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# Substitutional site of $Co^{2+}$ ions in single-crystalline $AgGaS_2$:$Co^{2+}$

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We investigated Co-doped $AgGaS_2$ single crystals in order to determine the substitutional site of $Co^{2+}$ ion in the crystal. The analysis of the absorption spectra shows that the $Co^{2+}$ ions are located at the Ga sites and yields the values of the crystal-field parameter $Dq = 359\ cm^{-1}$ and Racah parameter $B = 605\ cm^{-1}$. The lattice constants of Co-doped crystals were almost the same as those of undoped ones. All the Raman modes were observed to soften in the Co-doped crystals, and that also implies the $Co^{2+}$ ions occupy the Ga sites. [S0163-1829(96)03023-8]

3*d* transition-metal (TM) impurities in semiconducting materials have been used mainly to study the symmetry and the strength of the crystal field of host semiconducting materials. In binaries, TM impurities should take the place of cations. But in the case of ternary semiconductors, I-III-$VI_2$ or II-$III_2$-$VI_4$, which have two cation sites, we may ask which cation they replace. When TM impurities occupy one of the two sites, they display only the local site symmetry and the local strength of the crystal field. For $Zn_{1-x}Cd_xGa_2Se_4$, it was reported that $Co^{2+}$ ions may replace Ga atoms.[1] In this study we used the $Co^{2+}$ ion as the TM impurity in $AgGaS_2$ in order to discuss the substitutional sites of these impurities.

$AgGaS_2$ single crystal and Co-doped ones were synthesized by chemical transport reaction method using iodine as a transporting agent. The ampoules were heated in a two-zone furnace for 17 days. The temperature of the source zone was 900 °C and that of the growth zone was 750 °C. The color of undoped crystals was transparent yellow and that of the Co-doped ones was dark red. All of them were in rod form with the dimensions of about $3\times3\times20\ mm^3$.

The Co concentrations of the $AgGaS_2$:$Co^{2+}$ single crystal were measured by wavelength dispersion spectroscopy. In order to investigate the $Co^{2+}$ site in $AgGaS_2$, x-ray diffraction (XRD) analysis, Raman spectroscopy, and absorption spectroscopy were performed. The absorption spectra of $AgGaS_2$:$Co^{2+}$ were obtained with a VIS-NIR spectrophotometer (Shimadzu MPS-5000) at 10 K in the 185–3200-nm range and its resolution was less than 1 nm. The Raman modes were excited by the 514.5-nm line from an Ar-ion laser and the spectra were obtained at room temperature with the resolution of about $0.5\ cm^{-1}$.

The chalcopyrite structure differs from zinc blende in that there are two species of cation, and this produces two distinct types of distortion from cubic symmetry. Each anion is displaced from its zinc-blende site (anion displacement), the whole crystal is compressed along the tetragonal direction (tetragonal distortion), and the length of the Ag-S bond is longer than that of the Ga-S bond. In $AgGaS_2$, the anion displacement and the tetragonal distortion are unusually large in comparison with other chalcopyrite compounds.[2] Thus, as can be seen in Fig. 1, the symmetries of S atoms around each cation are much different from each other. The tetragonal distortion shortens the side of the cube in the *z* direction, which is made up of S atoms around each cation. In the Ga site the lengths of the sides in the *x*-*y* plane shorten but in the Ag site they become longer. As a result, the Ga atom is surrounded by an almost exactly regular tetrahedron ($T_d$) of S atoms, whose axes are rotated relative to the axes of the crystal.[3] On the other hand, with the tetragonal distortion and the displacements of S atoms the symmetry of S atoms around the Ag atom is lowered to the $D_{2d}$ symmetry (Fig. 1).

The optical absorption spectra of the Co-doped $AgGaS_2$

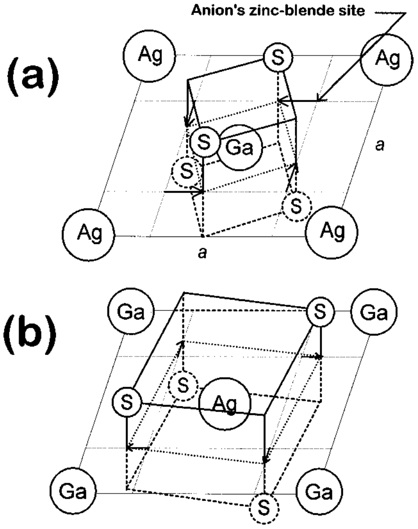

FIG. 1. The symmetries of S atoms around (a) Ga and (b) Ag. The arrows denote the anion displacements.

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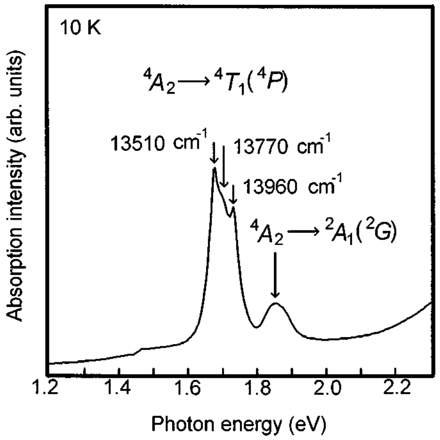

FIG. 2. The structure of the absorption band at 10 K near the band gap.

single crystal at 10 K are shown in Figs. 2 and 3. We observed eight impurity peaks at 5501, 5985, 6348, 6808, 13 510, 13 770, 13 960, and 14 960 $cm^{-1}$. The three lower energy peaks in Fig. 2 are attributed to the electronic transitions of $Co^{2+}$ from the ground state $^4A_2$ $(^4F)$ to $^4T_1(^4P)$ and the highest-energy peak at 14 960 $cm^{-1}$ is assigned to the transition from the ground state to $^2A_1(^2G)$. The four peaks in Fig. 2 correspond to the transitions to $^4T_1(^4F)$ state. The groupings of the absorption peaks of $Co^{2+}$ ion shown in Figs. 2 and 3 may indicate that the $T_d$ crystal field must be larger than the $D_{2d}$ crystal field or the spin-orbit interaction. As can be seen in Fig. 4, if the $D_{2d}$ crystal field is larger than the spin-orbit interaction, the $^4T_1$ states split into two (six) sublevels without (with) spin-orbit interaction. The energy-level splittings can be derived by a simple group theoretic calculation from a character table for point-symmetry groups.[4] If the $D_{2d}$ crystal field is less than the spin-orbit interaction, they split into three sublevels in the first-order spin-orbit interaction or four in the second order.[5] Therefore, the absorption spectra clearly show that the $Co^{2+}$ ions belong to the $T_d$ symmetry in which the effect of the $D_{2d}$ crystal field is negligible, and that means the $Co^{2+}$ ions at the Ga sites.

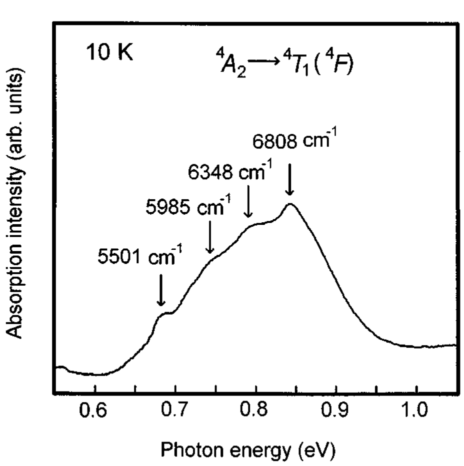

FIG. 3. The structure of the absorption band at 10 K in the infrared region.

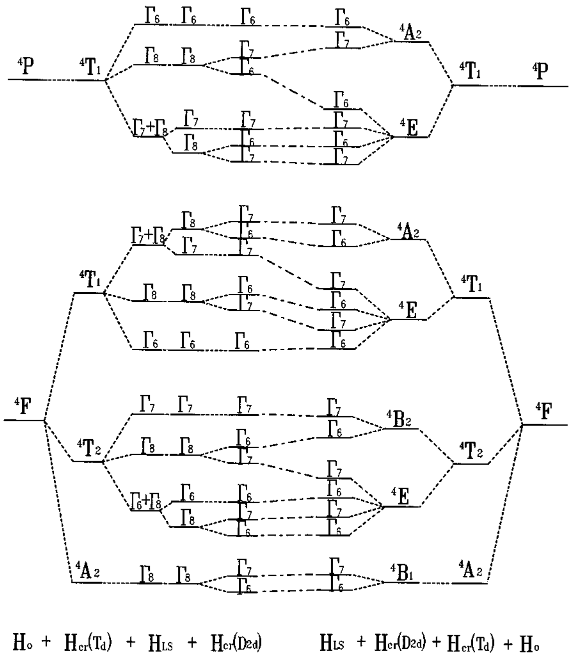

FIG. 4. Energy-level diagram for $Co^{2+}$ in $T_d$ and $D_{2d}$ crystal field with spin-orbit coupling predicted on the basis of group theory.

From the above data and the equations in Ref. 6, the crystal field parameter $Dq$ is 359 $cm^{-1}$ and the Racah parameter $B$, which characterizes the Coulomb repulsion of $3d$ electrons, is 605 $cm^{-1}$. These values are very close to those of $Co^{2+}$ in ZnS whose $Dq$ and $B$ are 375 and 610 $cm^{-1}$, respectively.[7] The S atoms in ZnS have the regular tetrahedral coordination and the Zn-S bond length is close to the Ga-S bond length in $AgGaS_2$.[2,7] Therefore the crystal field parameters also show that $Co^{2+}$ ions are in the $T_d$ crystal field, which implies the Co impurities replace the Ga atoms.

Raman spectra of $AgGaS_2$:$Co^{2+}$ crystals are shown in Fig. 5 and compared with that of $AgGaS_2$. One can observe that as the concentration of Co is increased from 0 to 0.14 and to 1.2 mole %, the energies of all Raman modes decrease

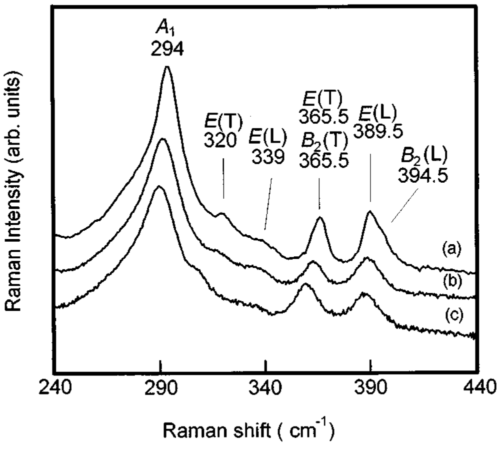

FIG. 5. The Raman spectra of $AgGaS_2$:$Co^{2+}$ single crystals. The Co concentrations are (a) 0%, (b) 0.14 mole %, and (c) 1.2 mole %.

gradually. From a simple least-square fitting, the lattice constants of these crystals were $a = 5.751 \pm 0.003$ Å and $c = 10.302 \pm 0.005$ Å for the undoped crystals, $a = 5.753 \pm 0.005$ Å and $c = 10.304 \pm 0.008$ Å for the doped ones of 0.14 mole %, and $a = 5.750 \pm 0.005$ Å and $c = 10.303 \pm 0.009$ Å for the doped ones of 1.2 mole %, and there was no considerable change. This indicates that the size of the unit cell does not contribute to the shifts of Raman modes in our case. The frequency shifts of the Raman modes may come from the mass effect and the electronegativity difference effect. The atomic weight of the Co atom is similar to that of a Ga atom but is much lighter than that of a Ag atom. Thus the mass effect will result in hardening of Raman modes if Co atoms replaced Ag atoms. As the electronegativity difference of two atoms involved in bonding increases, the binding force becomes stronger and the energy of phonon modes increases. The electronegativity difference of the Co-S bond is smaller than that of the Ga-S bond while larger than that of the Ag-S bond.[8] The incorporation of Co causes softening of the Ga-S related Raman modes but hardening of the Ag-S related ones.

The single $A_1$ mode at 294 $\mathrm{cm}^{-1}$ results from the motion of S atoms in the perpendicular direction to the *c* axis, with Ag and Ga atoms remaining at rest.[9] The mass effect of the stationary atom may be neglected and only the electronegativity difference effect may contribute to Raman shifts. If the $\mathrm{Co}^{2+}$ ions replace the Ga atoms, the energy of the $A_1$ mode must decrease, since the restoring force of the Co-S bond is weaker than that of Ga-S bond. $B_2$ modes [394.5 $\mathrm{cm}^{-1}(L)$ and 365.5 $\mathrm{cm}^{-1}(T)$] and $E$ modes [339 $\mathrm{cm}^{-1}(L)$, 320 $\mathrm{cm}^{-1}(T)$] involve the motion of S and Ga, which is independent of the Ag atom. Provided that the $\mathrm{Co}^{2+}$ ions occupy the sites of the Ag atoms, we should expect that the energies of these modes increase as the electronegativity difference increases. Other $E$ modes [389.5 $\mathrm{cm}^{-1}(L)$, 365.5 $\mathrm{cm}^{-1}(T)$] in Fig. 5 correspond to the motion of S and Ag, with Ga atoms being almost stationary.[10] If $\mathrm{Co}^{2+}$ ions are placed at the sites of Ga atoms, the electronegativity difference may result in softening of the mode, while the $\mathrm{Co}^{2+}$ ions at Ag sites harden the mode. Therefore, these results also show that the $\mathrm{Co}^{2+}$ ion is located at the Ga site not at the Ag site.

In conclusion, we discussed from the XRD analysis, absorption spectra and Raman spectroscopy that the $\mathrm{Co}^{2+}$ ions replace the Ga atoms in $\mathrm{AgGaS_2{:}Co^{2+}}$ single crystal. And the values of the crystal field parameter *Dq* and Racah parameter *B* are 359 and 605 $\mathrm{cm}^{-1}$, respectively, which are very close to those of $\mathrm{Co}^{2+}$ in ZnS.

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