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On the Structure of Cobalt Garnet, a New Synthetic Silicate Containing 8-Coordinated Cobalt(II)

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The X-ray structure of the CoO_8 unit in cobalt garnet, a new synthetic silicate of the composition $Co_3Al_2Si_3O_{12}$, is presented. The unit can be taken as a deformed cube, but its central Co^{II} is more regularly 8-coordinated than that in $[Co(NO_3)_4]^{2-}$ studied formerly by Bergman and Cotton.[5] The electronic spectrum and magnetic moment of cobalt garnet are discussed in comparison with those of two other silicates containing CoO_4 units.

Minerals are metallic complexes in nature, and their studies have played important roles in the development of crystal field theory.[1] Synthetic silicates are also of much interest from the standpoint of coordination chemistry.

This paper deals with the structure and some related properties of cobalt garnet, a new and interesting example of such synthetic silicates.

Experimental

Figure 1 and Table 1 were obtained using the data of Ohashi *et al.*[2] which are not explicity given in their original paper. Spectral measurements were made with a Hitachi Recording Spectrophotometer 323, using an electro-polished Al mirror as the standard. Magnetic measurements were made with a Shimadzu MB-2H Magnetic Balance, using Mohr's salt as the standard.

Results and Discussion

The structure of cobalt garnet, $Co_3Al_2Si_3O_{12}$, was recently analyzed by Ohashi *et al.*[2] This silicate was synthesized by the hydrothermal reaction of CoO, Al_2O_3 and SiO_2 at 900 °C and 50 kbar (1 bar=10^5 Pa), which took 3 h in a belt-type high pressure reaction vessel.[3] It has a structure which is common to natural garnets, *i.e.*, a three-dimensional network composed of tetrahedral SiO_4, octahedral AlO_6, and 8-coordinated $M^{II}O_8$ units.[4] Thus, in terms of coordination chemistry, it is a new example of 8-coordinated cobalt(II) complexes, of which only a limited number seems to be known at present.

A well-known example of such complexes is $[Co(NO_3)_4]^{2-}$, studied formerly by Bergman and Cotton.[5] In this complex, cobalt(II) is at the center of a dodecahedron of eight oxygen atoms, formed by the chelation of four nitrate ions around it. Two different sets of Co–O bonds exist, *i.e.*, one set of four bonds which are 2.03—2.11 Å long, and the other set of four bonds which are much longer (2.36—2.54 Å; 1 Å=10^{-1} nm). The dodecahedron can therefore be taken as a superposition of two deformed tetrahedra, one inside and the other outside, around the central cobalt(II).

The CoO_8 unit in cobalt garnet is, on the other hand, quite different in shape. Here the eight oxygen atoms around the central cobalt(II) form a severely deformed cube, as can be seen from the data in Fig. 1 and Table 1. Among the Co–O bonds, four are 2.21 Å long, and the other four are slightly longer (2.33 Å). The bonds of each set lie on a deformed plane ($O^AO^BO^CO^D$ and $O^EO^FO^GO^H$ in Fig. 1, respectively). The cobalt(II) in cobalt garnet is, therefore, much more "regularly" 8-coordinated than that in $[Co(NO_3)_4]^{2-}$.

To see the influence of such a structure on the electronic state of Co^{II}, the electronic spectrum and magnetic susceptibility of cobalt garnet were studied. The data on $Ca_2CoSi_2O_7$ and $Sr_2CoSi_2O_7$ with melilite structure,[6] containing tetrahedral CoO_4 units, were also obtained for the sake of comparison. These two compounds were

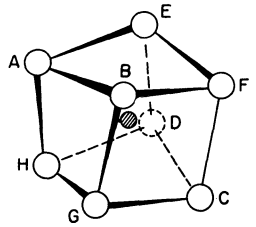

Fig. 1. Sketch of the CoO_8 unit in cobalt garnet. Each oxygen is bound tetrahedrally to two Co^{II}, each at the center of this type of CoO_8 unit, and also to a Si^{IV} and an Al^{III}, forming tetrahedral SiO_4 and octahedral AlO_6 units, respectively, around them.

Table 1. Bond lengths and angles of the polyhedron shown in Fig. 1.

Bond length	l/Å		
$Co-O^A=Co-O^B=Co-O^C=Co-O^D$	2.332(2)		
$Co-O^E=Co-O^F=Co-O^G=Co-O^H$	2.211(2)		
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
$\angle O^ACoO^B=\angle O^CCoO^D$	72.06	$\angle O^ACoO^E=\angle O^DCoO^H$	70.97
$\angle O^BCoO^C=\angle O^ACoO^D$	110.35	$\angle O^ACoO^G=\angle O^DCoO^F$	93.42
$\angle O^ACoO^C=\angle O^BCoO^D$	163.81	$\angle O^CCoO^G=\angle O^BCoO^F$	73.02
$\angle O^ECoO^F=\angle O^GCoO^H$	68.88	$\angle O^BCoO^H=\angle O^CCoO^E$	123.94
$\angle O^ECoO^H=\angle O^FCoO^G$	114.49		
$\angle O^ECoO^G=\angle O^FCoO^H$	161.05		

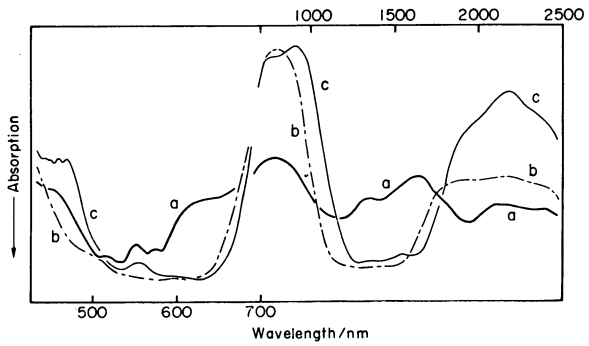

Fig. 2. Powder reflection spectra of cobalt garnet (a) and $Ca_2CoSi_2O_7$ (b) and $Sr_2CoSi_2O_7$ (c) with melilite structure.

synthesized by solid state reaction at 1 atm. The structure refinement of $Ca_2CoSi_2O_7$ has been carried out by Kimata.[7]

Figure 2 shows the reflection spectra of these three silicates. As a whole, there is a general resemblance between the spectrum of cobalt garnet and those of the other two, which, on the other hand, show the broad and split bands of tetrahedral Co^{II} ($\tilde{\nu}_3$ and $\tilde{\nu}_2$, or $^4A_2 \rightarrow {}^4T_1$ (P) and $\rightarrow {}^4T_1$(F)) at around 600 and 1300 nm, just like the spectrum of lusakite cited by Burns.[1] This resemblance is what one can expect, since the splitting of the d-orbitals in a quasi-cubic CoO_8 unit will be essentially similar to that in a tetrahedral CoO_4 unit.

One can now imagine that the ligand field strength (l.f.s.) in cobalt garnet will be nearly twice as large as in the two CoO_4 type silicates. In fact, the above-mentioned bands are shifted somewhat toward blue in cobalt garnet; moreover, a new set of bands appear at *ca.* 2000—2500 nm, which may correspond to the weak shoulders and humps observed on the curves of the CoO_4-type silicates at the same wavelength region, and may be due to the transition $\tilde{\nu}_1$, or $^4A_2 \rightarrow {}^4T_2$, which is sometimes observed in the infrared spectra of tetrahedral Co^{II} complexes. Nevertheless, all these spectral shifts are seemingly rather small, and one can even suppose that the l.f.s. of cobalt garnet and the other two silicates are quite comparable,†† although the broadness and complicated splittings of the bands hinder reliable comparison of the ligand field parameters.

The reason for the relatively weak l.f.s. in cobalt garnet may be in part found in the distortion of the cubic field, but it must be noted that the Co–O bond in it is much longer than the sum of the effective ionic radii of Co^{2+} (0.58 Å when 4-coordinated, as in melilite, and high-spin) and O^{2-} (1.38 Å when 4-coordinated, as in melilite and cobalt garnet).[8] In the case of Co-melilite, the Co–O bond length (1.926 Å) was slightly shorter than the corresponding sum (1.96 Å).[7]

†† This can be seen, for example, by comparing the data of Fig. 1 with those of Cotton *et al.* on the spectra of CoX_4^{2-} (X=Cl, Br, or I). The latter shows that the change from $CoCl_4^{2-}$ to $CoBr_4^{2-}$, where the l. f. s. (Dq) changes only less than 10%, causes quite remarkable shifts of $\tilde{\nu}_2$ and $\tilde{\nu}_3$.[9]

Table 2. μ_{eff} and θ values of the three silicates

Silicate	μ_{eff}/BM	θ/K
Cobalt garnet	4.57	−12
$Ca_2CoSi_2O_7$	4.17	−24
$Sr_2CoSi_2O_7$	4.13	−20

An apparent expansion of a metallic ion in going from 4- to 8-coordination was already reported to occur in many cases by Shannon,[8] who assigned an effective ionic radius of 0.90 Å to 8-coordinated Co^{II}, making use of the data of Bergman and Cotton.[5] Interestingly, this is in good agreement with the radius of Co^{2+} in cobalt garnet (0.89 Å), obtained by taking the mean of the two Co–O lengths in it and subtracting the radius of O^{2-} from it. Such an expansion, which should be due to the interligand repulsion and/or the attraction of O^{2-} ions toward the cations which are outside of the CoO_8 unit, will certainly enlarge the "box" of O atoms to accomodate Co^{II}, and diminish the l.f.s. acting on it considerably.†††

At any rate, therefore, it seems that the effect of the high coordination number in cobalt garnet is largely cancelled by this expansion, causing only relatively small changes in its spectral pattern in comparison with the two CoO_4-type silicates studied.[11]

The magnetic susceptibilities of the three silicates obey Curie-Weiss law down to liquid N_2 temperature, and the values of μ_{eff} and θ obtained from them are shown in Table 2. They are thus all high-spin d^7 complexes with no apparent magnetic anomaly.

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††† On the other hand, comparison of the spectra of the two CoO_4-type silicates indicates that the change from Ca to Sr lowers the values of $\tilde{\nu}_2$ and $\tilde{\nu}_3$, or weakens the l. f. s. around the Co^{2+} ions. This may be due to the expansion of the unit cell (the values of a(Å), c(Å), and V(Å^3) are: 7.844(1), 5.027(1), and 309.33(10) for $Ca_2CoSi_2O_7$, and 8.027(1), 5.161(1), and 332.55(9) for $Sr_2CoSi_2O_7$, respectively[10]), which will lead to the elongation of the Co–O bonds, and the decrease of the l. f. s.