since the stoichiometric composition may be n- or p-type depending on the Fe-to-Cu ratio. However, for $0.57 \leqslant x \leqslant 0.63$, the stoichiometric composition is close enough to the p-n transition for sulfur annealing to produce p-type samples and vacuum annealing to produce n-type samples.

The magnetic ordering temperatures T_c of some crystals and of as-prepared and annealed powders were measured with a vibrating coil magnetometer in a field of 100 Oe. The T_c values were found by extrapolating, to the temperature axis, the linear portion of the magnetic-moment-vs-temperature curve in the transition region. The data for the powders are shown in Fig. III-5. For the as-prepared and S-annealed samples, there is a strong, linear increase in T_c from $FeCr_2S_4$ to $Fe_{0.5}Co_{0.5}Cr_2S_4$, and a very gradual linear increase from this composition to $CuCr_2S_4$. A similar variation was observed by Haacke and Beegle[7] whose data, which were obtained by the Faraday method in a field of 10 kOe, are also shown in Fig. III-5. Their T_c values are systematically higher than ours. Differences of ~20°C can be attributed to their use of the higher field.

Except for $FeCr_2S_4$, the vacuum-annealed powders (therefore with lower S-to-metal ratios) with $x < 0.5$ have a substantially higher T_c than the as-prepared or S-annealed powders. Powders with $x > 0.5$ show a small decrease in T_c on vacuum annealing. This treatment caused $CuCr_2S_4$ to decompose to $CuCrS_2$ and Cr_2S_3. For all the crystals measured, the T_c values lie 20° to 30° below the line shown in Fig. III-5.

M. D. Banus
A. J. Strauss

C. NON-Γ DONOR LEVELS IN II-VI COMPOUNDS AND THEIR ALLOYS

As reported previously (see p. 28 in Ref. 4), the carrier concentration (n) in n-type CdTe heavily doped with the donor impurities Ga, In, Cl, or Br is strongly decreased by the application of hydrostatic pressure. We concluded from this observation that these impurities introduce donor levels into CdTe that are associated not with the lowest conduction band minimum at Γ (k = 0) but with higher minima. From the pressure dependence of n, we found that at atmospheric pressure these levels are all located above the Γ minimum, with the difference $(E_\Gamma - E_D)$ equal to −0.05 eV for Ga and Cl, −0.19 eV for In, and −0.26 eV for Br. Hysteresis experiments showed that at sufficiently low temperatures the transfer of electrons between the Γ minimum and any of these donor levels becomes too slow in either direction for electronic equilibrium to be achieved experimentally. Thus, the electron transfer is a thermally activated process, which we attributed to the fact that the donor levels are not associated with the Γ minimum.

Another phenomenon that results from the slow rate of electron transfer between the Γ minimum and the non-Γ donors at low temperatures is persistent photoconductivity, which we have observed in experiments at atmospheric pressure on both Cl- and Ga-doped samples. (These experiments are possible because the donor levels of Cl and Ga are so close to the Γ minimum that in heavily doped samples they are partially occupied by electrons at room temperature and below, whereas the In and Br levels are essentially empty at atmospheric pressure.) The results of one such experiment, performed on a Cl-doped sample with $n = 8 \times 10^{17}\ cm^{-3}$ at room temperature, are shown in Fig. III-6. The sample was first rapidly cooled in the dark by immersing it into liquid nitrogen. This caused a small increase in resistivity ρ due to the transfer of additional electrons to the Cl levels. The sample was then exposed to white light from a microscope lamp, which caused a decrease in ρ by exciting the electrons from the Cl levels to the Γ conduction band. When ρ reached a constant value, after the Cl levels were all empty, the lamp was switched off. As long as the sample remained at liquid nitrogen temperature, there was no detectable change in ρ, even for days. Finally, the sample was slowly heated in the dark. At first ρ decreased a little, but beginning at about 160°K it increased sharply until it reached the cooling curve and then slowly decreased again. The increase occurred when the transfer rate became high enough to permit the rapid return of excess electrons from the Γ conduction band to the Cl levels.

Persistent photoconductivity in Cl-doped CdTe has also been observed by MacMillan and Bube,[8] initially for samples which were nominally undoped but had been contaminated with Cl during annealing. In experiments on these samples and on some of our intentionally Cl-doped samples, they have measured the time constant for the decay of photoconductivity between 150° and 190°K, where the time constant changes from about 10^4 to about 1 sec. A plot of time constant on a logarithmic scale against reciprocal absolute temperature gives a straight line whose slope corresponds to an activation energy of 0.50 eV for the transfer of electrons from the Γ conduction band to the Cl donor levels. Extrapolation of this line gives time constants of about 10^{-5} sec at room temperature and about 10^{12} years at liquid nitrogen temperature.

In order to extend our investigation of non-Γ donors in the II-VI compounds, we have measured the effects of hydrostatic pressure and temperature on the resistivity and Hall coefficient of a number of $Cd_{1-x}Mg_xTe$, $Cd_{1-x}Zn_xTe$, and $CdTe_{1-x}Se_x$ alloy samples doped with Cl, Br, or In. The initial experiments have been restricted to alloys with values of x up to about 0.25. Over this composition range, the donor levels introduced by all three impurities are still non-Γ levels, since the carrier concentration at room temperature is strongly decreased by applying pressure. The limited data available indicate that the donor levels are rapidly lowered with respect to the Γ minimum by alloying with MgTe or ZnTe, and are rapidly raised by alloying with CdSe. Thus, the In level is 0.19 eV below the Γ minimum in $Cd_{0.75}Mg_{0.25}Te$, while the Cl level is 0.11 eV below the minimum in $Cd_{0.90}Zn_{0.10}Te$ but 0.17 eV above it in $CdTe_{0.90}Se_{0.10}$. (All the alloy compositions listed are nominal values.) For all samples, hysteresis effects are observed in pressure experiments at sufficiently low temperatures, and persistent photoconductivity is also observed at 77°K for samples in which the donor levels are low enough to be partially populated at that temperature.

Persistent photoconductivity at temperatures below about 125°K is observed[9] in n-type CdS doped with F, due to the slow rate of electron transfer at these temperatures between the Γ conduction-band minimum and a localized level lying 0.09 eV below the Γ minimum. It has been proposed[9] that this level is the second charge state of a double-acceptor center involving F; the double-acceptor model has also been proposed[10] to account for persistent photoconductivity and other phenomena in CdTe that are associated with a level of uncertain origin lying 0.06 eV below the Γ minimum. Alternatively, the observations on F-doped CdS could be explained by identifying the 0.09-eV level as a non-Γ donor level due to F. To investigate this possibility, we have measured the effect of hydrostatic pressure on the carrier concentration of an F-doped sample. The results support the non-Γ donor model, since the carrier concentration decreases by two orders of magnitude between atmospheric pressure and 13 kbars. Application of hydrostatic pressure to F-doped CdSe also results in a strong decrease in carrier concentration, indicating that F introduces a non-Γ donor level here also. The F-level in CdSe lies 0.26 eV above the Γ minimum at atmospheric pressure and 0.20 eV below it at 18 kbars.

G. W. Iseler
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D. OPTICAL REFLECTIVITY STUDIES ON THE METAL-INSULATOR TRANSITION IN $(V_{1-x}Cr_x)_2O_3$

McWhan and Remeika[11] have reported the pressure-temperature-composition phase diagram shown in Fig. III-7 for compositions close to V_2O_3 in the $(V_{1-x}Cr_x)_2O_3$ system. According to this diagram, which is based on electrical resistivity and x-ray diffraction measurements, at atmospheric pressure a first-order metal-to-insulator transition occurs with increasing temperature in a narrow range of compositions (x from about 0.005 to about 0.015). In measurements on single crystals in this composition range, we have observed abrupt changes in optical reflectivity as a function of temperature which are presumably associated with the metal-insulator transition. Such abrupt changes were not observed in previous reflectivity measurements.[12]

Single crystals typically 3 mm in diameter and 4 mm long were grown from the melt in a tri-arc furnace. Measurements on unoriented, mechanically polished samples were made with a split-beam optical system using two PbS detectors which operate over the photon energy range between 0.6 and 2.0 eV.

Two types of reflectivity-vs-temperature behavior were observed. For crystals of V_2O_3 and $(V_{0.998}Cr_{0.002})_2O_3$, the reflectivity decreased continuously with increasing temperature, as shown in Fig. III-8, and did not exhibit hysteresis. A somewhat anomalous variation occurred between 400° and 500°K, in the region of the phase diagram beyond the critical point terminating the metal-insulator phase boundary (see Fig. III-7). For samples with x = 0.005, 0.010, 0.014, and 0.019, however, abrupt and opposite changes in reflectivity were observed at two temperatures differing by as much as 75°K because of hysteresis. A typical reflectivity-vs-temperature curve is shown in Fig. III-9 for the sample with x = 0.014. Presumably, the increase in reflectivity on cooling is associated with the insulator-to-metal transition and the decrease in reflectivity on heating is associated with the reverse transition. The two transition temperatures and their average are listed in Table III-1 and plotted as a function of x in Fig. III-10. In agreement with the phase diagram of McWhan and Remeika,[11] the transition temperatures are in the vicinity of the phase boundary between the metal and insulating phases, and they decrease as the value of x increases. More detailed studies are planned on the relationship between the transition temperatures observed optically and those observed by electrical measurements.

J. Fan†
T. B. Reed
P. M. Raccah

E. IDENTIFICATION OF INTERMEDIATE-SPIN-STATE CATIONS

There are two limiting descriptions of the outer electrons in solids: crystal-field theory and band theory. Crystal-field theory treats the electrons as localized to a specific atomic site, and the localized-electron manifold is treated in lowest order as an ionic state. Localized outer-d-electrons, for example, have a ground-state energy for the d^n configuration that is stabilized

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ratio are sufficient to produce significant changes in a_o, which is reversibly increased by vacuum annealing and decreased by S annealing. Constant values of a_o were obtained by successive vacuum anneals after a total annealing time of 8 to 24 hours. These values can be fit fairly well by a straight line parallel to the Vegard's law line for the as-prepared powders but lying 0.025 Å higher. Presumably this line gives the a_o values for samples with compositions at the metal-rich limit of the homogeneity range for $Fe_{1-x}Cu_xCr_2S_4$. The lower line for the as-prepared powders presumably gives the a_o values for samples with compositions at the sulfur-rich limit of the homogeneity range. However, the a_o values for the transported crystals after sulfur annealing rarely reach this line.

M. D. Banus

E. NON-Γ DONOR LEVELS IN n-TYPE CdTe

The Group III elements Al, Ga and In and the Group VII elements Cl, Br and I are all effective donor impurities in CdTe. We have measured the effects of pressure and temperature on the resistivity and Hall coefficient of CdTe samples heavily doped with these elements. The resistivity values measured at room temperature are plotted on a logarithmic scale in Fig. II-15 as a function of hydrostatic pressure. Except for the samples containing Al and I, the resistivity increases markedly with increasing pressure. Hall coefficient measurements under pressure have shown that this increase in resistivity ρ is due almost entirely to a decrease in carrier concentration n, not to a decrease in mobility. The strongest effects are observed for the Cl-doped samples. Results in quantitative agreement with these have been reported by Foyt, Halsted and Paul[9] for nominally undoped samples of CdTe; we believe that these samples actually contained Cl.

Similar changes in carrier concentration with pressure have been observed for n-type samples of GaAs, GaSb and $GaAs_{1-x}P_x$ alloys.[10] They are generally attributed to the transfer of electrons from the lowest conduction band minimum at Γ into donor levels associated with higher minima, as these minima and therefore the donor levels are lowered relative to the Γ minimum by the application of pressure. Adopting this same explanation for the present results, we conclude that Cl, Br, Ga and In all introduce non-Γ donor levels into CdTe.

For each of these dopants, we have used the carrier concentrations measured in the pressure experiments to calculate the difference in energy between the donor level and the Γ minimum as a function of pressure. The differences are plotted as a function of pressure in Fig. II-16. For each impurity, the points can be very well represented by a straight line. The slopes of the four lines are similar, but those for Cl and Br are somewhat higher than those for Ga and In. Extrapolation of the lines to the ordinate gives the following values for the positions of the donor levels at atmospheric pressure: Ga, −0.05; Cl, −0.05; In, −0.19; and Br, −0.26 eV. The minus signs mean that each of the donor levels lies above the Γ minimum at atmospheric pressure.

No significant decrease in carrier concentration can be produced by pressure until the donor level is sufficiently close to the Fermi level. This suggests that we failed to observe pressure effects in samples doped with Al or I because these impurities introduce non-Γ levels located so far above the Γ minimum that the maximum pressure we used was too low to reduce the carrier concentration. Alternatively, the donor levels due to these impurities might be associated with the Γ minimum. There is no way to distinguish between these possibilities on the basis of our data.

In several cases the donor energy levels calculated from the room temperature data have been compared with ionization energies obtained by measuring the carrier concentration at various fixed pressures as a function of temperature. The results of these measurements on a Cl-doped sample are shown in Fig. II-17. At the two higher pressures, where the Cl donor level is below the Γ minimum, as the temperature is reduced below room temperature the carrier concentration initially decreases sharply as the electrons are transferred into the Cl levels. The ionization energies calculated from the data in this region are in good agreement with the values obtained from the room temperature measurements.

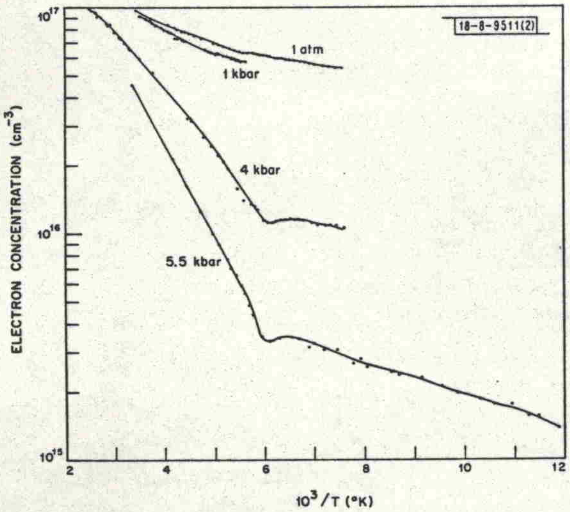

Fig. II-17. Carrier concentration vs reciprocal absolute temperature for Cl-doped CdTe at fixed hydrostatic pressures.

At about 160° to 170° K, the two higher pressure curves exhibit an abrupt decrease in slope. On the basis of our earlier study of S donors in GaSb,[11] we believed that this change in slope was probably due to a decrease in the rate of electron transfer sufficient to prevent equilibrium from being achieved between the conduction band and the Cl levels at low temperatures. This hypothesis was confirmed by two hysteresis experiments in which resistivity measurements were made as a function of temperature on a Cl-doped sample (1) cooled rapidly to 77° K at 4 kbar and then warmed slowly to room temperature at the same pressure, and (2) cooled rapidly to 77° K at 4 kbar and then warmed slowly to room temperature after the pressure had been reduced to 2 kbar.

Similar hysteresis phenomena have been observed in our pressure-temperature experiments on CdTe samples heavily doped with Br, Ga and In and also in transport and photoconductivity measurements on S-doped GaSb[11] and $GaAs_{1-x}P_x$.[12] In each of these cases, as well as in Cl-doped CdTe, the time constant for electron transfer between the donor levels and the Γ minimum increases strongly as the temperature decreases. Pressure experiments show that the donor levels are associated with higher conduction band minima. This correlation leads us to conclude that there is a causal relationship here – that is, the fact that electron transfer in these materials is a thermally activated process is a consequence of the fact that the donor levels involved are not associated with the Γ minimum.

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Bull. Amer. Phys. Soc. 16, 435 (1971)

HC 9 1/f Noise from Surface Interface and Oxide Trap States on Oxidized Silicon.* H.S.FU and C.T.SAH, Univ. Illinois, Urbana. -- A 1/f noise model including the SRH and the tunneling processes in epitaxial channel MOS transistor is developed. The interface states and the oxide trap states are generated using oxygen heat treatment techniques during device fabrication under reproducible and controlled conditions. Oxide trap concentrations are obtained from the C-V data at different frequencies. The theoretical noise power calculated using the experimental oxide trap concentrations agrees very well with the experimental noise data. Correspondence between the humps of the 1/f noise and the humps of the interface states and oxide trap states are obtained. The slopes of the frequency spectra of the noise power depend strongly on the oxide trap concentration profile. A linear relationship between the 1/f noise power and the fixed oxide charge density is also observed, indicating a linear dependence of the fixed oxide charge density on the chargeable oxide trap state density.

*Work supported in part by AFOSR and ARPA.

HC 10 Low Temperature Irradiations of p-type Silicon with 1 MeV Electrons*. N. D. Wilsey, Naval Research Laboratory. -- Silicon n/p solar cells have been irradiated over the temperature range from 90°K to 300°K to fluences of 10^{15} e/cm^2. The degradation of minority carrier lifetime in the base region of the cells was determined through measurements of minority carrier diffusion length. From the temperature dependence of the diffusion length, it is shown that the degradation of minority carrier lifetime in p-type silicon occurs primarily through an irradiation temperature independent (ITI) recombination center with an energy level at $E_v + 0.24$. This information is used to explain the temperature dependence of the photovoltaic parameters of irradiated silicon solar cells.[1]

*Work supported in part by the NASA Ames Research Center.

[1]R. J. Debs and N. R. Hanes, Conference Record of the Eighth IEEE Photovoltaic Specialists Conference, 155 (1970), N. D. Wilsey and R. J. Lambert, Ibid., 169.

THURSDAY AFTERNOON, 1 APRIL 1971 (D. R. FRANKEL presiding) OHIO ROOM AT 2:00 P.M.

Semiconductor Impurities

HD 1
Theory of Donor-Acceptor Pairing in Elmental Semiconductors. J.B.R. Franco*, M. Schoijet, Centro de Investigación y de Estudios Avanzados del I.P.N., Ap. Postal 14-740, México 14, D.F.--- A theory of pairing for donor-acceptor pairs with different states of charge in elemental semiconductors has been developed. A law of mass action for charged pairs

$$N_{OO}N_{-+}/N_{O+}N_{-O} = \exp\,(E_q/kT)$$

has been obtained, where E_q is the Coulombic interaction energy between positive donor and negative acceptor at nearest neighbor lattice sites.

* With a scholarship of the Instituto Nacional de la Investigación Científica.

HD 2 Effect of Hydrostatic Pressure on Electrical Properties of n-Type CdTe.* G. W. ISELER, J. A. KAFALAS and A. J. STRAUSS, Lincoln Lab., M.I.T. --Room temperature resistivity (ρ) measurements have been made at pressures up to 15 kbar on n-type CdTe samples with carrier concentrations ($n_{300°K}$) of 10^{15}-10^{18} cm^{-3}. For a sample heavily doped with Cl ($n_{300°K} = 8.6 \times 10^{17}$ cm^{-3}), ρ increases by a factor of 10^3 between 1 atm and 15 kbar, with $d \log \rho/dP = 0.22$ kbar^{-1} above 4 kbar. Hall coefficient measurements on this sample between atmospheric pressure and 7 kbar show that the electron mobility decreases by less than 50% over this range. For samples less heavily doped with Cl, the curves of ρ vs. P are initially much less steep, but eventually coincide with the one for the most heavily doped sample. These results are quantitatively the same as those previously reported[1] for nominally undoped samples. For samples doped with Br, I, Al, Ga, or In, pressure has much less effect on ρ.

*This work was sponsored by the Department of the Air Force.
[1]A. G. Foyt, R. E. Halsted, and W. Paul, Phys. Rev. Letters 16, 55 (1966).

HD 3 Kinetics of Electron Transfer in n-Type CdTe.* A. J. STRAUSS, G. W. ISELER, and J. A. KAFALAS, Lincoln Lab., M.I.T. --The increase in resistivity (ρ) between 300 and 77°K has been measured at fixed hydrostatic pressures up to 7 kbar for n-type CdTe samples doped with Cl. With increasing pressure $d \log \rho/d(1/T)$ increases, as expected if the increase in ρ at 300°K with increasing pressure (preceding Abstract) is due to transfer of electrons from the conduction band to a donor level associated with a higher-lying band.[1] For samples with $n_{300°K} \gtrsim 7 \times 10^{16}$ cm^{-3}, below 150°K the time constant for this process at high pressure becomes extremely long and persistent photoconductivity is observed at 1 atm. Persistent photoconductivity is also observed for samples doped with Br, I, Al, Ga, or In, but only below about 100°K. These results indicate that the hole traps recently reported[2] in nominally undoped n-type CdTe are due to Cl.

*This work was sponsored by the Department of the Air Force.
[1]A. G. Foyt, R. E. Halsted, and W. Paul, Phys. Rev. Letters 16, 55 (1966).
[2]H. F. Macmillan and R. H. Bube, Bull. Am. Phys. Soc. 15, 1615 (1970).

HD 4 Investigation of Shallow Acceptor States in Semiconductors.* A. BALDERESCHI and N. O. LIPARI, Univ. of Illinois.--Using angular momentum techniques, the effective mass theory for shallow acceptor states is reformulated in a simple way and a meaningful classification of these states is obtained. The eigenvalue problem is reduced[1] to simple radial hamiltonians which are solved for the lowest acceptor states. The energies