Spin-orbit coupling effects in $CdGa_2Se_4:Co^{2+}$ single crystals

Chang-Dae Kim,* Tong-San Cho, Jae-Kuen Kim, and Wha-Tek Kim
Department of Physics, Chonnam National University, Kwangju 505, Korea

Hong-Lee Park
Department of Physics, Yonsei University, Seoul 120, Korea

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Single crystals of $CdGa_2Se_4:Co^{2+}$ were grown by the chemical transport reaction method using iodine as a transporting medium. The optical absorption peaks observed at 4132, 4332, 5970, 6329, 12 903, and 13 793 cm^{-1} at 292 K can be explained in terms of the electronic transitions of Co^{2+} ion in S_4 symmetry. The crystal-field parameter Dq and the Racah parameter B were found to be 413 and 455 cm^{-1}, respectively. Also the absorption spectrum of $CdGa_2Se_4:Co^{2+}$ single crystals obtained at 77 K in the 700–800-nm region was analyzed using S_4 symmetry along with spin-orbit coupling effects.

$CdGa_2Se_4$ is a tetrahedrally coordinated semiconductor crystallizing in the defect chalcopyrite structure. Its space group is $S_4^2(I\bar{4})$. It is known as an ordered-vacancy compound having one-quarter of the cation sites unoccupied.[1] The structure of $CdGa_2Se_4$ can be considered as a three-dimensional (3D) superstructure of zinc blende, i.e., doubling of the zinc-blende unit cell along the c axis results in the $CdGa_2Se_4$ structure. Much attention has been paid to $CdGa_2Se_4$ and its optical properties. Abdullaev *et al.*[2] reported the band-gap transitions in the fundamental absorption edge region. Optical absorption studies were done by Kshirsagar and Sinha.[3] Photoconductivity,[4] photoluminescence,[5] and Raman scattering[6–8] have been studied in $CdGa_2Se_4$. However, there exists no published results to date about the optical properties of $CdGa_2Se_4$ doped with transition metals.

In this Brief Report we are going to present results on the crystal growth of $CdGa_2Se_4:Co^{2+}$ single crystals and its optical properties. In particular, the splittings of the highest energy level (^4A and ^4E) of the Co^{2+} ion in S_4 symmetry are analyzed in terms of the spin-orbit coupling effects in the $CdGa_2Se_4$ host.

Single crystals of $CdGa_2Se_4:Co^{2+}$ were grown by the chemical transport reaction (CTR) method using iodine as a transporting medium. The charged ampoule was evacuated at $\sim 1\times10^{-6}$ mm Hg, and the sealed ampoule was placed into a two-zone furnace at temperatures 750 to 900 °C. The single crystals of $CdGa_2Se_4:Co^{2+}$ grown had a lamella habit and an average size of $4\times3\times1.5$ mm^3. The crystal structure determined by x-ray diffraction analysis is a chalcopyrite structure with lattice constants $a=5.762$ Å, $c=10.833$ Å, which are in good agreement with the results obtained by Kshirsagar *et al.*[3] For optical measurements, the crystals of $CdGa_2Se_4:Co^{2+}$ were washed with ethyl alcohol in order to remove the iodine that has been physisorbed on the surface of the crystals. The absorption spectra were obtained with a VIS-NIR spectrophotometer (Shimadzu MPS-5000) in the 700–2500-nm range and a monochromator (Jarrel Ash, $f=\frac{1}{2}m$) in the 650–850-nm range. A cryogenic system (Air Products, CSA-202B) was used for low-temperature measurements.

The optical absorption spectrum of the Co-doped $CdGa_2Se_4$ single crystals at 292 K in the near-infrared region is shown in Fig. 1. We observed six absorption peaks with energies 4132, 4332, 5970, 6329, 12 903, and 13 793 cm^{-1} in the absorption regions which correspond to the transitions $^4A_2(^4F)\rightarrow{}^4T_2(^4F)$, $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$, $^4A_2(^4F)\rightarrow{}^4T_1(^4P)$ of the Co^{2+} ion in various semiconductors with T_d symmetry. The splitting of the energy levels of the Co^{2+} ion due to the reduction from T_d to S_4 symmetry can be predicted by group theoretical calculations. The energy levels of $^4T_2(^4F)$, $^4T_1(^4F)$, and $^4T_1(^4P)$ of Co^{2+} in T_d symmetry are, respectively, split into two levels as reducing to a lower symmetry of

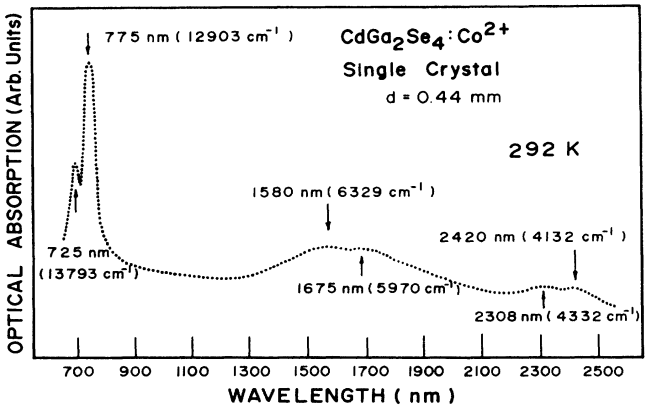

FIG. 1. Absorption spectrum of the $CdGa_2Se_4:Co^{2+}$ single crystals measured at 292 K in the 700–2500-nm region.

S_4. Six absorption lines in Fig. 2 are assigned to the allowed transitions from the ground state ^4B to the upper states of the Co^{2+} ion in S_4 symmetry. These predictions are in good agreement with the results of the optical absorption spectrum measured in the Co-doped $CdGa_2Se_4$ (see Figs. 1 and 2). As T_d symmetry is reduced to S_4 symmetry, the spacing of the low-symmetry splitting of the $^4T_2(^4F)$ energy level is ~ 200 cm^{-1}, which is similar to that of ~ 220 cm^{-1} obtained in a YAG:Co^{2+} single crystal (YAG represents yttrium aluminum garnet).[9] Thus the observed absorption lines are well assigned to the electronic transitions between the split energy levels of the Co^{2+} ion due to the reduction from T_d to $S4$ symmetry. The crystal field parameter Dq and the Racah parameter B, obtained from Fig. 1, are 413 and 455 cm^{-1}, respectively. The Dq value in the Co-doped $CdGa_2Se_4$ shows a good agreement with $Dq = 460$ cm^{-1} for tetrahedral Co^{2+} in the YAG:Co single crystal,[9] but shows considerable differences as compared with $Dq = 830$ cm^{-1} for tetrahedral Co^{3+}, $Dq = 920$ cm^{-1} for octahedral Co^{2+}, and $Dq = 1600$ cm^{-1} for octahedral Co^{3+} in the YAG:Co single crystal.[9] Thus we can conclude that cobalt atoms in the $CdGa_2Se_4$:Co single crystal occupy the tetrahedral sites of the $CdGa_2Se_4$ host lattice as Co^{2+} ions, then the reduction in symmetry is attributed to the cobalt atoms added to the $CdGa_2Se_4$ host.

To identify the fine structure in the transition region centered at 13 000 cm^{-1}, the optical absorption spectrum of $CdGa_2Se_4$:Co^{2+} single crystals was investigated at low temperatures. At 77 K we observed fourteen absorption peaks in the 12 500 to 14 200 cm^{-1} region as shown in Fig. 3. If we consider S_4 symmetry neglecting spin-orbit coupling, only two absorption lines are expected in these regions. Thus the observed results suggest that there exists the spin-orbit coupling effects of Co^{2+} in S_4 symmetry of $CdGa_2Se_4$. When the spin-orbit coupling effects are treated, using group theory, the ground state ^4B is split into two levels, and the first excited states are split into two levels for the ^4A state, four levels for ^4E state. Thus the lowering of symmetry from T_d to S_4 along with spin-orbit coupling effects can be exhibited as twelve absorption lines due to the transitions of the Co^{2+} ion from the ground state ^4B (doublet) to the upper states (doublet and quartet). The observed absorption spectrum of Fig. 3 is just what one would predict on the basis of the combined operation of S_4 symmetry and spin-orbit coupling. From the energy values of the optical absorption peaks of the $CdGa_2Se_4$:Co^{2+} single crystals, the energy levels of the Co^{2+} ion in S_4 symmetry

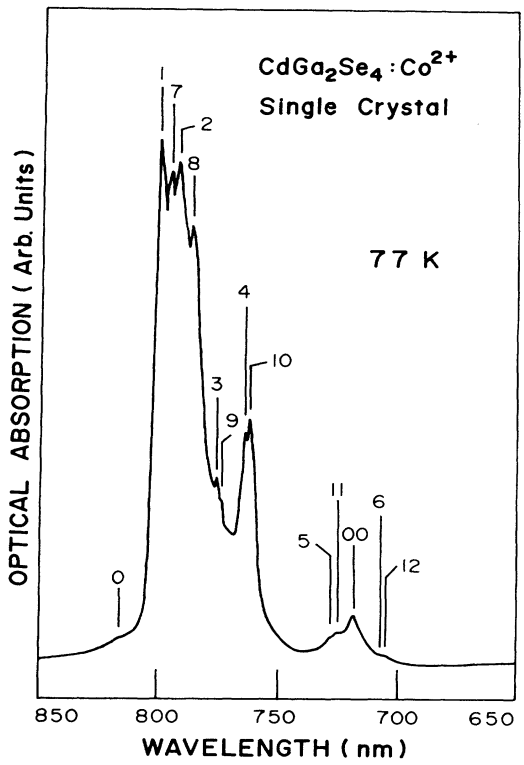

FIG. 3. Absorption spectrum of the $CdGa_2Se_4$:Co^{2+} single crystal measured at 77 K in the 650 to 850-nm region.

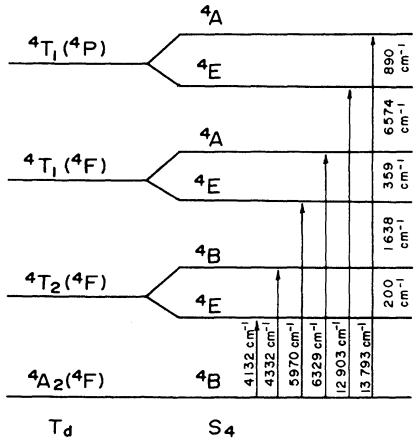

FIG. 2. Energy-level diagram for Co^{2+} due to the reduction in symmetry of the site from T_d to S_4 symmetry.

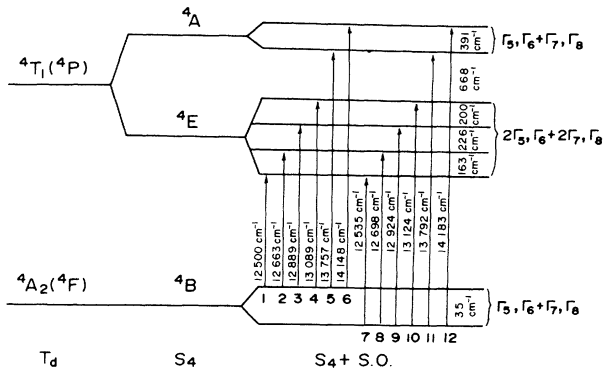

FIG. 4. Energy-level diagram for Co^{2+} in S_4 symmetry with spin-orbit coupling predicted on the basis of group theory (the transition numbers correspond to the numbers of the optical absorption peaks in Fig. 3).

along with spin-orbit coupling effects can be plotted on the basis of group theory as shown in Fig. 4. The spin-orbit splitting of the ground state ^4B obtained from Fig. 4 is the order of 35 cm^{-1}, which is a reasonable value compared with that of about 30 cm^{-1} in the YAG:Co^{2+} crystal.[9] However, the optical absorption peaks at 12 269 (peak 0 of Fig. 3) and 13 913 cm^{-1} (peak 00 of Fig. 3) cannot be explained by the spin-orbit coupling effects. It is considered that the unassigned transitions may relate to the defect levels which originate from the incorporation of cobalt atoms to the $CdGa_2Se_4$.

In summary, the optical absorption of the $CdGa_2Se_4$:Co^{2+} single crystals grown by the CTR method was investigated. The six absorption peaks observed at 292 K in the near-infrared region are attributed to the electronic transitions of Co^{2+} between the localized energy levels. At 77 K, the observed absorption spectrum of the $CdGa_2Se_4$:Co^{2+} single crystals in the 12 500 to 14 200 cm^{-1} region was assigned in terms of S_4 symmetry along with spin-orbit coupling effects.

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*Present address: Department of Physics, Mokpo National University, Mokpo 580, Republic of Korea.

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