a much wider temperature range. In the case of the oxygen-induced relaxation, the application of pressure is found to produce a fairly large increase in the relaxation time, the value at 9000 kg/cm<sup>2</sup> being about 1.7 times the value at 1 kg/cm<sup>2</sup>. The activation volume calculated with Eq. (2) from these measurements is about 1.7 cm<sup>3</sup>/mole, roughly equal to the molar volume of the dissolved oxygen atoms and about 20% of the molar volume of the vanadium atoms.

For the nitrogen-induced relaxation the increase in relaxation time with pressure is found to be about 40% less than in the case of oxygen, the value at 9000 kg/cm<sup>2</sup> being about 1.3 times the value at 1 kg/cm<sup>2</sup>. The activation volume calculated from these measurements is about 1.1 cm<sup>3</sup>/mole, which is somewhat smaller than the molar volume of dissolved nitrogen and about 13% of the molar volume of the vanadium atoms.

The value of the activation volume for nitrogen is considerably smaller than that for oxygen. On the basis of the ionic radii of the interstitial atoms alone, one might expect nitrogen to show a larger effect, since the nitrogen and oxygen ionic radii are 1.71 Å and 1.40 Å, respectively. However, any chemical affinity between oxygen and the vanadium atoms may cause the interstitial volume to be effectively larger for oxygen than for nitrogen.

The present results are in sharp distinction to those obtained by Bosman, Brommer, and Rathenau<sup>7,8</sup> in the analogous  $\alpha$ -iron-nitrogen and  $\alpha$ -iron-carbon systems. The activation volumes for interstitial oxygen and nitrogen in vanadium are apparently much larger than for nitrogen in iron, the value for oxygen being forty times larger and the value for nitrogen being thirty times larger. For carbon in  $\alpha$ -iron, Bosman,

Brommer, and Rathenau obtain a negative activation volume. At present, the reasons for this discrepancy are completely obscure. However, neither the present measurement nor that of Bosman *et al.* involve direct measurements of diffusion; possibly the processes are somewhat more complicated than generally supposed. It is hoped that this situation may be clarified by additional experiments.

#### ACKNOWLEDGMENT

The authors wish to express their sincere thanks to Professor C. A. Wert for suggesting the suitability of the vanadium-oxygen and vanadium-nitrogen systems, and for his kindness in providing the vanadium samples. The authors also wish to thank Mr. James Boyd for assistance in making some of the measurements.

## Electron Effective Masses of InAs and GaAs as a Function of Temperature and Doping

MANUEL CARDONA

Laboratories RCA Ltd., Zurich, Switzerland

(Received September 19, 1960)

The electron effective masses of several GaAs and InAs samples at room and liquid nitrogen temperatures have been determined from Faraday rotation and infrared reflectivity measurements. An increase in effective mass with increasing carrier concentration has been found in both materials. This increase can be quantitatively interpreted in InAs in terms of the nonparabolic nature of the conduction band. In GaAs the increase in effective mass with doping suggests the existence of another set of conduction band minima above the lowest (000) minimum. The measured temperature variation of the effective mass can be attributed to two mechanisms: the increase in effective mass produced by the spread in the Fermi distribution because of the nonparabolic shape of the band, and the variation in the band structure produced by the thermal expansion of the lattice.

The Faraday rotation due to the interband transitions has been measured in GaAs and InAs. This rotation is clockwise along the direction of motion of the radiation and the magnetic field for GaAs and counterclockwise for InAs. This effect is compared with the corresponding effect in other semiconductors.

### 1. INTRODUCTION

THE variation of the electron effective mass with temperature found experimentally in Ge<sup>1,2</sup> has been interpreted as due to the slight nonparabolicity of the energy band and the variation of the corresponding energy gap with volume.<sup>1</sup> The temperature variation of the effective mass produced by the nonparabolicity of the band and the one due to the change of the energy gap have opposite signs for the III-V semiconductors with a lowest (000) conduction band minimum. Hence, a very small variation of the effective mass with temperature should be expected for these semiconductors. This conclusion has been experimentally confirmed by the author, who found a temperature variation smaller than

2% between 80 and 297°K in the electron effective mass of GaAs and InP as determined from the infrared reflectivity of these materials.<sup>3</sup>

A large increase in the electron effective mass of InSb with increasing carrier concentration has been found by several authors.<sup>4,5</sup> This effect can be explained in terms of the strong nonparabolic character of the conduction band of this material, produced by the small energy gap. A somewhat smaller effect should be expected for InAs and a much smaller one for GaAs.

In this paper, infrared reflectivity and Faraday rotation measurements on InAs and GaAs at several temperatures and dopings are reported. The electron effective

<sup>3</sup> M. Cardona, to be reported at the Prague Conference on Semiconductors, August-September, 1960.

<sup>4</sup> W. G. Spitzer and H. Y. Fan, *Phys. Rev.* **106**, 882 (1957).

<sup>5</sup> S. D. Smith, T. S. Moss, and K. W. Taylor, *J. Phys. Chem. Solids* **11**, 131 (1959).

<sup>1</sup> M. Cardona, W. Paul, and H. Brooks, *Helv. Phys. Acta* (to be published).

<sup>2</sup> D. Geist, *Z. Physik* **137**, 335 (1959).