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Low Symmetry Crystal Field Splitting of $^4T_1$ States of Co^{2+} in $CuGaS_2$

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The optical absorption spectra of $CuGaS_2$:Co are observed at a room temperature and at 2K in near infrared and visible regions, the low energy side of the absorption edge (20,000 cm^{-1}) of the host crystal. The spectra show a broad band in the vicinity of 7,000 cm^{-1} and a fine structured band around 13,000 cm^{-1}.

The fine structure of the upper band is analyzed by calculating the energy level scheme taking account of a low symmetry (D_{2d}) crystal field and the spin-orbit coupling in addition to the cubic (T_d) field.

A reasonable choice of the parameters reproduces the observed spectra fairly well and give the g-shifts and zero field splitting constant which agree quite well with the observed values by Kaufmann *et al.* (Solid State Commun. **15** (1974) 1881).

§ 1. Introduction

The I-III-VI$_2$ compounds have been attracting attention of many workers and among them chalcopyrite $CuFeS_2$ in which we have been particularly interested is believed to be the only magnetic substance, which is an antiferromagnet of a high Néel temperature. In order to get some idea about the electronic structure of $CuFeS_2$, recently we worked on the optical spectra of $CuGaS_2$: Fe experimentally[1-4] and theoretically.[5-7] Then we clarified the origins of the observed intense absorption band and of the pretty low energy emission line and suggested that the g-values and zero-field splitting constant D determined through the ESR technique[8] could be reasonably interpreted if a moderate strength of the low symmetry crystal field was assumed. Although the low symmetry field is quite expected from the distorted crystal structure of this substance, its strength is unknown yet by an optical study because the absorption band so far observed is so broad that no fine structures are detected. However, it is quite necessary to know its strength for comprehensive understanding of the properties of $CuFeS_2$ since there are many important features determined mainly by the low symmetry field.

The purpose of the present article is to determine the strength of the low symmetry field in $CuGaS_2$. We have found that $CuGaS_2$: Co is suitable for this purpose. Its optical absorption spectra show rather complicated fine structure in near infrared and visible regions in contrast with the case of Mn, Fe, or Ni in $CuGaS_2$. We calculate energy level scheme of a Co^{2+} ion under an appropriate low symmetry crystal field and the spin-orbit interaction in the framework of the crystal field theory.[9] Cobalt is a particularly suitable probe to make such analysis in the sense that it is in a unique divalent state in the $CuGaS_2$ crystal[10] and so there is no need, at least, for the present analysis to take into account complications of charge transferred states; in contrast both trivalent and divalent states are equally feasible for iron and, in fact, taking into account mixing of these two is inevitable for interpretation of the optical spectra.[1-7]

Large components of the low symmetry crystal field are expected to be a D_{2d} type in this crystal, though the rigorous site symmetry of metal ions is an S_4 type. The D_{2d} crystal field is represented in terms of two parameters, P and Q, defined in § 3. Besides them, there are several parameters to be fixed, the

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Racah parameters, B and C, of intraatomic Coulomb repulsion, a spin-orbit coupling constant ζ, and a cubic crystal field parameter $10\,Dq$. We determine these parameters so that they reproduce available experimental data, the optical absorption spectra described in the next section and the ground state spin Hamiltonian determined by Kaufmann *et al.*[10] We obtain $P=700\,\text{cm}^{-1}$ and $Q=344\,\text{cm}^{-1}$, together with $B=500\,\text{cm}^{-1}$, $C=2200\,\text{cm}^{-1}$, $\zeta=533\,\text{cm}^{-1}$, and $10\,Dq=4300\,\text{cm}^{-1}$. The values of the low symmetry field parameters are smaller by an order than the cubic field parameter as expected in our previous treatment of $CuGaS_2$:Fe.

§ 2. Experiments

Single crystals of $CuGaS_2$:$Co_{0.006}$ used in this work were obtained by the chemical transport method with Iodine as a carrier. Doping of Co was achieved by adding a suitable amount of CoS powder to the starting materials (1/2 $Cu_2S+Ga+3/2\,S$). Concentration of Co in the crystals is only nominal.

Typical size of the obtained crystal is $2\times2\times1\,\text{cm}^3$. The crystals were polished to 30-150μm thickness for the use of optical studies. The specimen has a metallic luster but shows dark reddish-brown color in the transmitted light.

The room temperature crystal spectrum in the range 5,000 cm^{-1} to 20,000 cm^{-1} was obtained with a Cary model-14 spectrophotometer. The thickness of the specimen used in this study was 30 μm. The spectrum of the sample together with that of undoped $CuGaS_2$ is shown in Fig. 1. It is seen in this figure that Co ion in $CuGaS_2$ exhibits several structures in the low energy side of the absorption edge (20,000 cm^{-1}) of the host crystal; a broad band in the vicinity of 7,000 cm^{-1}, a structured band with a peak around 13,000 cm^{-1} and a broad shoulder-like structure stitched to the absorption edge.

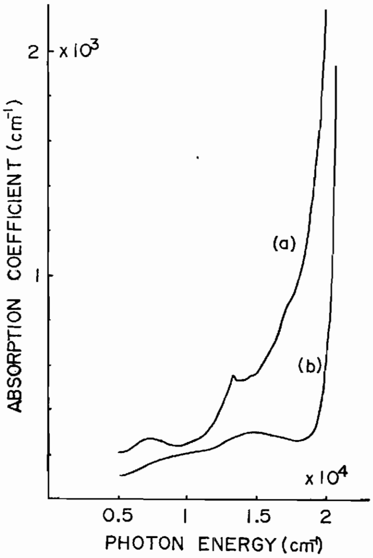

Fig. 1. a) Overall profile of absorption spectrum of $CuGaS_2$:$Co_{0.006}$ at room temperature.
b) That of undoped $CuGaS_2$.

The structured band around 13,000 cm^{-1} was further investigated at a low temperature. This measurement was carried out in an immersion dewer with liquid helium pumped to 2 K. The specimen used in this experiment was 158 μm thick. A Spex model-1800 Czerny-Turner monochrometer with a 1,200 G/mm grating (1 μm-braze), an EMI-9558 photomultiplier and a PAR model-124 Lock-in amplifier were employed for this experiment. The obtained spectrum between 12,500 cm^{-1} and 14,100 cm^{-1} is illustrated in Fig. 2.

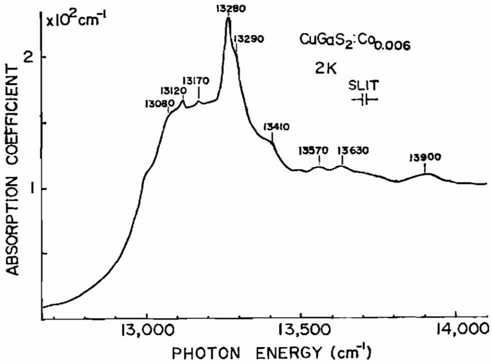

Fig. 2. Fine structure of the absorption band in the region of 12,500~14,000 cm^{-1} at 2 K.

Although polarization dependence of the spectrum was found, only unpolarized spectrum is shown here since the surface of the specimen was not a well-defined crystal plane.

As shown in Fig. 2 the 13,000 cm^{-1}-band is split into a number of bands, some of which are rather sharp. The most intense band at 13,280 cm^{-1} consists of several components, the separation of which is poor due to the experimental limitations. Higher energy side of the spectrum is much obscured due to the superposition of a broad shoulder like structure near the absorption edge.

The total oscillator strength of the 13,000cm^{-1}-band is of the order of 10^{-8} at room temperature.

§ 3. Theoretical Considerations

3.1 *Cubic field and overall profile of optical spectra*

The crystal structure of I-III-VI$_2$ compounds is of chalcopyrite type as shown in Fig. 3. The space group is $D_{2d}^{12}(I\bar{4}2d)$ and the site symmetry of metal ions is $S_4(\bar{4})$. These compounds and their binary analogs, II-VI compounds, manifest many electronic and optical properties similar to each other; overall profile of optical spectra of Co^{2+} ion in CuGaS$_2$ is similar to those in ZnO and ZnS.[11] This suggests that the main feature of energy level scheme of Co^{2+} ion in the I-III-VI$_2$ compounds is determined by the tetrahedral crystal field. At first, taking a tetrahedral crystal field, we calculate the energy levels of Co^{2+} ion in the framework of the crystal field theory.[9]

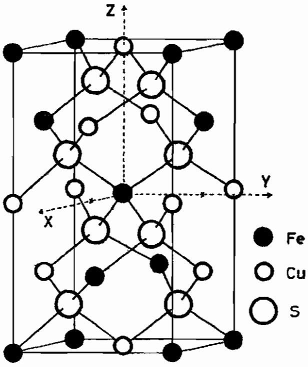

Fig. 3. Crystal structure of chalcopyrite and the coordinate system.

The energy levels are expressed in terms of B, C, and Dq, where B and C are Racah parameters for Coulomb repulsion and Dq is the cubic field parameter. The calculated energy levels of the d^7 configuration are illustrated in Fig. 4. (Some of the energy levels were calculated previously by Tanabe and Sugano.[9]) Here we take 4.4 for the value of C/B, adjusted for Co^{2+} in ZnS.[11] The values of B and Dq in CuGaS$_2$ are determined so that the calculated energy differences between the ground state $^4A_2$ and two $^4T_1$ states fit to the peaks of the two absorption bands in Fig. 1, because it is highly reasonable from intensity consideration that the two peaks mainly from the allowed transitions in the tetrahedral crystal field. The so adjusted values of B and Dq are 500 cm^{-1} and 430 cm^{-1}, respectively, not very different from the values 610 cm^{-1} and 375 cm^{-1} for ZnS.[11] Note that for our adopting value $Dq/B=0.86$ three energy levels $^4T_1(2)$, $^2T_2(1)$, and $^2A_1$ come very close to each other as seen in Fig. 4. It will be shown in a later subsection that this fact explains so complicate optical structure in Fig. 2.

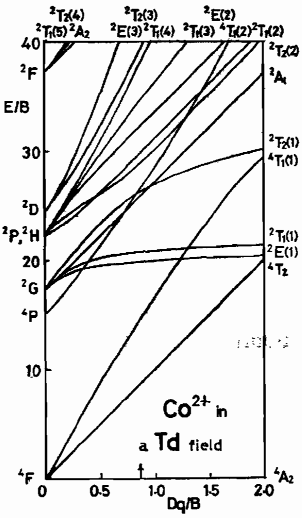

Fig. 4. Energy diagram for d^7 in the T_d symmetry field vs Dq/B. The value of C/B is 4.4. Since $^4T_1$, ^2E, $^2T_1$, and $^2T_2$ states occur more than twice, they are distinguished by numbering in the parenthesis in the order of increasing energy.

The wave functions of the two states $^4T_1(1)$, $^4T_1(2)$ and also of the state $^2T_2(1)$, the energy of which is very close to that of $^4T_1(2)$ as seen in Fig. 4, are

$$\begin{aligned}\Psi(^4T_1(1)M\mu) = &-0.6952\Phi(t_2{}^4(^3T_1)e^3 : {}^4T_1M\mu)\\ &+0.7188\Phi(t_2{}^5e^2(^3A_2) : {}^4T_1M\mu)\ , \quad (3.1)\end{aligned}$$

$$\begin{aligned}\Psi(^4T_1(2)M\mu) = &\,0.7188\Phi(t_2{}^4(^3T_1)e^3 : {}^4T_1M\mu)\\ &+0.6952\Phi(t_2{}^5e^2(^3A_2) : {}^4T_1M\mu)\ , \quad (3.2)\end{aligned}$$

$$\begin{aligned}\Psi(^2T_2(1)M\mu) = &\,0.6971\Phi(t_2{}^3(^2T_2)e^4 : {}^2T_2M\mu)\\ &+0.6075\Phi(t_2{}^4(^3T_1)e^3 : {}^2T_2M\mu)\\ &+0.2375\Phi(t_2{}^4(^1T_2)e^3 : {}^2T_2M\mu)\\ &-0.2170\Phi(t_2{}^5e^2(^1A_1) : {}^2T_2M\mu)\\ &+0.2037\Phi(t_2{}^5e^2(^1E) : {}^2T_2M\mu)\ , \quad (3.3)\end{aligned}$$

where M is $\pm 3/2$ or $\pm 1/2$ for $^4T_1$ and $\pm 1/2$ for $^2T_2$, and μ is α, β, or γ for $^4T_1$ and ξ, η, or ζ for $^2T_2$. The symmetries denoted symbolically are $\alpha \propto L_x$, $\beta \propto L_y$, $\gamma \propto L_z$, $\xi \propto x$ or yz, $\eta \propto y$ or zx, and $\zeta \propto z$ or xy, where the cubic axis are taken as in Fig. 3.

3.2 *Low symmetry crystal field and spin Hamiltonian*

Each metal ion in the II-VI compounds is surrounded tetrahedrally by four chalcogen ions, but the tetrahedron in I-III-VI_2 compounds have two distorted aspects. The first is a uniaxial compression in the c-axis direction and the second is an internal strain arising from the systematic rotation of the tetrahedron about c-axis. Thus, the coordination of the nearest neighbor chalcogen ions has a D_{2d} symmetry, although the full site symmetry of metal ions is S_4. In the present paper, we take the D_{2d} field as the low symmetry crystal field.

The potential of the D_{2d} crystal field is given by

$$V(D_{2d})=E^{(2)}(r)[3z^2-r^2]+E^{(4)}(r)\times\left[z^4-\frac{x^4+y^4}{2}-\frac{6}{7}\left\{z^2-\frac{x^2+y^2}{2}\right\}r^2\right]. \tag{3.4}$$

Matrix elements of $V(D_{2d})$ based on the five $3d$ orbital functions (u, v, ξ, η, ζ), where $u\propto 3z^2-r^2$ and $v\propto x^2-y^2$, are represented by using two parameters.

$$\langle\xi|V(D_{2d})|\xi\rangle=\langle\eta|V(D_{2d})|\eta\rangle =-\frac{1}{2}\langle\zeta|V(D_{2d})|\zeta\rangle=-\frac{1}{2\sqrt{3}}P, \tag{3.5}$$

$$\langle u|V(D_{2d})|u\rangle=-\langle v|V(D_{2d})|v\rangle=-\frac{1}{2}Q. \tag{3.6}$$

The effective spin Hamiltonian of the ground state ${}^4A_2$ depends on the low symmetry crystal field parameters P and Q. The spin Hamiltonian in the D_{2d} crystal field is written as

$$H_s=g_{/\!/}\mu_BH_zS_z+g_{\perp}\mu_B(H_xS_x+H_yS_y) +D\left[S_z^2-\frac{1}{3}S(S+1)\right]. \tag{3.7}$$

The g-values and D are represented as

$$g_{/\!/}=2+\frac{8}{3}\frac{k\zeta}{10Dq+X_0} \tag{3.8}$$

$$g_{\perp}=2+\frac{8}{3}\frac{k\zeta}{10Dq-(1/2)X_0} \tag{3.9}$$

$$D=\frac{4\zeta^2}{9}\left[\frac{1}{10Dq-(1/2)X_0}-\frac{1}{10Dq+X_0}\right] +\frac{1}{36}\sum_{n=1}^{5}|\langle{}^4A_2||V_{so}||{}^2T_2(n)\rangle|^2 \times\left[\frac{1}{E_n({}^2T_2)-(1/2)X_n}-\frac{1}{E_n({}^2T_2)+X_n}\right] \tag{3.10}$$

where $\zeta(=-3\lambda)$ is the spin-orbit interaction parameter, $k\equiv i/2\langle v|l_z|\zeta\rangle$, $X_0\equiv(1/\sqrt{3})P-(1/2)Q$, and $X_n\equiv(1/\sqrt{3})\langle{}^2T_2(n)||V(D_{2d})||{}^2T_2(n)\rangle$. The detailed forms of

$$\langle{}^4A_2||V_{so}||{}^2T_2(n)\rangle,\ \langle{}^2T_2(n)||V(D_{2d})||{}^2T_2(n)\rangle,$$

and $E_n({}^2T_2)$ are given in Appendix.

Recently, Kaufmann *et al.*[10] obtained the values of $g_{/\!/}$, $g_{\perp}$, and D for Co^{2+} in $CuGaS_2$ through ESR analysis. Their values are $g_{/\!/}=2.2147\pm0.0010$, $g_{\perp}=2.2326\pm0.0020$, and $|2D|=5.8\pm0.5$ cm^{-1}. Using these g-values and eqs. (3.8) and (3.9), we obtain $k\zeta=364.9\,\text{cm}^{-1}$ and $X_0=232.2$ cm^{-1}. The second term in eq. (3.10) is small compared to the first term which arises from the ${}^4T_2$ state. If we take into account only the ${}^4T_2$ term for the calculation of D, then we obtain $\zeta=595.5\,\text{cm}^{-1}$ ($\lambda=-198.5\,\text{cm}^{-1}$) and find D positive. This value is larger than the free ion value $\zeta=533\,\text{cm}^{-1}$. Weakliem[11] also obtained such anomalously high values of ζ 585 cm^{-1} for Co^{2+}:ZnS and 630 cm^{-1} for Co^{2+}:ZnO from the analysis of the optical spectra. If the second term of eq. (3.10) is retained for the calculation of D, it is expected to obtain a less value of ζ. Since, anyway, the spin-orbit interaction in Co^{2+} ion seems to be hardly reduced in the tetrahedral bonding crystals, we adopt the free ion value 533 cm^{-1} for ζ. Then, we get 0.69 for the reduction factor k of orbital angular momentum in the crystal. There remains the only parameter P (or Q) unfixed.

3.3 *Details of calculation*

3.3.1 *Energy levels*

We calculate the energy level splittings of the level bunch [${}^4T_1(2)$, ${}^2T_2(1)$, ${}^2A_1$] due to the

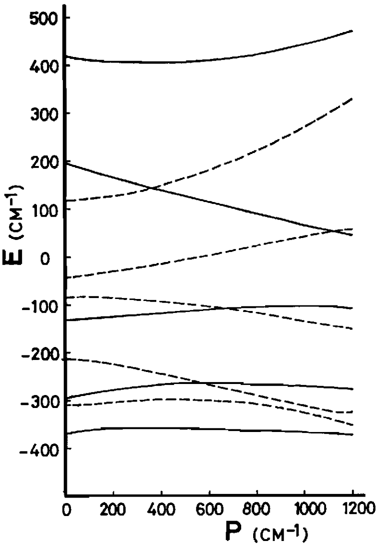

Fig. 5. Energy splitting diagram for the [${}^4T_1(2)$, ${}^2T_2(1)$, ${}^2A_1$] level bunch vs P. The solid lines represent the Γ_6 states and the dashed lines the Γ_7 states. The values of the parameters used are $B=500\text{cm}^{-1}$, $C=2200\text{cm}^{-1}$, $Dq=430\text{cm}^{-1}$, $\zeta=533\,\text{cm}^{-1}$, and $1/\sqrt{3}\,P-1/2Q=232.2\,\text{cm}^{-1}$.

low smmetry crystal field $V(D_{2d})$ and the spin orbit interaction for various values of P, using the adjusted values of the parameters, $B=500\,\mathrm{cm}^{-1}$, $C=2200\,\mathrm{cm}^{-1}$, $Dq=430\,\mathrm{cm}^{-1}$, $\zeta=533\,\mathrm{cm}^{-1}$, and $(1/\sqrt{3})P-(1/2)Q=232.2\,\mathrm{cm}^{-1}$. The split levels are classified into two groups, Γ_6 and Γ_7, where both Γ_6 and Γ_7 denote doubly degenerate irreducible representations of the D_{2d} double group. The obtained level scheme is shown in Fig. 5.

3.3.2 *Absorption intensity*

We calculate intensities of the optical transitions to the ${}^4T_1(1)$ state and the level bunch $[{}^4T_1(2), {}^2T_2(1), {}^2A_1]$ from the lowest level of the ground state ${}^4A_2$. The lowest level turns out to have Γ_6 symmetry in case $D>0$. The observed transitions are due to an electric dipole in Co^{2+}:ZnO and Co^{2+}:ZnS.[11] Judging from the fact and the magnitude of the observed intensities, we assume that the transitions in Co^{2+}:CuGaS_2 are also due to an electric dipole. Optical transitions between the ${}^4A_2$ state and the ${}^4T_1$ states become allowed by mixing of odd parity orbitals with the d orbitals for lack of inversion symmetry in the T_d crystal field.

We obtained the relative intensities of the transitions to all levels of the ${}^4T_1(1)$ state and the level bunch $[{}^4T_1(2), {}^4T_2(1), {}^2A_1]$. The total intensity of the transition to the ${}^4T_1(1)$ state is one half of that to the level bunch. It is seen from Fig. 1 that this calculated intensity ratio is in harmony with the observed spectra. The calculated intensity pattern for the level bunch is shown for $P=700\,\mathrm{cm}^{-1}$ in Fig. 6. The calculated pattern is in reasonable agreement with the observed spectra in Fig. 2, although the calculated relative intensity of the highest energy peak is too high compared with the experiment. The calculated patterns are rather insensitive to P, so that we obtain similar patterns to Fig. 6 in a range of P from $600\,\mathrm{cm}^{-1}$ to $800\,\mathrm{cm}^{-1}$: We cannot fix precisely the value of P. As one possible choice we adopt $P=700\,\mathrm{cm}^{-1}$ and $Q=344\,\mathrm{cm}^{-1}$ for the low symmetry field parameters. Using the values for P and Q, we calculate the intensity pattern for the ${}^4T_1(1)$ state and give it in Fig. 7. The total splitting agrees reasonably with the experiment, but a detailed comparison is not possible since we could not detect fine structures of the lower absorption band as yet. Further experimental study is in progress.

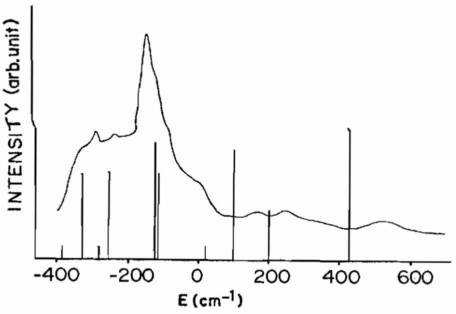

Fig. 6. The calculated absorption spectra in the energy region of the $[{}^4T_1(2), {}^2T_2(1), {}^2A_1]$ level bunch in case of $P=700\,\mathrm{cm}^{-1}$ and $Q=344\,\mathrm{cm}^{-1}$. The observed spectra are also shown for comparison.

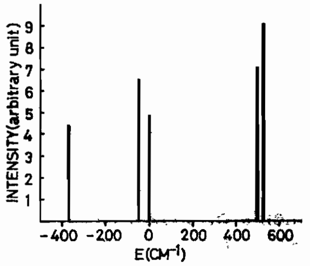

Fig. 7. The calculated absorption spectra in the energy region of the ${}^4T_1(1)$ state for $P=700\,\mathrm{cm}^{-1}$ and $Q=344\,\mathrm{cm}^{-1}$.

3.3.3 *Anisotropy constant D*

By substituting the values of the parameters fixed above into eq. (3.10), we get $D=2.54\,\mathrm{cm}^{-1}$. This is in a good agreement with the observed value $2.9\pm0.3\,\mathrm{cm}^{-1}$. The contribution of the ${}^2T_2$ states amounts to 9% of the calculated D.

§ 4. Concluding Remarks

We have obtained $P=700\,\mathrm{cm}^{-1}$ and $Q=344\,\mathrm{cm}^{-1}$, which reproduce the observed absorption spectra fairly well. These values are smaller by an order than the cubic field parameter $10\,Dq=4300\,\mathrm{cm}^{-1}$. Thus, it is reasonably justified to treat the low symmetry field as a perturbation of the cubic field for the I-III-VI_2 compounds. In the crystal the Racah parameter B of Coloumb repulsion is reduced to a half of the value ($997\,\mathrm{cm}^{-1}$) for a free Co^{2+} ion and the orbital angular momenta of d electrons are also reduced to 69% of the free ion values. On the other hand, the spin-orbit coupling constant ζ is not reduced even in the crystal. The same situations occur in cases of Co^{2+} ions in ZnO, ZnS, and CdS.[11] This is rather unusual for transition metal ions in crystals, however.

Detailed calculations of the electronic structure of a Co^{2+} ion and its vicinity are necessary for understanding of the reason why ζ of Co^{2+} ions are hardly reduced in the tetrahedral bonding crystals. These calculations, along with more refined experimental studies, are in progress.

Appendix

n	$E_n(^2T_2)$	$\langle ^2T_2(n)\|V(D_{2d})\|^2T_2(n)\rangle$	$\langle ^4A_2\|V_{so}\|^2T_2(n)\rangle$
1	$26.123B$	$0.3368P-0.1176Q$	$-4.845\,i\zeta$
2	$28.768B$	$0.6262P-0.3527Q$	$-1.230\,i\zeta$
3	$38.630B$	$-0.5453P+1.2202Q$	$1.186\,i\zeta$
4	$46.633B$	$0.3012P+0.2312Q$	$1.159\,i\zeta$
5	$72.046B$	$-0.7188P-0.9810Q$	$-0.516\,i\zeta$

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