

## Optical study of the one-dimensional Ising-like antiferromagnet CsCoBr<sub>3</sub>

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The polarized, single-crystal absorption spectra of spin  $S = \frac{1}{2}$  Ising-like antiferromagnet CsCoBr<sub>3</sub> have been investigated in the visible to near-infrared region at various temperatures between 15 and 300 K. The observed absorption bands are attributed to the Co<sup>2+</sup> crystal-field energy states of the  $d^7$  electronic configuration. A fine structure is observed at the low-energy side of the band due to a spin-allowed  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  transition. From its interval of progression, the fine structure is concluded to arise from the electronic coupling with the  $A_{1g}$  phonon. It is found, from a comparison with the temperature dependence of the Raman band, that a spin-forbidden band is enhanced by the one-dimensional (1D) short-range antiferromagnetic spin-exchange interaction. The same temperature behavior as in the case of the 1D Heisenberg antiferromagnet is confirmed to appear for the magnon sideband in the 1D Ising-like antiferromagnet.

### I. INTRODUCTION

Considerable interest has been given to the  $ABX_3$ -type (where  $A$  is an alkali ion,  $B$  is a transition-metal ion, and  $X$  is a halide ion) magnets with hexagonal crystal structure since they exhibit one-dimensional (1D) magnetic behavior. Of the various  $ABX_3$  magnets, the cobalt salts CsCoCl<sub>3</sub>, CsCoBr<sub>3</sub>, and RbCoCl<sub>3</sub> are known as examples of a spin  $S = \frac{1}{2}$  1D Ising-like antiferromagnet.<sup>1-7</sup> From this point, these Co salts attract our interest. All three magnets have two kinds of Néel temperatures,  $T_{N1}$  and  $T_{N2}$  ( $< T_{N1}$ ). At low temperatures below  $T_{N2}$ , they exhibit the triangular-lattice antiferromagnetic (AF) spin ordering, while, in the temperature region between  $T_{N2}$  and  $T_{N1}$ , one-third of the AF ordering chains along the  $c$  axis are disordered but two thirds remain antiferromagnetically coupled in the  $a$ - $b$  plane. Above  $T_{N1}$ , they exhibit a strong 1D AF short-range order along the  $c$  axis.

In addition to the nonoptical measurements, the optical-absorption<sup>8-12</sup> and Raman<sup>1-7,13</sup> measurements have been done on these Co salts. Unlike the cases of CsCoCl<sub>3</sub> and RbCoCl<sub>3</sub>,<sup>8-12</sup> however, there has been no report on the absorption spectrum of CsCoBr<sub>3</sub> in the uv to the near-infrared region. In this paper we study the visible-to-infrared absorption spectra of CsCoBr<sub>3</sub> to obtain information about the magnetism of the Ising-like AF material.

### II. EXPERIMENTAL RESULTS

Single crystals of CsCoBr<sub>3</sub> were prepared from a stoichiometric amount of CsBr and anhydrous CoBr<sub>2</sub> which was thoroughly dried in a silica tube at about 150°C for 3 d. The tube was then sealed under vacuum and slowly lowered in a vertical Bridgman furnace. The crystals were cleaved easily along the  $c$  axis. The crystal used for the absorption measurement had dimensions of about  $5 \times 5 \times 0.4$  mm<sup>3</sup>. Absorption spectra were obtained using a

Shimadzu MPS-50L or UV-260 spectrophotometer. A Glan prism was used as a polarizer. The crystal was cooled in an Osaka Sanso Cryo-Mini cryostat which allows cooling down to 15 K.

Figure 1 shows the absorption spectra of CsCoBr<sub>3</sub> at 15 K in the 480–2500-nm region, measured using the polarized light with the electric vector  $E$  parallel or perpendicular to the crystal  $c$  axis. Several bands seem to appear in the low-wavelength region below 480 nm, but they are too intense to observe their peaks.

The visible-infrared spectra of CsCoBr<sub>3</sub> are similar to not only those of CsCoCl<sub>3</sub> and RbCoCl<sub>3</sub>,<sup>8</sup> but also those of KCoF<sub>3</sub>, CoBr<sub>2</sub>, CoCl<sub>2</sub>,<sup>14</sup> and RbCoF<sub>3</sub>,<sup>15</sup> indicating that all the absorption bands observed in the visible to near-infrared region are ascribed to the Co<sup>2+</sup> ion. However, a quite different point, which is not observed in other salts, is found in CsCoBr<sub>3</sub> on the lowest-energy band appearing around 1700 nm. This band has a fine structure with several sharp lines at the low-energy side, as seen in Figs. 1 and 2. These sharp lines appear to remain constant as temperature is increased, although the main band with a broad peak around 1700 nm grows and becomes broad (Fig. 3).

The similarity of the CsCoBr<sub>3</sub> absorption spectra with the other Co salts is also found in the temperature ( $T$ ) dependence of the absorption bands. In Fig. 3 the line shape of the low-energy bands is shown at various temperatures. As in the cases of various Co salts (see, e.g., Ref. 15), the lowest-energy band grows with increasing temperature at high temperatures. The intensity increases in proportion to temperatures above 50 K, but it is almost constant below 50 K. The similar  $T$  dependence is observed for the small band with a peak at 825 nm at 15 K (see Fig. 3).

In addition to such  $T$ -dependent bands, we have observed several bands whose peak height decreases with increasing temperature. Of them, there is a weak absorption band with a broad peak at 510 nm which appears in

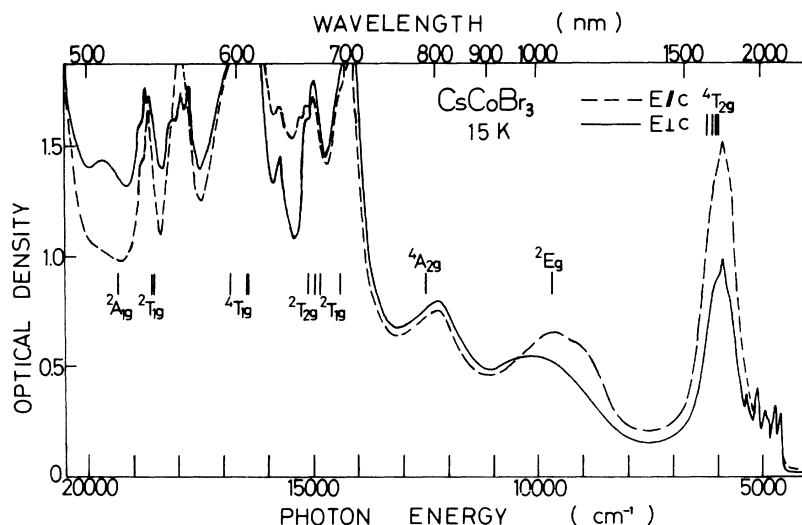


FIG. 1. Polarized ( $E_{||c}$  and  $E_{\perp c}$ , where  $E$  represents the electric vector of incident light, and  $c$  represents the crystal  $c$  axis) absorption spectra of  $\text{CsCoBr}_3$  crystal at 15 K. The vertical lines show the positions of  $\text{Co}^{2+}$  energy levels in the cubic crystal field calculated by Ferguson *et al.* (Ref. 14).

the  $E_{\perp c}$  spectrum but not in the  $E_{||c}$  spectrum. Unlike the other bands, the 510-nm band is well separated from its neighboring bands, indicating that it is possible to estimate the band intensity precisely. In Fig. 4 (open circles), we show the  $T$  dependence of intensity (i.e., band area) of the 510-nm band.

### III. DISCUSSION

Ferguson, Wood, and Knox have obtained good agreement between the observed and calculated absorption-

band positions  $\text{CoBr}_2$ .<sup>14</sup> Their calculation of  $\text{Co}^{2+}$  energy levels in the cubic crystal field was done using values of  $Dq = 640$ ,  $B = 760$ ,  $C/B = 4.40$ , and  $\zeta = 420 \text{ cm}^{-1}$ , where  $Dq$  is the crystal-field parameter,  $B$  and  $C$  are the Racah parameters, and  $\zeta$  is the spin-orbit coupling constant. The calculated energy-level positions are shown in Fig. 1 by the vertical lines. When we compare these levels with the observed  $\text{CsCoBr}_3$  bands we find good agreement between them. Therefore, we will be allowed to use the level assignment, which is shown in this figure, for the  $\text{CsCoBr}_3$  absorption bands. This band assignment is consistent with

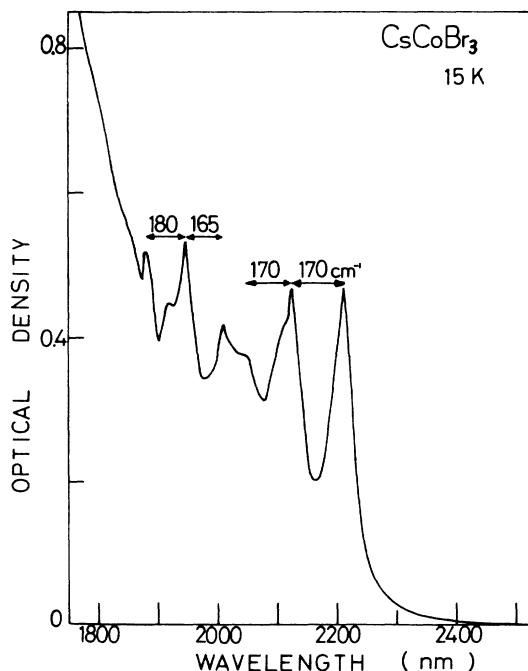


FIG. 2. Fine structure observed at the low-energy side of the 1700-nm band of  $\text{CsCoBr}_3$  at 15 K.

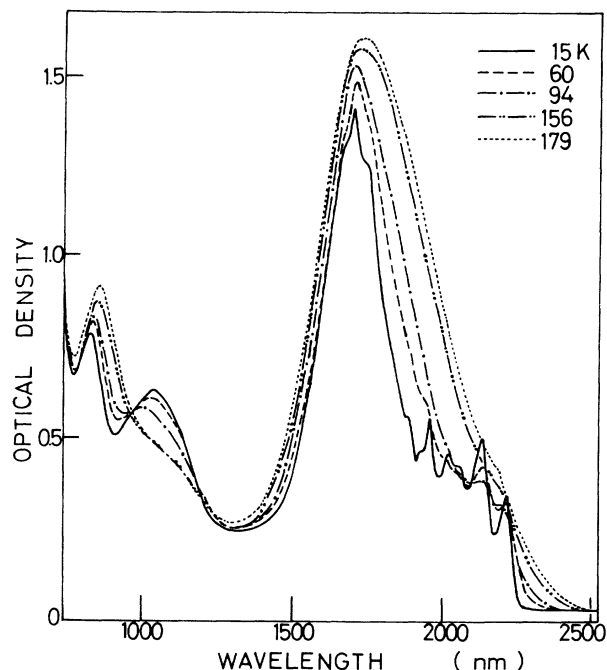


FIG. 3. Near-infrared absorption spectra of  $\text{CsCoBr}_3$  at various temperatures.

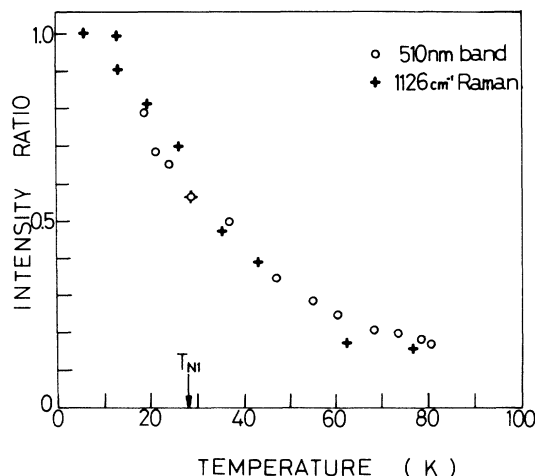


FIG. 4. Temperature dependence of the intensity of the 510-nm absorption band (open circles), compared with the intensity of the  $1126\text{-cm}^{-1}$  exciton band obtained by Raman measurement by Johnstone and Dubicki (Ref. 2) (crosses). The two kinds of data were plotted to have the same value at 26 K.

the cases of  $\text{CsCoCl}_3$  and  $\text{RbCoCl}_3$  made by Putnik and Holt.<sup>8</sup>

The ground state of  $\text{Co}^{2+}$  is  ${}^4T_{1g}$ . Three parity-forbidden but spin-allowed states are found in Fig. 1, i.e.,  ${}^4T_{2g}$ ,  ${}^4A_{2g}$ , and  ${}^4T_{1g}$  in order of increasing energy. These spin-allowed bands obtain their absorption intensities mainly by the electron-phonon interaction, while the spin- and parity-forbidden bands in the magnetic crystals obtain their absorption by the magnetic interaction (see, e.g., Ref. 16). As mentioned above, the 825-nm band shows the  $T$  dependence of the well-known  $\coth(h\nu/2k_B T)$  law. This band is quite close to the calculated  ${}^4A_{2g}$  energy-level position. Therefore, it is quite reasonable that the 825-nm band is attributable to the spin-allowed  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  transition just as in the case of the spin-allowed 1700-nm band. So far, the absorption band due to the  ${}^4T_{1g} \rightarrow {}^2E_g$  transition has not been observed clearly in Co salts.<sup>8,14,15</sup> As shown in Fig. 1, however, the spin-forbidden band is obviously observed in  $\text{CsCoBr}_3$ .

Hauser and Gudel have studied the absorption spectra of  $\text{CsVCl}_3$ ,  $\text{CsVBr}_3$ , and  $\text{CsVI}_3$  AF crystals<sup>17</sup> which have the same crystal structure as  $\text{CsCoCl}_3$  and  $\text{CsCoBr}_3$ . The vanadium ion  $\text{V}^{2+}$  has the electron configuration of  $d^3$  with a ground state of  ${}^4A_{2g}$ , which is complementary to  $\text{Co}^{2+}$  with  $d^7$  electron configuration. Therefore, the  $\text{Cs-VX}_3$  crystal is expected to exhibit behavior similar to the  $\text{CsCoX}_3$  crystal. Hauser and Gudel have observed well-resolved vibronic structure with a progression on the low-energy tail of the spin-allowed  ${}^4T_{2g}$  and  ${}^4T_{1g}$  absorption bands. The observed vibration interval is 256, 160, and  $118\text{ cm}^{-1}$  for  $\text{CsVCl}_3$ ,  $\text{CsVBr}_3$ , and  $\text{CsVI}_3$ , respectively, which are quite close to the frequencies of the totally symmetric  $A_{1g}$  phonon mode.<sup>17</sup>

The structure observed at the  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  1700-nm band of  $\text{CsCoBr}_3$  has a progression with an interval of about  $170\text{ cm}^{-1}$  (see Fig. 2). According to the Raman

measurement,<sup>2,5</sup> the  $A_{1g}$  phonon mode has an energy of  $168\text{ cm}^{-1}$  for  $\text{CsCoBr}_3$  and  $262.5\text{ cm}^{-1}$  for  $\text{CsCoCl}_3$ . Putnik and Holt have observed a vibronic structure on the absorption band appearing in the 460–475-nm region in  $\text{CsCoCl}_3$  and also in  $\text{RbCoCl}_3$ .<sup>8</sup> Our observed interval of progression is about  $225\text{ cm}^{-1}$ , which does not agree with the expected  $262.5\text{ cm}^{-1}$ . The interval, however, is in good agreement with the expected  $168\text{ cm}^{-1}$  just as the cases of  $\text{CsVCl}_3$  and  $\text{CsVBr}_3$ .

The fine structure of the  $\text{Co}^{2+}$  lowest-energy band at 1700 nm has also been found in the corresponding absorption band in  $(\text{QH})_2\text{CoCl}_4$  and in Co-doped  $\text{Cs}_2\text{ZnCl}_4$  and  $[\text{N}(\text{CH}_2)_4]\text{ZnCl}_4$ .<sup>18</sup> They are observed to have a progression of the same vibration mode with an interval of about  $270\text{ cm}^{-1}$ . The value is close to the  $A_{1g}$  phonon frequency of Co chlorides, i.e.,  $256\text{ cm}^{-1}$  of  $\text{CsVCl}_3$  and  $262.5\text{ cm}^{-1}$  of  $\text{CsCoCl}_3$ . Therefore, taking into account that the vibration interval depends mainly on that kind of halide ion but depends on neither the alkali-metal ion nor transition-metal ion, the fine structure observed in the 1700-nm band in  $\text{CsCoBr}_3$  is ascribed to the  $A_{1g}$  phonon.

In  $\text{CsCoCl}_3$ , one has been interested in sharp bands due to hot and cold magnon sidebands in the spin-forbidden  ${}^4T_{1g} \rightarrow {}^2T_{1g}$  absorption band appearing around 535 nm.<sup>8–12</sup> In our crystal, we also observed the several lines in the  ${}^4T_{1g} \rightarrow {}^2T_{1g}$  absorption band located around 540 nm, but they are unresolved from each other and, moreover, their linewidths are so broad that it is difficult to make an identification for these lines exactly.

Here we concentrate our attention on the weak 510-nm band observed in the  $E \perp c$  spectrum. The corresponding band in  $\text{CsCoCl}_3$  was observed in the 460–475-nm region. Unlike the case of  $\text{CsCoCl}_3$ , the 510-nm band has not a vibronic structure. We tried to find the fine structure but we could not find it clearly. The 510-nm band shows the decrease with increasing temperature as seen in Fig. 4. To understand the origin of the 510-nm band, we compare the  $T$  dependence with that of a Raman band observed by Johnstone and Dubicki.<sup>2</sup> In Fig. 4 the Raman intensity of an exciton line at  $1126\text{ cm}^{-1}$  is plotted. The Raman intensity falls slowly at first, then more rapidly with increasing temperature, but decreases very slowly above 60 K. It is found that the 510-nm band intensity shows a quite similar  $T$  dependence as the exciton line. The behavior of the exciton line is ascribed to a spin-dependent mechanism involving pairs of  $\text{Co}^{2+}$  ions, i.e., spin-correlation function  $\langle S_i \cdot S_j \rangle$ .<sup>2,6</sup> Therefore, it is concluded that the character of magnetic short-range order in this material appears in the 510-nm band.

The intensity of the 510-nm band never becomes zero at  $T_{N1}$  [ $=28.3\text{ K}$  (Ref. 7)] and decreases gradually above  $T_{N1}$ . This is characteristic of 1D Heisenberg AF material.<sup>17,19</sup> In fact the  $T$  dependence of the exciton line observed by the Raman measurement does not agree with that of the spin-correlation function in the 3D system.<sup>2</sup> This is in agreement with the fact that  $\text{CsCoBr}_3$  has a strong AF short-range interaction along the  $c$  axis because, in the 1D system, the phase transition from 3D magnetic order to paramagnetic disorder is not as abrupt as in the case of the 3D system, and the spin-correlation function extends over a relatively wide temperature region

above  $T_N$ .

In conclusion, the same behavior as that observed in the 1D Heisenberg antiferromagnet is confirmed to appear for the magnon sideband in the 1D Ising-like  $\text{CsCoBr}_3$  antiferromagnet.

The Néel temperature of  $\text{CsCoBr}_3$  is  $T_{N1} = 28.3$  K and  $T_{N2} \cong 10$  K, and its intra- and interchain nearest-neighbor exchange interactions are  $J = -54.1 \text{ cm}^{-1}$  and  $J' = -3.2 \text{ cm}^{-1}$ , respectively.<sup>7</sup> Our present measurement was done at temperatures above 15 K. We tried to find the magnetic phase transition at 28.3 K by the absorption spectra when the crystal was warmed gradually from 15 K. Neither abrupt change nor critical behavior, however, were

observed in the spectral line shape around  $T_{N1}$ . This is consistent with the existence of strong 1D spin coupling (i.e.,  $|J| \gg |J'|$ ) in  $\text{CsCoBr}_3$ .

Information about the magnetic long-range order has not been obtained in the present temperature range. To check a presence of transverse spin ordering for  $\text{CsCoBr}_3$ ,<sup>20</sup> which does not appear in  $\text{CsCoCl}_3$ , an absorption study below  $T_{N2}$  will be done in the near future.

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