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Electrical and Optical Properties of Rare Earth Doped Cadmium Fluoride Single Crystals

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Single crystals of CdF_2 have been doped with all rare earth elements and with Y, Sc, and U. Firing these crystals in a Cd atmosphere or under vacuum at 500° produced samples having electronic, n-type conductivity for all the dopants except La, Ce, Pr, Eu, and U. The temperature dependences of the resistivity, Hall coefficient, and mobility were similar for all crystals containing conductivity-producing dopants and were similar to the temperature dependences expected for impurity conduction. Optical absorption measurements indicated that no divalent rare earth ions (except Eu^{+2}) and no U^{+3} ions were present in the crystals either before or after heat treatment. Absorption studies on all the conducting crystals showed essentially identical infrared absorption that increased in intensity with wave length and that decreased in intensity between 300 and 77°K. but not between 77 and 6°K. Yellow to yellow-green phosphorescent and thermoluminescent radiation was observed and was very similar for all the unfired crystals containing conductivity-producing dopants. Chemical oxidation potentials were used to explain the existence of M^{+3} and U^{+4} ions and the absence of M^{+2} (except Eu^{+2}) and U^{+3} ions both in the untreated and in the Cd treated samples. The presence of ions in either the +2 or the +4 oxidation state was used to explain the absence of conductivity in some of the doped crystals. The following model for the conductivity and the associated infrared absorption is proposed. The impurity states giving rise to conduction are formed by the sharing of one electron among the twelve Cd nearest neighbors to the substituted M^{+3} dopant. The associated optical absorption is caused by charge transfer between these cadmium "impurity" states.

Introduction

Recently Prener and Kingsley[2,3] showed that CdF_2 doped with certain rare earth elements or with yttrium became an electronic conductor when treated in cadmium vapor at elevated temperatures. The conducting crystals were colored blue. The color was caused by an optical absorption whose absorption coefficient varied as $\lambda^{3.0}$ or $\lambda^{3.5}$ depending on dopant concentrations[2] and was explained by free-electron absorption[2] or transitions between the donor and conduction band states.[4] A mechanism for the production of conductivity was proposed[2,3] in which Cd atoms react with the charge-compensating F^- interstitial ions, which diffuse to the crystal surface, forming more CdF_2 and releasing electrons that are bound weakly to the trivalent dopant ions, giving rise to a hydrogenic donor level[4] and n-type conductivity. The diffusion of the interstitial F^- to the surface should, most probably, increase the symmetry of the crystal field at the substituted trivalent ion site, making it cubic.

This paper reports further experiments on doped CdF_2 crystals that exhibit electronic conductivity, a very interesting and unusual behavior for such an ionic material. Studies were made on Bridgman-grown single crystals, doped at the 0.1 mole % level, both before and after firing in cadmium vapor. Optical absorption spectra were run at 300, 77, and 6°K. for various dopants, and the visible fluorescent, phosphorescent, and thermoluminescent emissions, under 2537 and 3660 Å. excitation, were observed visually. Electrical data, conductivity and Hall effect, were taken at 300 and 77°K. and also as a function of temperature for selected samples.

Experimental

Starting Materials.—CdF_2 was prepared by a method similar to that of Rubenstein and Banks.[5] Reagent grade $CdCO_3$ was dissolved in aqueous ammonia and the fluoride precipitated and boiled repeatedly with concentrated aqueous hydrofluoric acid. The dried powder was then melted in a platinum crucible in a flowing argon atmosphere.[6] This material yielded crystals that generally showed evidence of a slight impurity as indicated by a shoulder on the ultraviolet absorption edge around 2800 Å. This absorption was removed after three or four crystallizations or zone passes in zone refining runs. Ultimately the absorption spectrum was similar to that of Prener and Kingsley.[6] However, the results reported here were obtained on crystals that generally had some absorption in the 2800 Å. region.

Dopants were added to the CdF_2 as the metal trifluorides in all cases except two in which Sc_2O_3 and Y_2O_3 were used. No pretreatment procedures were used on any of the dopant materials, which were generally slightly hydrated.

Crystal Growth.—Single crystals were grown using a Bridgman–Stockbarger technique similar to that previously described for CaF_2.[7] A graphite crucible was lowered through the furnace at about 10 mm./hr. in a flowing argon atmosphere. The grown crystals were about 10 mm. in diameter and 10 to 50 mm. long. No segregation of any of the rare earth elements, yttrium, scandium, or uranium was detectable either visually or through the optical and electrical studies reported below. This implied segregation coefficient (the ratio of the concentration in the solid to the concentration in the liquid) of near unity is true for all dopants at least to the 1 mole % level and probably higher.

Heat Treatment.—Two methods of heat treatment were found to yield conductivity in the CdF_2:M^{+3} crystals. The first was firing in cadmium vapor.[2] The crystal and a piece of high purity cadmium metal were heated at 500° for 1 hr. in a sealed, evacuated (about 10^{-6} mm. pressure) quartz tube. Identical conditions were used in the second method except that no cadmium metal was used. In each case the clear, colorless crystals turned

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[1] Department of Chemistry, State University College, Fredonia, N. Y.

[2] J. D. Kingsley and J. S. Prener, *Phys. Rev. Letters*, **8**, 315 (1962).

[3] J. S. Prener and J. D. Kingsley, *J. Chem. Phys.*, **38**, 667 (1963).

[4] J. S. Prener and H. H. Woodbury, "Physics of Semiconductors, Proceedings, 7th International Conference," Paris, 1964, p. 1231.

[5] M. Rubenstein and E. Banks, *J. Electrochem. Soc.*, **106**, 404 (1959).

[6] J. S. Prener and J. D. Kingsley, *J. Chem. Phys.*, **35**, 2256 (1961).

[7] P. F. Weller and J. E. Scardefield, *J. Electrochem. Soc.*, **111**, 1009 (1964).

TABLE I

VALUES FOR THE RESISTIVITY, HALL COEFFICIENT, CARRIER CONCENTRATION, AND HALL MOBILITY AT 300 AND 77°K. FOR SEVERAL DOPED CdF_2 CRYSTALS

Sample no.	Dopant (0.1 mole %)	ρ, ohm cm. 300°K.	ρ, ohm cm. 77°K.	$-R_H$, cm.^{3}/coulomb (300°K.)	n, e$^-$/cm.^{3} (300°K.)	μ_H, cm.^{2}/v. sec. (300°K.)
55	TbF_3	2.70	935.	11.	6.0×10^{17}	3.5
22	ErF_3	0.745	75.8	4.8	1.3×10^{18}	6.8
41	YbF_3	0.144	4.76	1.8	3.5×10^{18}	13.
60	YF_3	0.177	2.17	1.4	4.3×10^{18}	8.3
60V	YF_3	0.480	20.2	3.1	2.0×10^{18}	6.5
102	Y_2O_3	0.186	3.20	1.4	4.5×10^{18}	7.5
103	Sc_2O_3	0.167	2.38	1.8	3.5×10^{18}	10.

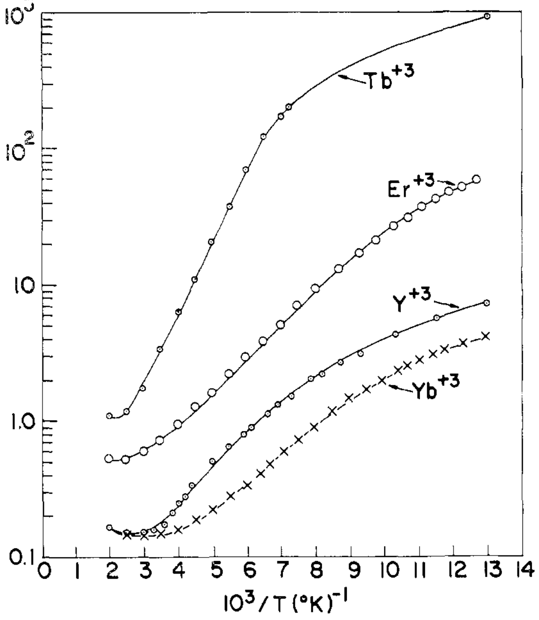

Figure 1.—Log ρ *vs.* $10^3/T$ for CdF_2 single crystals doped with 0.1 mole % TbF_3, ErF_3, YbF_3, and YF_3.

a deep blue after just a few minutes at 500°. The "vacuum only" treatment seemed to be slightly less effective as is indicated by the resistivity and carrier concentrations for samples 60 and 60V in Table I. Since no free cadmium was detected in the "vacuum only" runs, it seems likely that fluorine was pumped from the crystal. The interstitial fluoride, charge-compensating, ions are prime candidates for removal. This seems to be more supporting evidence for the mechanism proposed[3] for the "cadmium fired" case.

Conductivity and Hall Effect.—The conductivity and Hall effect were measured using standard direct current techniques and apparatus[8] between 77 and 600°K. Samples were cut ultrasonically giving an eight-armed Hall "spider." The soldered indium metal contacts were ohmic at room temperature and generally gave slightly nonlinear *I–V* characteristics at 77°K. Even though the contacts appeared to be reasonably good, the measurements at the lower temperatures were often subject to drift and noise. Measurements above 300°K. encountered different difficulties. A running pressure of about 10^{-3} mm. was used. After completing the run (from 77 to 600°K.) a surface film was always present and the crystal bulk was changed as evidenced by a lightening or disappearance of the blue color. Other experiments have shown that either a pressure of less than 10^{-5} mm. or an inert atmosphere that is considerably more pure than that generally obtained commercially is needed to prevent this behavior. A high vacuum, however, might lead to cadmium and/or fluorine removal which could continually change the observed properties.

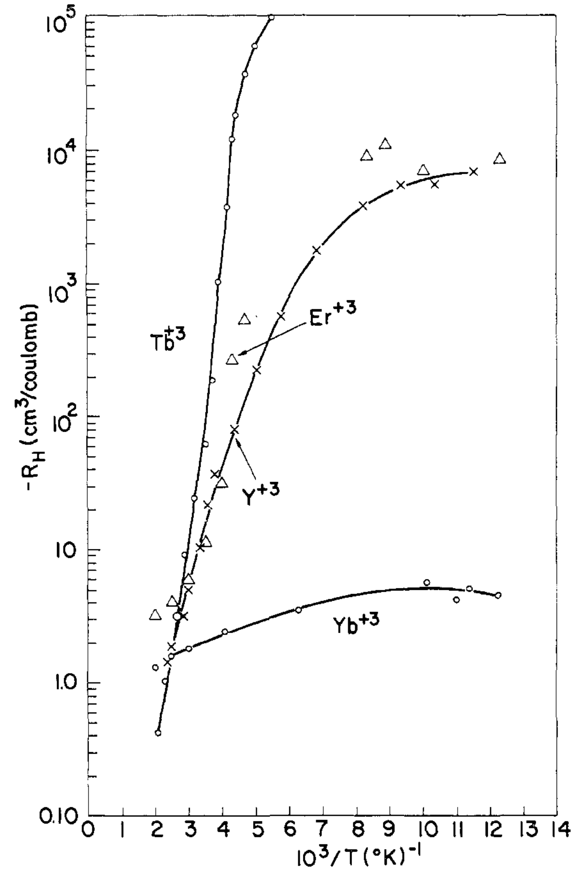

Figure 2.—Log (Hall coefficient) *vs.* $10^3/T$ for the samples shown in Figure 1.

All of the CdF_2 crystals measured were doped at the 0.1 mole % level. It was found that the dopants fell into two distinct groups. One group composed of Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc yielded crystals with a room temperature, n-type resistivity of about 1 ohm cm. The other group composed of La, Ce, Pr, Eu, and U yielded crystals with a room temperature resistivity of about 10^7 ohm cm., similar to that of "pure" CdF_2. The electrical properties observed for crystals containing dopants of the first group were very similar as is shown in Table I and Figures 1–3. Figure 1 shows the increase and subsequent leveling off of the resistivity with decreasing temperature. Figure 2 shows the apparent maximum of the Hall coefficient with changing temperature. Figure 3 shows the decrease in mobility at low temperatures. These electrical characteristics all strongly indicate impurity conduction (impurity banding). From the slope of the log ρ *vs.* $1/T$ curve for Tb^{+3} in Figure 1 a donor activation energy, E_D, of 0.10 e.v. can be calculated. This value is similar to that reported by Prener and Woodbury[4] for Yb^{+3} doping.

Optical Absorption Spectra.—Absorption spectra of selected samples before and after heat treatment were run on a Cary

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[8] See, for example, E. H. Putley, "The Hall Effect and Related Phenomena," Butterworths, London, 1960, Chapter 2.

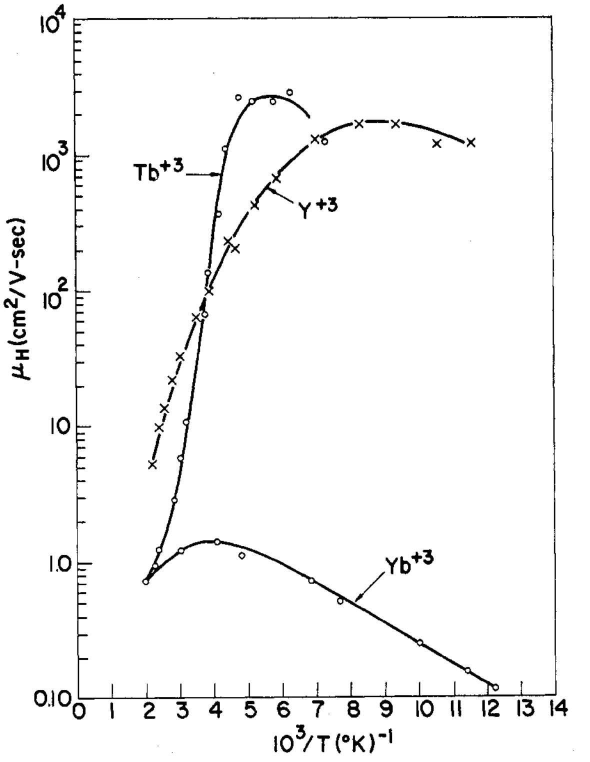

Figure 3.—Log (Hall mobility) *vs.* $10^3/T$ for the samples shown in Figures 1 and 2.

Model 14 spectrophotometer at 300, 77, and 6°K. Two specific problems were investigated. The first was a study of the effect of Cd firing on the symmetry of the crystal field at the site of the various M^{+3} ions. The second was a study of the relation between the intense infrared absorption of the conducting crystals and free carrier absorption.

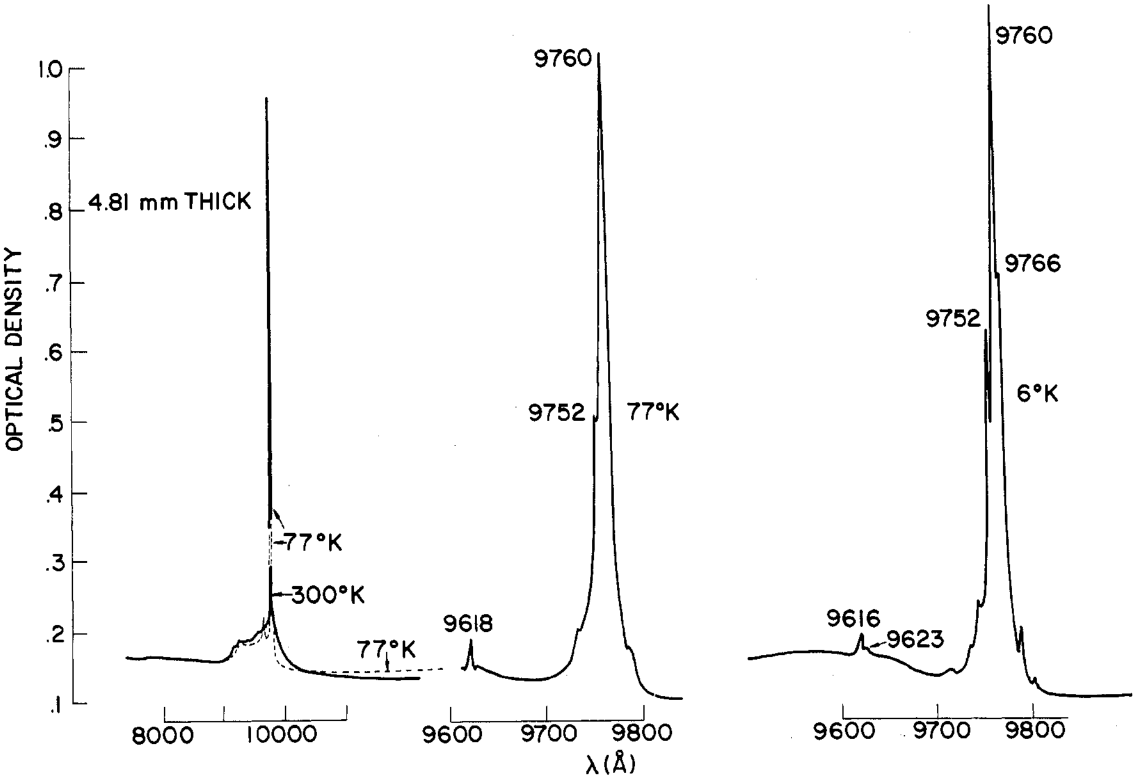

Figure 4.—Absorption spectrum for no. 10 CdF_2:0.1 mole % YbF_3 single crystal at 300, 77, and 6°K.

The first problem is illustrated in Figure 4, which shows the absorption spectrum of Yb^{+3} in CdF_2 at 300, 77, and 6°K. before Cd firing. After the sample was Cd fired, the Yb^{+3} spectrum was superimposed on the rapidly rising infrared absorption of the conducting crystal and was rather difficult to study. Consequently, resolution was not as good as in the unfired sample. It did appear, however, that the main absorption peak in the Cd fired crystal was asymmetric and was split in a similar fashion to the peak before Cd firing. There did not seem to be any large differences in the Yb^{+3} absorption spectra in the before and after Cd fired samples.

Similar results were found for Pr^{+3} and Er^{+3} doped CdF_2. The absorption spectra before and after Cd firing showed no observable differences. Detection of any changes with Er doping was difficult since all of the Er absorption coefficients were quite small.

These absorption results on untreated and Cd treated Yb, Pr, and Er doped crystals indicate no observable changes in the dopant crystal field symmetries upon Cd firing. In the case of Pr this is not too surprising since conductivity is not produced and, consequently, not many interstitial F^- ions are removed. If, however, conduction does depend on interstitial F^- removal, as seems to be the case,[3] then some change in the very peculiar Yb^{+3} spectrum (only one strong absorption line) shown in Figure 4 was expected upon Cd firing since about 10% of the Yb^{+3} ions present were uncompensated. It might be that the resolution in the Cd fired sample was not good enough to detect a change, say in the ratio of intensities of the 9620 and 9760 Å. lines, caused by only 10% of the ions present.

The second problem above was considered by studying the temperature dependence of the intense infrared absorption of the conducting crystals (absorption coefficient variation approximately λ^3).[2] There was a decrease in absorption of about a factor of four in going from 300 to 77°K. The curves at 77 and 6°K., however, were superimposable. There was an increase in resistivity of about a factor of 30 in going from 300 to 77°K. The resistivity at 4°K., however, was very high, as indicated by e.p.r.

TABLE II

VISIBLE FLUORESCENCE, PHOSPHORESCENCE, AND THERMOLUMINESCENCE UNDER 2537 Å. EXCITATION OBSERVED VISUALLY FOR CRYSTALS OF CdF_2:0.1 MOLE % MF_3[a]

Dopant	Fluorescence 300°K.	Fluorescence 77°K.	Phosphorescence 300°K.	Phosphorescence 77°K.	Thermo-luminescence 77 → 300°K.
La	s yellow	s yellow	s yellow	s yellow-orange	s yellow
La + Cd_v	s yellow	s yellow	s yellow	s yellow-orange	s yellow
Ce	None	None	None	None	vw green
Ce + Cd_v	None	None	None	None	vw green
Pr	w pink	w pink	Yellow-green	Yellow-pink	w yellow-green
Pr + Cd_v	w pink	w pink	None	Pink	w yellow-green
Eu	s pink	s pink	Yellow	Bluish white	Yellow
Eu + Cd_v	s pink	s pink	None	None	Yellow
Tb	s yellow-green	s yellow-green	s yellow-green	s yellow-green	s yellow-green
Tb + Cd_v	None	None	None	None	None
Er	w pink	w pink	Green	Yellow	s yellow-green
Er + Cd_v	None	None	None	None	None
Yb	w pink	w pink	Yellow-green	Yellow-green	w yellow-green
Yb + Cd_v	None	None	None	None	None
Y	w pink	w pink	Yellow-green	Yellow-green	w yellow-green
Y + Cd_v	None	None	None	None	None
U	None	None	None	None	None
U + Cd_v	None	None	None	None	None

[a] The entry labeled + Cd_v gives the results after treating the crystals in cadmium vapor at 500°. Very weak, weak, and strong are denoted by vw, w, and s, respectively.

measurements. Since the samples had high resistivity at 4°K. and the infrared absorption was still very strong, it seems probable that the absorption is not caused by free electrons. Further indication of this is given by CdF_2:In^{+3} samples[9] which are very dark red but have an infrared spectrum similar to the blue crystals, which are conducting at room temperature but not at 77°K. and which have *increasing* absorption with decreasing temperature.

Visible Fluorescence, Phosphorescence, and Thermoluminescence.—The visible fluorescent, phosphorescent, and thermoluminescent emissions under 2537 and 3660 Å. excitation from low-pressure mercury pen lamps were observed visually. The 3660 Å. line gave fairly strong fluorescence only with the Sm and Eu doped samples, phosphorescence (yellow to green) only with Eu, and thermoluminescence (yellow to green) only with Tb, Er, Yb, Lu, and Sc.

The visible fluorescent, phosphorescent, and thermoluminescent emissions of the doped CdF_2 crystals listed in Table II for 2537 Å. excitation are interesting since the dopants fall into categories that appear to be the same as the ones described above for the electrical properties. La, Ce, Pr, Eu, and U showed much different emission characteristics than did the other rare earth dopants. The lifetime of the Eu phosphorescence was much longer than those of any of the other crystals, the order of several minutes. La showed strong yellow emission that did not change upon Cd firing. Ce and U gave essentially no visible emissions. Pr was quite similar to the "conducting ions" but did show some phosphorescence and thermoluminescence after Cd treatment.

On the other hand, all of the conductivity-producing dopants gave very similar emission properties, yellow to yellow-green phosphorescence and thermoluminescence, both of which were quenched upon Cd firing. All of the phosphorescence lifetimes were several seconds and were longer at 77°K. than at 300°K.

Discussion

Doping Experiments.—It has been suggested[7] that chemical oxidation potentials are of use in deciding what chemical species will be present when dopants are added to a highly ionic solid. Investigation of these potentials[10] shows that rare earth metals and divalent rare earth ions (RE^{+2}), except Eu^{+2}, are very good reducing agents. In contrast cadmium is a poor reducing agent. In this context, it was suggested[7] that RE^{+2} ions (Eu^{+2} excepted) could not be obtained in any but ionic solids of highly electropositive elements, such as alkali and alkaline earth halides. CdF_2, therefore, can be doped with RE^{+3} and possibly RE^{+4} ions, but with the exception of Eu^{+2}, no measurable concentration of any RE^{+2} ion can be obtained.

In order to verify this idea, CdF_2 crystals were doped with all of the rare earth trifluorides, and with YF_3, ScF_3, and UF_3. Except for Eu and U dopants, only trivalent ions were observed by optical absorption or e.p.r. measurements in the untreated crystals. In the case of Eu an equilibrium concentration of Eu^{+2} and Eu^{+3} existed. E.p.r. studies indicated a Eu^{+2} concentration of about 10^{17} cc.$^{-1}$ with 0.1 mole % total Eu (about 3×10^{19} Eu/cc.). With U, however, only the U^{+4} ion was found to be present. No trace of U^{+3} was indicated as is seen in the absorption spectrum in Figure 5. The very intense visible and infrared absorption bands of U^{+3} are completely absent.[11] A few very weak bands were found in the visible centered around 4300, 4460, 4650, 5300, and 6400–6600 Å. Three very strong bands occurred in the ultraviolet at 2450, 2530, and 2610 Å.

An explanation of the behavior of Eu and U dopants can be given by considering the oxidation potentials for the reactions

$$2U^{+3} + Cd^{+2} \rightleftarrows 2U^{+4} + Cd \qquad (1)$$

$$2Eu^{+3} + Cd \rightleftarrows 2Eu^{+2} + Cd^{+2} \qquad (2)$$

The aqueous potentials[10] give values of $E°_U = 0.217$ and $E°_{Eu} = -0.027$ v. for the standard oxidation potentials for the reactions as written. The equilibrium

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(9) P. F. Weller, to be published.

(10) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(11) See, for example, R. S. Title, P. P. Sorokin, M. J. Stevenson, G. D. Pettit, J. E. Scardefield, and J. R. Lankard, *Phys. Rev.*, **128**, 62 (1962).

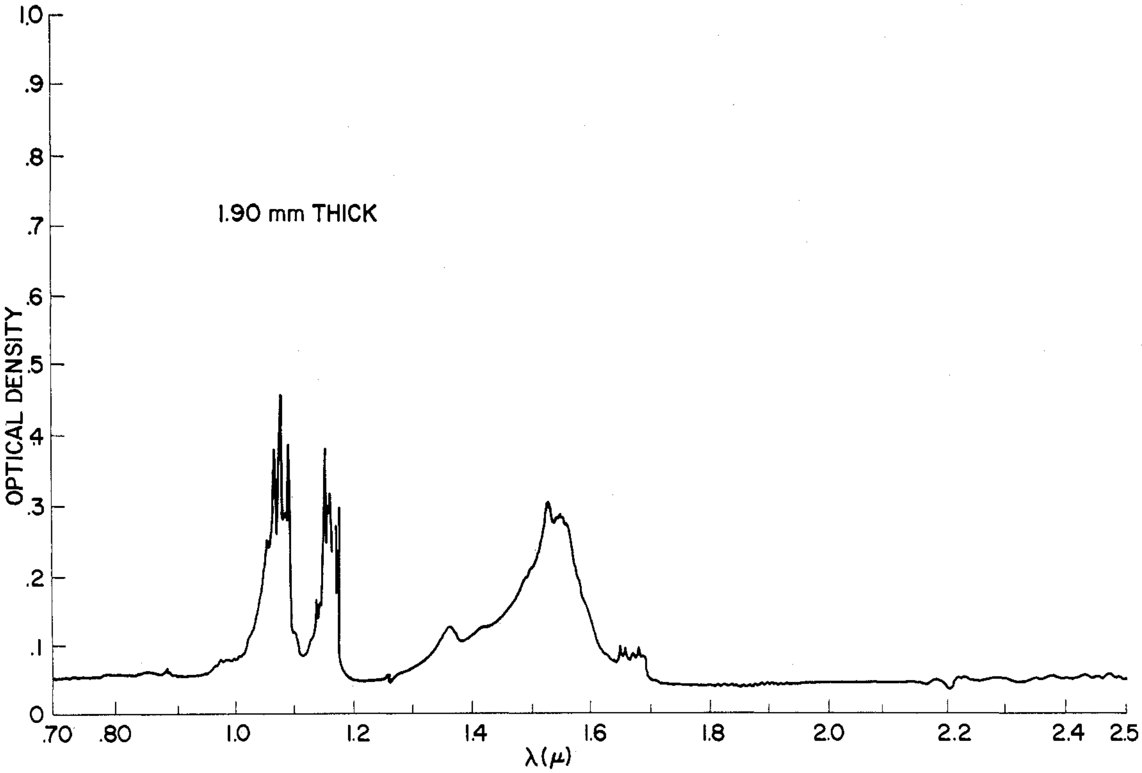

Figure 5.—Absorption spectrum of CdF_2:0.1 mole % U^{+4} at 77°K. Note the absence of any lines, indicative of U^{+3}, in the 1.8–2.5 μ region.

concentration of U^{+3} will be very small while the concentration of Eu^{+2} will be somewhat larger than that of U^{+3} but still smaller than that of Eu^{+3}.

Attempts were made to reduce the trivalent dopants and U^{+4} by heating in a cadmium atmosphere, by solid state electrolysis, and by ultraviolet and X-ray irradiation. γ-Ray irradiation has also been used.[12] The cadmium firings gave blue, conducting crystals, except for La, Ce, Pr, Eu, and U doping, while the other treatments had little or no effect. No RE^{+2} or U^{+3} ions could be detected optically or paramagnetically in the treated crystals except for Eu^{+2}. The Eu^{+2} concentration increased about one order of magnitude upon Cd firing.

These experimental observations and the above oxidation potential arguments indicate two things: (1) The application of chemical oxidation potentials (even the aqueous values which neglect complexing in the fused salt) in predicting what chemical species will exist in doped, highly ionic solids has validity. (2) RE^{+2} ions that can be detected optically or paramagnetically are not obtainable in CdF_2 (except for Eu^{+2}).

Semiconducting or Insulating Crystals.—As noted above, Cd fired CdF_2:M^{+3} crystals can be either semiconductors or insulators. One important characteristic of the dopants that do not yield conducting crystals seems to be the tendency to form oxidation states other than +3. Europium is the most clear-cut case. It has been indicated above, and previously,[2] that Eu^{+2} is formed in CdF_2, particularly after Cd firing. Instead of the electrons being released to the lattice (conduction band) by the Cd treatment, they are simply trapped by the Eu^{+3} ion. It can be thought of as a chemical reduction as in eq. 2 or, possibly more correctly, as

$$2Eu^{+3} + 2F^- + Cd \rightleftarrows 2Eu^{+2} + CdF_2 \quad (3)$$

where the $2F^-$ ions indicate the interstitial ions necessary for charge compensation. The Eu, then, forms a trapping or "deep donor" level. The level does not seem to be too deep, however, since the Eu doped samples are also blue while they are held above about 300° in a Cd atmosphere.

Nonconduction in the U doped samples might also be expected. It was indicated above that only U^{+4} exists in CdF_2. That Cd fired samples, then, are not conducting is caused by the presence of U^{+4} ions. A probable charge compensation mechanism is that of two interstitial fluoride ions, possibly nearest neighbors to the U^{+4}. The removal of these F^- interstitials is necessary for conductivity (to uncompensate the U^{+4}, *i.e.*, to release the charge-compensating electrons to the lattice rather than having them localized at an interstitial fluorine). However, the energy required to remove the F^- ion from the U^{+4} will be greater than that for the case of a M^{+3} dopant, *i.e.*, the U^{+4}–F^- binding energy is greater since the U has an effective charge of +2. This is, in effect, saying that Cd metal is not a strong enough reducing agent to reduce U^{+4} to U^{+3} as is shown in eq. 1.

That La, Ce, and Pr do not yield conductivity in Cd fired CdF_2 is not as easily explained. Several reasons can be considered, no one of which is completely satis-

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[12] H. A. Weakliem, Project Defender Report No. NONR-4133(00) ARPA No. 306-62 (Aug. 20, 1964).

factory. The first factor is the possible presence of Ce^{+4} and Pr^{+4}. (Tb might also be expected to show a Tb^{+4} oxidation state, although it is generally less stable than Ce^{+4} and Pr^{+4}. As is seen in Table I and Figure 1, Tb doped samples do produce conductivity in CdF_2. This conductivity, however, is less than that obtained with the other rare earths.) The presence of these +4 oxidation states would have the same effect as that described above for U^{+4}. A second factor is the tendency of La, Ce, and Pr to show higher coordination in their REF_3 compounds than do the other rare earths—except Nd. This would indicate a stronger attraction for the charge-compensating, interstitial F^- and consequently reduced tendency for conduction. It seems, then, that La^{+3} might not yield conductivity since it is too large and prefers a high coordination number whereas Ce and Pr, while preferring higher coordination, might also form M^{+4} ions.

The Donor Level and Associated Properties.—When a Cd atom and an interstitial F^- ion react at the CdF_2 surface[3] and form more CdF_2, an electron is generated (two electrons per CdF_2 molecule). This electron can either be localized, as it is in the case of Eu^{+2} described above, or it can be donated to the entire lattice and give rise to electronic conductivity. It is proposed that the donor levels in Cd fired $CdF_2{:}M^{+3}$ crystals are formed by the sharing of the generated electron by the 12 Cd nearest neighbors to the substituted M^{+3}. This allows for a "resonance" stabilized Cd^+ state. Depending on the number of these states, either a shallow donor level is formed (about 0.10 e.v.), since there is a local perturbation on the conduction band, or, as the number of the states increase, impurity conduction becomes important since tunneling or "hopping" of electrons becomes more favorable. This would account for the differences observed in the behaviors of the resistivity, Hall coefficient, and mobility with temperature for the various dopants, Tb^{+3} and Yb^{+3}, for example. In the case of Tb^{+3} the overlap between "impurity" states is not as great as it is for Yb^{+3} and impurity conduction becomes important at much lower temperatures, as is evidenced by the almost immediate decrease in μ_H with temperature for Yb^{+3} doping.

The strong infrared absorption associated with the conduction can then be explained on the basis of charge transfer between these Cd "impurity" states. The charge transfer might be visualized, for example, as a transfer of an electron from one "Cd^+—M^{+3}—Cd^{+2}" complex to another with the formation of a "Cd^+—M^{+3}—Cd^+" excited state. An increase in the number of "impurity" centers would increase the infrared absorption.

The phosphorescent and thermoluminescent behavior of the crystals can also be related to these Cd "impurity" states. Before Cd firing, all of the crystals containing conductivity-producing dopants exhibit yellow to yellow-green phosphorescent and thermoluminescent emission under 2537 Å. (4.9 e.v.) excitation but not under 3660 Å. (3.4 e.v.) excitation. The following process is proposed. An electron is excited from the F^- interstitial charge compensator into the conduction band by the incident ultraviolet radiation. This locates the F^- interstitial level between 3.4 and 4.9 e.v. below the conduction band edge. The excited electrons then undergo nonradiative decay into the "impurity" centers where they are trapped until a F atom can recapture the electron. The yellow to yellow-green phosphorescent emission would be associated with electron capture by the diffusing F atom and subsequent regeneration of the F^- interstitial ion. The thermoluminescent emission can be regarded in the same way. At 77°K. the diffusion of the F atom is too slow to permit rapid recapture of the excited electron. Hence, the emission upon warming and the very long phosphorescent lifetimes at 77°K. After Cd firing the emissions were quenched in the conducting samples. This would be expected since the "impurity" levels would be partially filled (particularly at 77°K.) and there would be fewer F^- interstitial charge compensators present.

Any disruption of the "resonance" effect among the 12 nearest neighbor Cd ions would destroy the possibility for electronic conductivity and, concurrently, the associated infrared absorption. These disruptions could come about in several ways: (1) The presence of M^{+3} ions such as La, Ce, and Pr whose tendency toward higher coordination indicates a more tightly bound charge compensator, such as an interstitial F^-. The presence of M^{+4} ions, as with U^{+4} and possibly Ce^{+4} and Pr^{+4}, makes the F^- interstitial even harder to remove. (2) The presence of a chemical species with a relatively large attraction for an electron, such as Eu^{+3}. The electron would then be trapped at the Eu^{+3} forming an Eu^{+2} ion rather than shared by the neighboring Cd^{+2} ions. (3) The replacement of one of the 12 Cd ions by a different M^{+2} or M^{+3} ion.

Conclusions

(1) The presence of certain chemical species in highly ionic solids can be predicted on the basis of chemical oxidation potentials. For example, no RE^{+2} ions except Eu^{+2} can exist in CdF_2 nor can CdF_2 be doped with U^{+3}.

(2) Electronic, n-type conductivity is produced in CdF_2 crystals doped with Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc by Cd or vacuum firing at 500° but not with La, Ce, Pr, Eu, or U doping. Room temperature resistivities are all around 1 ohm cm., electron concentrations around 10^{18} e^-/cc., and mobilities about 10 cm.^{2}/v. sec. in the conducting crystals.

(3) That certain dopants do not yield conductivity can be explained on the basis of unwanted oxidation states, as with Eu^{+2} or U^{+4}, or on the basis of an ion with a tendency toward high coordination, as with La^{+3}, Ce^{+3}, and Pr^{+3}.

(4) The temperature dependences of the resistivity, Hall coefficient, and mobility indicate impurity conduction.

(5) The intense infrared absorption of the Cd or vacuum treated samples (yielding blue crystals) decreases between 300 and 77°K. but is identical at 77 and 6°K. It is essentially the same for all conductivity-producing dopants.

(6) The visible phosphorescence and thermoluminescence are very similar with all conductivity-producing dopants. They are both yellow to yellow-green, and the phosphorescent lifetimes are of the order of seconds.

(7) The electron-donor levels and impurity conduction levels can be associated with an electron shared by the 12 Cd nearest neighbors to the substituted M^{+3}. Then charge transfer between the Cd "impurity" levels can account for the intense infrared absorption observed in the conducting crystals.

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Mössbauer Spectra of Tin Dithiolates[1a]

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The Mössbauer spectra of several compounds of Sn(IV) with 1,2-ethanedithiolate (EDT) and 3,4-toluenedithiolate (TDT) were measured. Evidence was obtained for a nontetrahedral configuration for $Sn(EDT)_2$ and a polymeric structure for $Sn(TDT)_2$. The mixed compounds of dimethyl- and diphenyltin(IV) with EDT and TDT show large quadrupole splittings. The formation of an adduct, for example with pyridine or 1,10-phenanthroline, which increases the coordination number of the tin, in all cases results in a more negative isomer shift, indicating a lower s electron density on the tin. EDT and TDT form equally covalent bonds with Sn(IV). Methyl tin compounds have larger quadrupole splittings than the corresponding phenyl compounds.

Introduction

A number of compounds containing Sn(IV) combined with a 1,2-dithiol were examined using Mössbauer spectroscopy. One of our objectives was a comparison of the two bis(dithiolates), $Sn(EDT)_2$ and $Sn(TDT)_2$, where EDT indicates the 1,2-ethanedithiolate anion, $^{-}SC_2H_4S^{-}$, and TDT indicates the 3,4-toluenedithiolate anion, $CH_3C_6H_3S_2{}^{2-}$. The latter tin compound has two unusual properties: a bright red color (useful for analytical purposes[2,3]) and very low solubility in any nonreacting solvent. These properties have been attributed to a polymeric structure achieved *via* intermolecular bonding by bridging sulfur atoms, giving tin a coordination number of six.[4] It was our purpose to clarify further the nature of the bonding to tin in this compound. In the course of this work a number of other compounds containing EDT or TDT along with various other ligands were examined.

The Mössbauer absorption spectra of all the compounds studied are simple doublets. The splitting, Δ, is due to a nuclear quadrupole interaction and is thus a direct measure of the electric field gradient at the tin nucleus or, in qualitative terms, a measure of the deviation of the surrounding electron cloud from cubic symmetry. The average line position, δ, also called the center, or isomer, shift is a measure of the s electron density at the tin nucleus. All numerical values of δ and Δ are given in velocity units, mm./sec. The source used in this work was Mg_2Sn at room temperature, and all δ values are referred to it.

The isomer shifts of tin compounds cover a range of over 4 mm./sec. At the positive end of the range are the ionic Sn(II) salts, the tin having about two s electrons (*i.e.*, $5s^2$), and at the negative end the ionic Sn(IV) salts. (Positive velocity, corresponding in tin to large s electron density, means the source and absorber are approaching each other.) In about the center of the range is gray tin which has four completely covalent sp^3 bonds, corresponding roughly to one s electron, there being some 5p shielding. (We ignore in this discussion the first four electron shells which constitute a core essentially unaffected by bond formation.) In Mg_2Sn the tin has a slightly lower electron density than gray tin. For comparison, the closest approximation to a bare Sn^{4+} core occurs in SnF_4, which is about 2.4 mm./sec. negative with respect to Mg_2Sn. Covalent compounds of four-coordinated tin, such as SnI_4, $SnBr_4$, and $Sn(C_6H_5)_4$, fall in the range 0.1 to 0.5 mm./sec. negative with respect to Mg_2Sn.

In this paper we will be concerned mostly with δ values between 0.4 and 1.0 mm./sec. negative with respect to Mg_2Sn, corresponding to essentially covalent

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