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Electronic Conduction and Defect Equilibria in CdO Single Crystals

F. P. KOFFYBERG

Department of Physics, Brock University, St. Catharines, Ontario, Canada

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Measurements of the equilibrium carrier concentration in pure, degenerate CdO single crystals grown by an iodine vapor transport process and quenched after equilibration with oxygen in the pressure range from 2×10^{-4} to 1.00 atm at temperatures from 605 to 828°C show that the donor defect is doubly ionized. The dependence of carrier concentration on oxygen pressure and temperature can be explained satisfactorily on the basis of a model in which the conduction band deviates from the simple parabolic shape by the addition of donor energy levels. The free energy of formation of the donors is 1.95 eV, which differs from the vacancy formation energy as deduced from previous oxygen diffusion measurements. However, the measured donor concentrations are in good agreement with the defect concentrations determined from previous chemical, electrical, and diffusion measurements. The carrier mobility at room temperature is determined only in part by ionized donor scattering.

1. Introduction

Cadmium oxide is a *n*-type semiconductor with nearly metallic conductivity. Previous work on thin films (*1*) and on polycrystalline specimens (*2*, *3*) has established that increasing temperature and decreasing oxygen pressure during specimen preparation results in increased conductivity, indicating that the conductivity is related to a deficiency of oxygen in the CdO lattice. The concentration of the principal defect in non-stoichiometric CdO has been measured by several different methods and interpreted in several ways. From lattice parameter measurement on pure and doped powder specimens, Cimino and Marezzio (*4*) concluded that Cd interstitials were present in a concentration of $1.5 \times 10^{19}/\text{cm}^3$. Using a direct chemical analysis Engell (*5*) measured a Cadmium excess of 0.055% ($2 \times 10^{19}/\text{cm}^3$) in a sample sintered in air at 650°C. Haul and Just (*6*) deduced an oxygen vacancy concentration of $1.7 \times 10^{19}/\text{cm}^3$ from oxygen tracer diffusion measurements in material equilibriated at 790°C and 0.16 atm O_2. Finkenrath and von Ortenberg (*3*) and Koffyberg (*7*) measured free carrier concentrations of 10^{18}–$10^{20}/\text{cm}^3$ in quenched polycrystalline (*3*) and single crystal (*7*) specimens and concluded that the carriers were produced by the ionization of atomic defects. With the exception of (*3*) and (*7*), the reliability of the data from these studies is open to question, either because of the type of specimen used or of lack of careful control of the experimental conditions or a combination of both factors.

The aim of the present work was twofold. Primarily we wished to obtain data under well-defined conditions on pure CdO single crystals. We studied the Hall coefficient R_H and conductivity σ as a function of temperature and oxygen pressure with which the crystal was in equilibrium. Our second objective was to attempt to identify the primary defect in nonstoichiometric CdO by a detailed consideration of the defect formation and ionization equilibria.

In Section 2 below, the methods of specimen preparation and measurement are outlined. The results are described in Section 3, and in Section 4 we show that they can be interpreted in terms of a doubly ionized defect donor that has zero ionization energy, that is, whose energy levels are in the conduction band. It is also pointed out that the simple mass-action formalism used by previous workers (*2*, *11*) cannot be applied to this material. The electron mobility will be shown to be predominantly determined by defect scattering. While the results of the present study confirm that the free carriers are produced by the ionization of lattice defects, the precise nature of the defect remains unresolved.

2. Experimental

2.1. Crystal Preparation

Single crystals have been prepared by injection of Cd vapor into a stream of oxygen, and by a vapor transport method using iodine as the transporting agent. In a variation of a procedure used by Scharowsky (*8*) for the growth of ZnO crystals, metallic Cd was vaporized at 400–500°C in a nitrogen stream; the Cd vapor was mixed at 700–800°C with oxygen in front of a MgO or quartz substrate. Small crystals (0.2 mm) grew as an agglomerate on the substrate; their small size was apparently due to failure to control the nucleation rate. Usable crystals were grown by transporting CdO via the volatile CdI_2 in a closed quartz ampoule. The ampoule (18-cm length by 3-cm i.d.) was charged at one end with 6 g of 99.999% CdO powder and thoroughly outgassed; 10–20 mg I_2 was sublimed into the ampoule before sealing off. Transport took place in a gradient of 80–120°C at an average temperature of 950°C. Good nucleation was achieved by first placing the growth-end of the ampoule at the highest temperature of a horizontal single-zone furnace and then pulling the ampoule at a rate of 1 mm/hr through the usual bell-shaped temperature profile until the charge temperature was 1000°C. After one to two weeks single crystals of maximum 3-mm edge length were obtained; the ampoule was then air-quenched and the crystals pried loose from the inner quartz wall to which they adhered strongly. After light etching the (111) faces showed numerous slip lines and a maximum etch pit density of $10^7/cm^2$. The only impurities detected by emission spectrography were Cu, Na, Si and Mg; these were present at the 10–30 ppm level. All results reported later were obtained on crystals grown by this iodine transport process.

2.2. Measuring Procedures

Samples were prepared by grinding thin slabs (0.3 × 1.2 × 1.2 mm) from the as-grown crystals. After polishing they were lightly etched in dilute HCl and annealed in commercial high-purity argon–oxygen mixtures; the time necessary to reach equilibrium concentrations of the defect (as judged by the constancy of the values of the conductivity and Hall coefficient after intermittent quenching) ranged from nine days at 605°C to one day at 827°C. The samples were quenched from the annealing temperature to room temperature in the annealing gas mixture; after quenching their bulk and surface conductivity were identical. The time needed for quenching to room temperature was approximately 5 sec; deliberately increasing this time to 100 sec had no effect on the measured bulk properties. The conductivity and Hall constant were measured by the van der Pauw method using spring-loaded tungsten or rhodium contacts which were ohmic and nonrectifying. At room temperature dc methods were used; the use of 27 c/s, ac instrumentation with tuned amplifiers at other temperatures avoided complications due to small thermoelectric voltages in the lead wires.

3. Results

For all specimens both the conductivity σ and the Hall constant R_H were independent of the directions of current flow and magnetic field. In the range from 2 to 7 kG R_H was found to be independent of magnetic field strength, in contradiction with previous results obtained by Wright and Bastin (*16*) on compressed powder specimens. All crystals were measured at room temperature after quenching from equilibration at temperatures T_a between 605 and 827°C with oxygen pressures P_a ranging from 1.00 atm to 2.30×10^{-4} atm. In addition, R_H was measured on a few relatively large quenched crystals, surrounded by the annealing gas mixture, from 83°K up to the annealing temperature T_a. Within the precision of these measurements (±3%) R_H did not vary with temperature in this range. In addition, R_H was found to be independent both of the quenching procedure and of the thermal history of the crystal before quenching. Carrier concentrations n_0, calculated from the room temperature

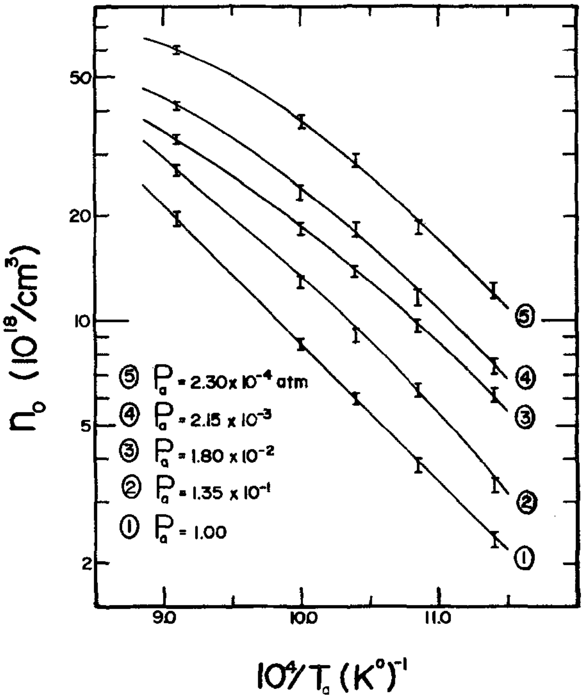

FIG. 1. Carrier concentrations n_0 as a function of equilibrium temperature T_a and equilibrium oxygen pressure P_a.

values of R_H according to $n_0 = r/R_H e$, where r is the Hall factor and e the electronic charge, are shown in Fig. 1 as a function of equilibrium temperature T_a and oxygen pressure P_a; the data points represent measurements on 12 different crystals. In these results r is set equal to 1.00, for reasons to be discussed in Section 4 below. The room temperature mobilities μ_H, calculated from $\mu_H = R_H \sigma$ are shown in Fig. 4 as a function of n_0.

4. Discussion

The lack of dependence of R_H on quenching procedure, on thermal history of the crystal before quenching, and on temperature up to T_a indicates that the electrically active defects generated at annealing temperature T_a were retained during quenching to room temperature. The Hall factor r depends in general on the degree of degeneracy and the carrier scattering mechanism (*9*). Calculations, based on the usual model of a parabolic conduction band or on the modified conduction band model which will be discussed later, show that all our specimens are fully degenerate at room temperature so that the Hall factor is equal to unity. Consequently, the carrier concentrations calculated from room temperature R_H values and shown in Fig. 1 represent equilibrium concentrations at temperatures T_a and oxygen pressures P_a. The lack of temperature dependence of R_H in the range from 83 to 900°K indicates that all donors are completely ionized. In the following, therefore, we shall take the donor ionization energy to be zero. It is clear that the results presented in Fig. 1 support a defect model in which the carriers come from donors generated in a crystal which at high temperature loses oxygen to the ambient atmosphere. At large oxygen pressure and small carrier concentration this process can be characterized by an apparent activation energy of 0.79 eV, as calculated from the data points at $P_a = 1.00$ atm in Fig. 1; however, at large carrier concentrations the activation energy clearly becomes a function of n_0.

Since there is no indication of any donor ionization process either at low or at high temperatures, we may rule out the presence of neutral or singly-ionized electrically active defects. Consequently, the major defect reaction in CdO may be written in general form as

$$\text{perfect lattice} \leftrightarrows \mathrm{D}^{++} + 2e + \tfrac{1}{2}\mathrm{O}_2, \qquad (1)$$

where D^{++} is either a doubly-ionized oxygen vacancy or a cadmium interstitial. When reaction (1) has proceeded to equilibrium, the thermodynamic potentials μ of the species involved are related by

$$\mathrm{O} = \mu_{\mathrm{D}^{++}} + \tfrac{1}{2}\mu_{\mathrm{O}_2} + 2\mu_e. \qquad (2)$$

Substituting the usual concentration and pressure dependence of $\mu_{\mathrm{D}^{++}}$ and μ_{O_2}, Eq. (2) becomes

$$0 = (\mu^0_{\mathrm{D}^{++}} + \tfrac{1}{2}\mu^0_{\mathrm{O}_2} + 2E_c) + kT_a(\ln[\mathrm{D}^{++}] + \tfrac{1}{2}\ln P_a + 2\eta). \qquad (3)$$

In this equation the first term is the standard free energy of the reaction (1), E_c is the energy at the bottom of the conduction band and $\eta = (\mu_e - E_c)/kT$ is the reduced Fermi energy of the carriers. In pure crystals electroneutrality requires that $n_0 = 2[\mathrm{D}^{++}]$; this relation is satisfied in our specimens since the concentration of aliovalent impurity ions is much smaller than n_0. The dependence of η on n_0 can be determined in principle if the density of states in the conduction band is either known from independent data or can be calculated from a physically acceptable model. In the absence of independent and reliable data, we will have to assume a model for the density of states. From Eq. (3) it follows that an acceptable model must satisfy at least two criteria: It should give a term $A \equiv [\ln(\tfrac{1}{2}n_0) + \tfrac{1}{2}\ln P_a + 2\eta]$ which is independent of n_0 and P_a; secondly, there should be a linear relationship between A and $1/T_a$, the slope being proportional to the standard free energy of reaction (1).

In our attempt to account for the present results we shall begin by making the commonly used assumption of a parabolic conduction band with a density of states $g(E)$ given by

$$g(E) = 4\pi(2m^*/h^2)^{3/2}(E - E_c)^{1/2}, \qquad (4)$$

where m^* is the electron effective mass assumed to be constant. The general expression for the carrier concentration,

$$n_0 = \int g(E)\cdot[1 + \exp(E - \mu_c)/kT]^{-1}\cdot dE, \qquad (5)$$

then reduces to (*10*):

$$n_0 = 2[2\pi m^* kT/h^2]^{3/2}\cdot F_{1/2}(\eta) \equiv N_c F_{1/2}(\eta), \qquad (6)$$

where $F_{1/2}(\eta)$ is the Fermi–Dirac integral of order $\tfrac{1}{2}$.

If in addition we assume that the carrier concentration is nondegenerate, we can make the approximation,

$$F_{1/2}(\eta) \simeq \exp(-\eta). \qquad (7)$$

Substitution of (7) and (6) into (3) shows that at constant temperature the carrier concentration n_0 should be proportional to $P_a^{-1/6}$, since the quantity A, introduced previously, becomes equal to $[2\ln N_c + \ln\tfrac{1}{2} + \tfrac{1}{2}\ln P_a - 3\ln n_0]$. In effect, the model combining both the assumptions of a parabolic conduction band and of nondegeneracy is equivalent to the formalism of the simple mass-action law as applied to Eq. (1).

We have attempted to fit our values of n_0 at constant T_a to a relation of the type $n_0 \propto P^{-1/q}$; at low carrier concentration an approximate fit can be obtained with $q \simeq 6$. However, with increasing carrier concentration the value of q increases; $q \simeq 10$ at the largest experimental values of n_0. It is clear that this simple model, which predicts a constant value of $q = 6$, cannot account satisfactorily for our results. This conclusion is supported by the failure of previous workers (*2*, *11*) to fit CdO conductivity data to a relation of the type $\sigma \propto P_{O_2}^{-1/q}$; these previous attempts gave q values ranging from 6 to 14.

The simple mass-action type model described in the previous paragraph can be easily modified to take proper account of the degeneracy of the electrons by abandoning the approximation of Eq. (7). Using the tabulated values (*10*) of the Fermi–Dirac integral $F_{1/2}(\eta)$, we have calculated the quantity A from our experimental values of n_0 and P_a. However, the calculated values of A failed to satisfy the two criteria enumerated previously. We may, therefore, conclude that a model with a simple parabolic conduction band, as expressed in Eq. (4), with or without degeneracy, cannot properly account for the observed carrier concentrations in CdO.

The principal feature of the simple model, i.e., the assumption of a parabolic conduction band unperturbed by the donor energy levels, may also be the cause of its failure at large donor and carrier concentrations. In most semiconductors the donor energy level is separated by an energy gap from the bottom of the conduction band when the donor concentration is small. With increasing donor concentration this energy gap decreases, resulting eventually in zero donor ionization energy. This process has been observed and interpreted in Germanium (*12*). Results obtained by Altwein et al. (*13*) on the conductivity of Li-doped CdO films lend support to the assumption that it takes place in CdO as well. Their results show that in films with a small donor concentration the conductivity is a temperature-activated process, apparently caused by the ionization of the donors; however, with increasing carrier concentration this ionization energy is found to decrease continuously. We may expect, using a crude hydrogenic model for the donor energy levels, that the ionization energy will become zero when the average distance between donors is approximately equal to the Bohr radius of a conduction electron in CdO. An order-of-magnitude estimate shows that this occurs in CdO at carrier concentrations of 10^{18}–$10^{19}/\mathrm{cm}^3$, in fair agreement with our experimental results. In CdO specimens with large carrier concentrations we may therefore expect that the donor energy levels will be situated at an energy at least equal to E_c, resulting in a density of states at the bottom of the conduction band which will be larger than $g(E)$.

Theoretical considerations, as for example in (*14*), indicate that the number of additional states $g'(E)$, contributed by the donor energy levels to the bottom of the conduction band, is not strictly proportional to the number of donors but increases less rapidly than the donor concentration $[\mathrm{D}^{++}]$. The exact dependence of $g'(E)$ on $[\mathrm{D}^{++}]$ or on the carrier concentration n_0 cannot as yet be calculated from first principles. In our calculations we will assume that all the additional states are at energy E_c, and that the dependence of $g'(E_c)$ on n_0 is given by the relation,

$$g'(E_c) = n_0 \cdot \left(\frac{n_0}{C_0}\right)^{-\alpha} \tag{8}$$

with C_0 and α as adjustable parameters. The dependence of η on n_0 is then given by

$$\begin{aligned} n_0 &= \int \{g(E) + g'(E_c)\} \cdot [1 + \exp(E - \mu_c)/kT]^{-1} \cdot dE \\ &= N_c F_{1/2}(\eta) + \frac{g'(E_c)}{1 + \exp(-\eta)}. \end{aligned} \tag{9}$$

We have calculated the quantity A from our experimental data, using Eqs. (9), (8), and (3); the parameters C_0 and α were adjusted until the calculated values of A satisfied the first criterion enumerated previously, i.e., until A became independent of n_0 and P_a at the temperatures T_a used in the experiments. In these calculations m^* was set equal to $0.14\ m_0$, the value of the effective mass obtained from an analysis (15) of the reflection spectrum of CdO; however, the final values of C_0 and α were found to be rather insensitive to small variations in the value used for m^*. The results of our calculations are shown in Fig. 2b as a plot of A versus $\log(n_0)$ for the parameter values $C_0 = 2.2 \times 10^{18}/\mathrm{cm}^3$ and $\alpha = 0.14$; the lack of dependence of A on n_0 indicates clearly that our model accounts in a satisfactory manner for our experimental results. Further calculations show that the assumption that $g'(E_c)$ is not proportional to n_0 is essential to the success of our model. As an example we show in Fig. 2a the results of a calculation of A for the parameter value $\alpha = 0$; the dependence of A on n_0 in this case shows

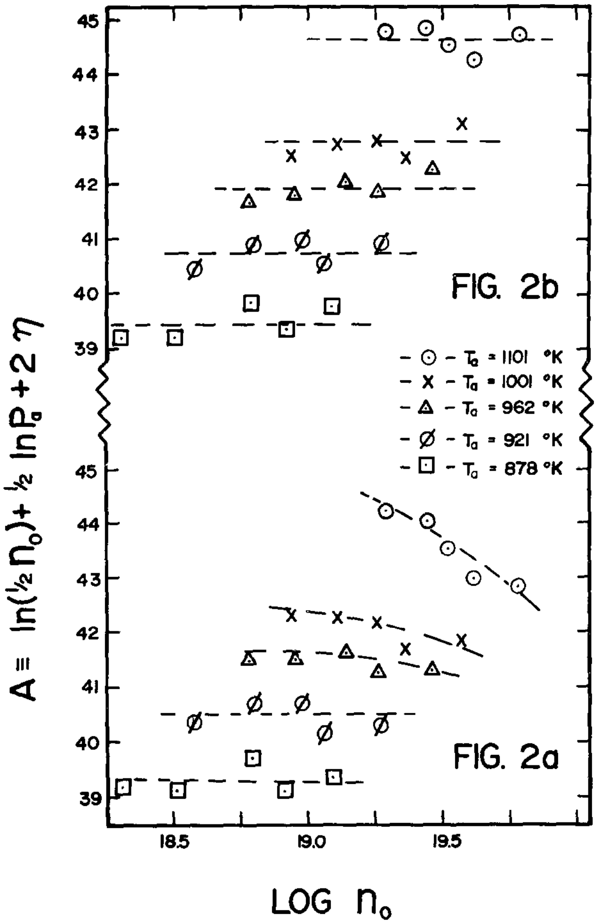

FIG. 2. The quantity $A \equiv [\ln(\frac{1}{2}n_0) + \frac{1}{2}\ln P_a + 2\eta]$ as a function of n_0 calculated from Eqs. (3), (8), and (9), at different equilibrium temperatures T_a, for two sets of parameters: (a) $\alpha = 0$ and (b) $\alpha = -0.14$, $C_0 = 2.2 \times 10^{18}$.

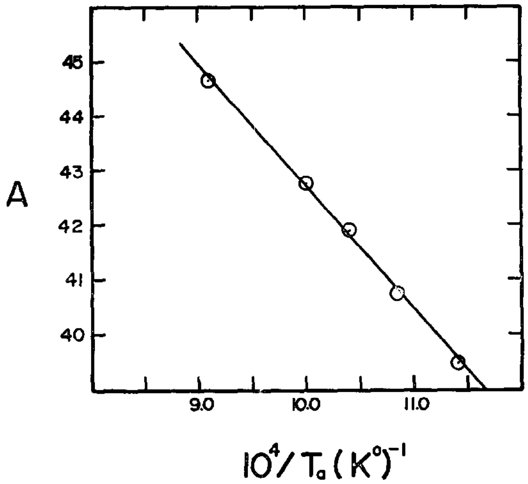

FIG. 3. The quantity $A \equiv [\ln\frac{1}{2}(n_0) + \ln P_a + 2\eta]$ obtained from Fig. 2(b) as a function of the equilibrium temperature T_a.

that the number of additional states $g'(E_c)$ cannot be equal to n_0.

As an additional test of the validity of our model we have plotted the value of A, taken from Fig. 2b, versus $1/T_a$ in Fig. (3); a straight line is obtained giving a value of 1.95 ± 0.08 eV for the standard free energy of reaction (1).

Although our model incorporates qualitatively the main features of the theory of heavily doped semiconductors (*14*), it is obviously oversimplified; the assumption that all the additional states $g'(E)$ are at energy E_c and the use of a constant effective mass m^* cannot be entirely correct. Previous measurements (*15*) of the optical reflectivity of CdO show that the conduction band is highly nonparabolic when the carrier concentration is large; our results are in agreement with this conclusion and show, in addition, that, at least for $n_0 < 5 \times 10^{19}/\mathrm{cm}^3$, the nonparabolicity may be the result of the incorporation of the donor energy levels into the conduction band.

The value of 1.95 eV for the free energy of the defect reaction (1) agrees favorably with the value of 1.8 eV calculated from Hall measurements on polycrystalline CdO (*3*). To our knowledge, the only other quantitative data on the energy of defect formation in CdO are those obtained by Haul and Just (*6*) from oxygen tracer diffusion measurements on CdO powders. In pure CdO they found an activation energy for diffusion $\Delta H_1 = 4.0 \pm 0.17$ eV, whereas in material heavily doped with Li_2O the activation energy was $\Delta H_2 = 2.6 \pm 0.43$ eV. Since the diffusion coefficient at constant temperature was proportional to $P_{O_2}^{-1/6}$ [as calculated by us from Fig. 3 of Ref. (*6*)], the defect active in the diffusion process is probably a doubly charged oxygen vacancy. The energy of formation of this defect would therefore be equal to $3(\Delta H_1 - \Delta H_2) = 4.2 \pm 1.4$ eV. This is twice as large as the energy determined from Hall effect measurements. The disagreement between the values of the defect formation energies obtained from oxygen diffusion and Hall effect measurements strongly suggests that different defects are involved in these two processes; however, the curious fact remains that both measurements give approximately equal defect concentrations at comparable temperatures and presssures. The experimental temperature dependence of n_0 is inconsistent with the assumption that two defects, with considerably different energies of formation, are simultaneously present in our crystals in approximately equal concentrations.

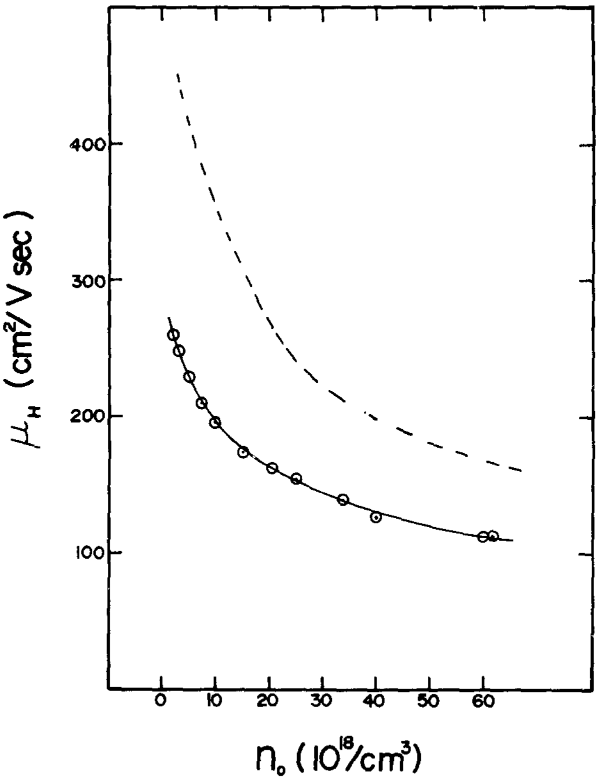

FIG. 4. The variation of the room temperature Hall mobility μ_H with carrier concentration n_0; –o– experimental data; --- calculated from ionized-donor scattering.

However, in view of the uncertainties in the evaluation of diffusion measurements made by the ^{18}O isotopic exchange technique [e.g., ref. (*17*)], the discrepancy between Haul's results and ours may be more apparent than real.

Although the main subject of this paper is a discussion of the carrier concentration, we will include a short preliminary report on the Hall mobilities as well. The room temperature mobilities μ_H are shown in Fig. (4) as a function of n_0; the continuous decrease of mobility with increasing carrier concentration suggests that scattering by the ionized donors may be the dominant process limiting the mobility. We have calculated the mobility assuming that ionized-donor scattering is the only scattering process at room temperature; the result of this calculation is also shown in Fig. (4). Although the calculated mobility decreases with n_0 in a fashion similar to the experimental mobility, it is clear that, in addition to ionized donor scattering, other scattering processes are active as well in our crystals. A detailed analysis will be reported when measurements of the temperature dependence of the mobility are completed.

Note added in proof: Additional evidence, for NMR measurements, for the merging of the donor energy levels with the conduction band in CdO has recently been published by D. C. Look, *Phys. Rev.* **184**, 705 (1969).

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