Pressure study of the crystal-field splitting of Co²⁺ in CdTe

J. Gardavský,* A. Werner, and H. D. Hochheimer

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 16 June 1981)

Pressure-induced changes of the crystal-field splitting of Co^{2+} in CdTe have been studied using optical-absorption measurements in the infrared region (0.25–1.35 eV). Hydrostatic pressure in the range from 0 to 11 GPa was generated in a diamond anvil cell. The phase transition at 3.3 GPa from the ZnS to NaCl structure is accompanied by a change of the gap energy from about 1.4 eV to less than 0.25 eV. The gap does not increase to values larger than 0.25 eV up to 11 GPa, where a second phase transition to a white tin structure occurs. The pressure shift of the transitions between the crystal-field-split electronic energy levels of Co^{2+} [$^4A_2(^4F)$ $-^4T_1(^4F)$, $^4A_2(^4F) - ^4T_2(^4F)$, and $^4A_2(^4F) - ^4T_1(^4P)$] in the ZnS structure are discussed with respect to changes of the interatomic distances and of the ionicity of the CdTe host crystal with pressure.

I. INTRODUCTION

Crystal-field theory (CFT) has proven to be a useful theoretical framework for the understanding of optical-absorption spectra as well as of the emission spectra due to electronic transitions between the localized energy levels of transition-metal impurities in crystal hosts.[1] Pressure-dependent effects, both on the absorption[2,3] and emission bands[4] can be described by the changes of the crystal-field parameter Dq, and of the Racah parameters B and C.[3] Especially the emission spectra of the compound $Al_2O_3:Cr^{3+}$ (ruby) are of great interest, as the linear pressure dependence of the R_1 ruby fluorescence allows the use of ruby as a pressure calibrant in optical high-pressure diamond anvils.[5,6] The linear shift of the emission bands as a function of pressure is also observed for impurity ions in Al_2O_3 which are isoelectronic to Cr^{3+}. This linear shift seems to be connected with the fact that in these compounds no phase transitions are impending. Munro[3] has shown that within the framework of CFT this linear frequency shift can be explained by a scaling theory, under the assumption that the scaling factors are essentially properties of the host. In this paper we study how the occurrence of a phase transition in the host influences the frequency shift of the impurity bands, and to what extent, if at all, a linear scaling theory can be applied below and near a phase transition.

As a candidate for such a study we choose CdTe, which at room temperature undergoes a phase transition from the ZnS to the NaCl structure at about 3.3 GPa,[7] changing the symmetry from T_d to O_h. Cobalt ions, substituting for cadmium in cadmium chalcogenide host lattices, provide a convenient transition-metal ion impurity, as suggested also by other types of external- and internal-field measurements like electroabsorption[8] and uniaxial stress effects.[9]

Our measurements show that $\Delta(Dq)$ as a function of pressure is strongly nonlinear. We can explain this nonlinearity by a change of the Phillip's ionicity with pressure. The measurement of the pressure dependence of the crystal-field splitting in $CdTe:Co^{2+}$ thus provides a tool to study the pressure dependence of the Phillip's ionicity.

II. EXPERIMENTAL

Crystals of $CdTe:Co^{2+}$ have been prepared by the directional freezing method.[10] The doping element was added to the initial compounds in metallic form (purity 99.999%). The concentration ratio of Co^{2+} to Cd^{2+} determined by chemical analysis and by comparison of calculated and measured oscillator strengths is of the order of 10^{-5}. Pressure was generated in a high-pressure diamond cell. An inconel gasket 120 μm thick with a 200-μm aperture served as the pressure chamber. As samples we used about 60-μm-thick pieces cleaved along the planes (110) with a diameter of about 100 μm. The free space between the sample and the border of the gasket hole was filled with fine CdTe powder. The usual 1:4 ethanol-methanol mixture was used as pressure medium and the pressure generated was measured by the well-known ruby fluorescence technique.[5]

The absorption spectra were taken at room temperature in the region of 0.25 to 1.35 eV using a 100-W halogen lamp, a Jobin Yvon 0.6-m monochromator with gratings 300 to 600 g/mm, and cooled InSb detector (ORP-13, VALVO). The monochromatized light was focused by a Beck mirror objective on the sample in the diamond anvil cell. The light intensity

transmitted by the sample in the cell was then imaged on the entrance slit of the detector.

III. RESULTS

Figure 1 shows results for the absorption coefficient α at room temperature as a function of the photon energy, with the sample outside the diamond anvil cell. The appearance as well as the relative positions of the three bands agree with group-theoretical predictions assuming a local T_d symmetry of Co^{2+}. This strongly supports the idea that Co^{2+} is a substitutional impurity. As an insert we have drawn α at 0 and 2.23 GPa taken with the sample inside the diamond anvil cell. We see that the bands broaden considerably due to the fact that we had to work with large slit widths to get a reasonable intensity of the bands. To clarify the origin and the notation of the bands we have added the scheme of the crystal-field splitting of the ^4F ground state as well as the first excited ^4P state of Co^{2+}. The transition $^4A_2$-$^4T_2$ (O^4F) is orbitally forbidden and therefore very weak. The band due to the transition $^4A_2$-$^4T_1$ (^4P) appears on the tail of the direct absorption edge (energy gap 1.4 eV). Taking the spectra of the sample in the diamond anvil cell the $^4T_1$ (^4P) band could not be resolved, and therefore the corresponding spectral region has been omitted in Fig. 1. Nevertheless it was possible to obtain the pressure shift of this band by determining the shift of its low-energy side in the interval of 1.30–1.35 eV. From spectra like those shown in Fig. 1 we have determined ΔE of the three bands as function of pressure as shown in Fig. 2.

FIG. 2. Observed pressure shifts of the absorption bands of $CdTe:Co^{2+}$. In addition, the pressure dependence of ΔE_i is transformed to a R (Co^{2+}-Te^{2-} distance) dependence using our high-pressure x-ray data.

The statistical error in ΔE is about ± 5 meV and is indicated in Fig. 2. To convert the pressure dependence of ΔE to one of the interatomic distance R, we have measured the lattice constant of $CdTe:Co^{2+}$ as function of pressure (Fig. 3) using an energy dispersive x-ray diffraction method and a diamond anvil cell. In the zinc sulfide structure R is connected to the lattice parameter a by $R = \sqrt{3}/4a$.

Above the phase transition from the zinc sulfide to the NaCl structure at about 3.3 GPa it turned out that the value of the direct energy gap is smaller than 0.25 eV. The gap does not increase to a value larger than 0.25 eV up to a pressure of 11 GPa where a second phase transition to a white tin structure occurs. The small energy gap prevents the measurement of the absorption bands in the NaCl structure. To check the possibility of destruction of the sample the pressure
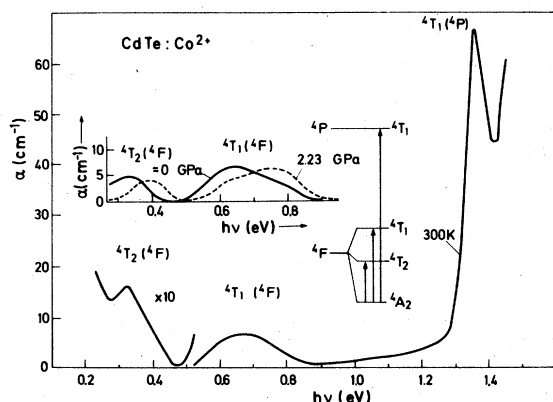

FIG. 1. Absorption coefficient α as function of the photon energy $h\nu$ at zero pressure. The transitions between crystal-field-split levels of Co^{2+} in CdTe responsible for the bands are displayed schematically in the figure. The inset shows the same spectrum taken at nearly zero pressure (solid line) and 2.23 GPa (dashed line) with the sample inside a diamond anvil cell.
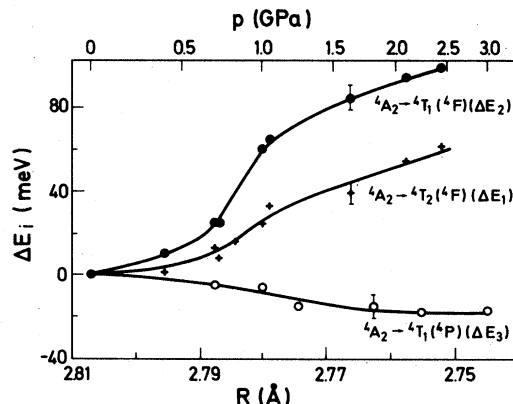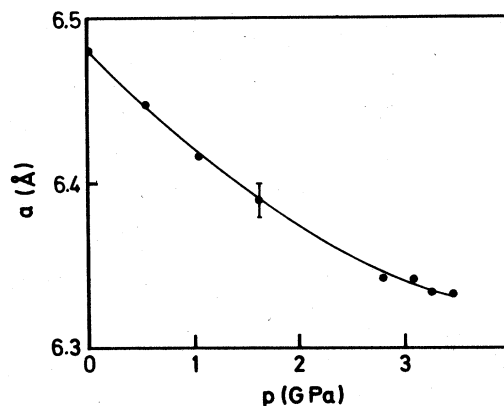

FIG. 3. Lattice constant of CdTe as function of pressure. The distance R is given by $R = \sqrt{3}/4a$ for a ZnS structure.

was released below 3 GPa, where the absorption bands could again be observed.

IV. DATA ANALYSIS AND DISCUSSION

Co^{2+} has the electronic configuration of argon and in addition seven electrons in the $3d$ state $(3d^7)$. According to Hund's rule the ground state is a $^4F_{9/2}$ state, i.e., a state which has an orbital degeneracy of 7. Group theory predicts that the orbital degeneracy will be partially lifted under the crystal field of T_d symmetry and that the ^4F state splits into a $^4A_2$, $^4T_2$, and $^4T_1$ state (see Fig. 1). The first ^4P excited state of Co^{2+} does not split and transforms like the representation $^4T_1$. The number 4 indicates the spin degeneracy $(2S+1)$ which is not lifted by the crystal field. Sugano, Tanabe, and Kamimura[1] have shown that the band positions of the three transitions shown in Fig. 1 are connected with the CFT parameter Dq and with the Racah parameter B as follows

$$E_1 = E(^4A_2(^4F) \rightarrow {}^4T_2(^4F)) = 10Dq \quad , \qquad (1)$$

$$E_2 = E(^4A_2(^4F) \rightarrow {}^4T_1(^4F))$$
$$= \tfrac{3}{2}(10Dq) + \tfrac{15}{2}B - \tfrac{1}{2}b \quad , \qquad (2)$$

$$E_3 = (^4A_2(^4F) \rightarrow {}^4T_1(^4P))$$
$$= \tfrac{3}{2}(10Dq) + \tfrac{15}{2}B + \tfrac{1}{2}b \quad , \qquad (3)$$

with the term interaction parameter between $^4T_1(^4F)$ and $^4T_1(^4P)$

$$b = [(10Dq - 9B)^2 + 144B^2]^{1/2} \quad .$$

Taking the total differential of Eqs. (1)–(3) leads to

$$\Delta E_1 = 10\Delta(Dq) \quad , \qquad (4)$$

$$\Delta E_2 = \left[15 - 5\frac{10Dq - 9B}{b} \right] \Delta(Dq)$$
$$+ \left[7.5 + \frac{18}{4}\frac{10Dq - 9B}{b} - 72\frac{B}{b} \right] \Delta B \quad , \quad (5)$$

$$\Delta E_3 = \left[15 + 5\frac{10Dq - 9B}{b} \right] \Delta(Dq)$$
$$+ \left[7.5 - \frac{18}{4}\frac{10Dq - 9B}{b} + 72\frac{B}{b} \right] \Delta B \quad . \quad (6)$$

Equation (4) connects directly the shift of the first absorption band $[A_2(F) \rightarrow T_2(F)]$ with the change of the crystal-field parameter Dq. Adding Eqs. (5) and (6) finally yields an expression for the change of the Racah parameter B,

$$\Delta B = \tfrac{1}{15}(\Delta E_2 + \Delta E_3 - 3\Delta E_1) \quad . \qquad (7)$$

Using the measured values of $\Delta E_i (i = 1, 2, 3)$ (Fig.

2) and Eqs. (4) and (7) we have calculated the pressure induced changes of Dq and B plotted in Fig. 4. We can see that ΔB is decreasing with decreasing lattice constant, indicating an increase of covalency of the impurity-host interaction with increasing pressure, which is in good agreement with the CFT[3] and experimental results by Stephens and Drickamer.[11]

The behavior of $\Delta(Dq)$ as function of ΔR is shown in detail once more in Fig. 5. Applying Munro's scaling theory[3] in the simple linear approximation does not reproduce the experimental curve. Instead of fitting the experimental data by including higher order terms in the expansion of Munro's scaling parameter[3] as a function of p, we have pursued an idea of Hennel.[12] He has pointed out that for a number of transition-metal impurities in $A_{III}B_V$ and $A_{II}B_{VI}$ semiconductors, there exists an empirical linear relation between $10Dq = \Delta$ and the crystal ionicity f_i expressed in Phillip's scale.[13] Therefore we consider Dq not only as function of R but also as function of f_i

$$Dq(R, f_i) = Dq(R, 0) - f_i[Dq(R, 0) - Dq(R, 1)] \quad . \qquad (8)$$

The total differential of $Dq(R, f_i)$ is given by

$$\Delta(Dq(R, f_i)) = \left[\frac{\partial Dq(R, f_i)}{\partial R} \right]_{f_i = f_{i0}}$$
$$\times \Delta R + \left[\frac{\partial Dq(R, f_i)}{\partial f_i} \right]_{R = R_0} \Delta f_i \quad , \quad (9)$$

with constant f_{i0} and R_0 where the index zero refers to zero pressure. Using Eq. (8) and the fact that $Dq(R)$ is proportional to R^{-5} (see Ref. 1) to calculate $\partial Dq/\partial R$ and $\partial Dq/\partial f_i$ we get for the change of the Phillip's ionicity f_i as a function of ΔR the fol-
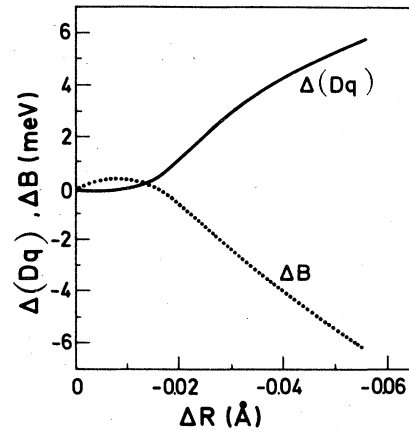

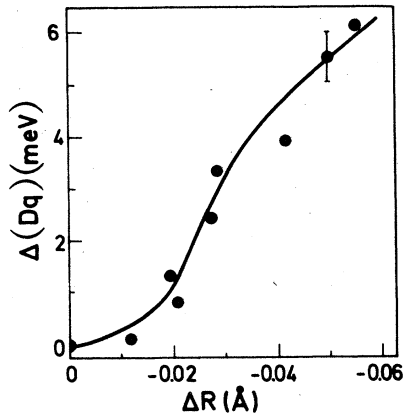FIG. 4. Change of the crystal-field theory parameter Dq and of the Racah parameter B with ΔR.

FIG. 5. Change of the crystal-field parameter Dq as function of ΔR. The solid line is visual aid and no fit to the data.

FIG. 6. Change of the Phillips ionicity f_i of CdTe:Co^{2+} with ΔR. The solid line is a visual aid and no fit to the data. The dashed straight line is calculated using the assumption (Ref. 14) $\partial C/\partial R = 0$. C is the ionic contribution to the E_g, the energy gap between bonding and antibonding states (see Ref. 13).

lowing expression

$$\Delta f_i = \frac{[\Delta(Dq(R,f_i)) - (5/R_0)Dq(R_0,f_{i0})\Delta R]}{[Dq(R_0,0) - Dq(R_0,1)]} \quad (10)$$

Taking the values for $[Dq(R_0,0) - Dq(R_0,1)]$ $= 52.95$ meV from Hennel[12] and $Dq(R_0,f_{i0}) = 34$ meV from our zero-pressure measurement as well as our values of $\Delta(Dq(R,f_i))$ at various pressures, we obtain Δf_i as function of ΔR shown in Fig. 6.

For pressures above 0.5 GPa the ionicity is decreasing with pressure. This behavior is expected from the increase of the covalency, indicated by the pressure dependence of ΔB. A small ionicity increase between 0 and 0.5 GPa may correlate with a red shift of the optical band gap, followed then by a blue shift at higher pressures.[14]

In order to test the assumption of Camphausen et al.[15] that $\partial C/\partial R = 0$ for pure CdTe also in the case of CdTe:Co^{2+} we use the definition of f_i as well as the R dependence of the homopolar gap E_h given in Ref. 13 to calculate Δf_i with the restriction $\partial C/\partial R = 0$

$$f_i = \frac{C^2}{C^2 + E_h^2} \quad , \quad (11)$$

$$E_h \sim R^{-2.5} \quad . \quad (12)$$

Here C is the ionic contribution to E_g, the energy gap[13] between bonding and antibonding states $E_g^2 = E_h^2 + C^2$. Differentiation of Eqs. (11) and (12) and using $\partial C/\partial R = 0$ yields

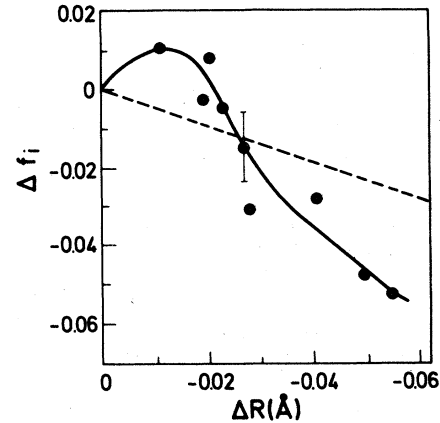$$\Delta f_i = f_i(1 - f_i)5\frac{\Delta R}{R} \quad (13)$$

shown as dashed line in Fig. 6. Obviously the assumption of $\partial C/\partial R = 0$ is not valid.

V. SUMMARY

We have shown that the measurement of the pressure shift of the crystal-field splitting of Co^{2+} in CdTe allows one to calculate the change of the Phillip's ionicity f_i with pressure without information about the pressure dependence of the low-frequency limit of the real part of the electronic dielectric constant. Usually this information is obtained by Kramers-Kronig transformation of the absorptive part $[\epsilon_2(\omega)]$ of the complex dielectric function. However, this method requires an excellent photometric accuracy, which is difficult to obtain in high-pressure experiments. Furthermore, we find that the ionic contribution C to the energy gap E_g is pressure dependent.

ACKNOWLEDGMENTS

*On leave from the Institute of Physics of the Charles University Prague, 12116 Praha 2, Czechoslovakia.

[1] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).

[2] C. S. Kelley, J. Chem. Phys. 59, 5737 (1973).

[3] R. G. Munro, J. Chem. Phys. 67, 3146 (1977), and references therein.

[4] D. Curie, D. E. Berry, and F. Williams, J. Lumin. 18/19, 823 (1979), and references therein.

[5] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. 46, 2774 (1975).

[6] H. E. King, Jr., and Ch. T. Prewitt, Rev. Sci. Instrum. 51, 1037 (1980).

[7] A. Onodera, Rev. Phys. Chem. Jpn. 39, 18 (1969).

[8] J. Gardavský and R. Boyn, Phys. Status Solidi (b) 68, 575 (1975).

[9] G. Ruszczynski and R. Boyn, Phys. Status Solidi (b) 67, K127 (1975).

[10] M. Popova and P. Polivka, Czech. J. Phys. B 23, 110 (1973).

[11] D. R. Stephens and H. G. Drickamer, J. Chem. Phys. 34, 937 (1961).

[12] A. M. Hennel, Phys. Status Solidi (b) 72, K9 (1975), and references therein.

[13] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[14] A. L. Edwards and H. G. Drickamer, Phys. Rev. 122, 1149 (1961).

[15] D. L. Camphausen, G. A. Neville Connell, and W. Paul, Phys. Rev. Lett. 26, 184 (1971).