

## OPTICAL SPECTRA OF CHROMIUM, NICKEL, AND COBALT-CONTAINING PYROXENES

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### ABSTRACT

Spectra have been obtained on synthetic  $\text{NaCrSi}_2\text{O}_6$  (jadeite type);  $\text{CaMg}_{1-x}\text{Co}_x\text{Si}_2\text{O}_6$ , and  $\text{CaMg}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$  (diopside type);  $\text{Mg}_{1-x}\text{Co}_x\text{SiO}_3$  and  $\text{Mg}_{1-x}\text{Ni}_x\text{SiO}_3$  (clinoenstatite type). All compounds exhibit spectra characteristic of the transition metal ions in an octahedral field. Only the cobalt compounds have spectra with the expected additional splittings from site distortion. The crystal field parameters  $Dq$  and  $B$  were calculated for all compounds and were used to show that  $\text{Ni}^{2+}$  orders on the  $M2$  site in clinoenstatite while  $\text{Co}^{2+}$  is predominantly on  $M(1)$ .

### INTRODUCTION

There has been a flood of papers describing the optical absorption spectra of iron in various minerals. Among the most interesting of these minerals are the iron-containing pyroxenes. The octahedral-field energy levels of  $\text{Fe}^{2+}$  are further split by the distorted field of the pyroxene cation coordination polyhedra. The result is a complex set of bands in the optical spectrum whose assignment and crystallographic interpretation has not yet been satisfactorily resolved. (Burns, 1966; White and Keester, 1966; Bancroft and Burns, 1967; White and Keester, 1967; Burns and Fyfe, 1967; Burns, 1968; Burns (1969).

An alternate route to interpretation of the spectra of natural pyroxenes is to examine the spectra of synthetic materials containing other ions of the first transition series. A further impetus is the possibility of mantle or lunar pyroxenes which contain more than trace amounts of transition elements other than iron.

This paper reports the optical spectra of pyroxene structures containing  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$ . The only spectra of these ions in metasilicates are those reported for a  $\text{Cr}^{3+}$ -containing diopside by Neuhaus and Reichartz (1958) Neuhaus (1960) and Grum-Grzhimailo (1960) and for some  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  containing metasilicates and metagermanates by Kaspar (1968).

Synthetic nickel diopside ( $\text{CaNiSi}_2\text{O}_6$ ) was prepared a number of years ago by Gjessing (1941) and was recently encountered by Biggar (1969) in a study of the system  $\text{CaO-NiO-SiO}_2$ . Biggar (1969) also suggested that cobalt diopside ( $\text{CaCoSi}_2\text{O}_6$ ) could be synthesized.

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Ureyite ( $\text{NaCrSi}_2\text{O}_6$ ) occurs naturally in meteorites and has been synthesized by Frondel and Klein (1965). Nickel metasilicate ( $\text{NiSiO}_3$ ) is unstable at atmospheric pressure (Biggar, 1969) and has not been prepared in any high-pressure studies. Cobalt metasilicate ( $\text{CoSiO}_3$ ) is also unstable at atmospheric pressure (Masse and Muan, 1965) but has been synthesized by Akimoto *et al.* (1965) at 20 kb and 800°C. Campbell and Roeder (1968) found that up to 13 mole percent  $\text{NiSiO}_3$  could be substituted into  $\text{MgSiO}_3$  at one atmosphere and 1400°C. No data are available on the extent of  $\text{CoSiO}_3$  substitution into  $\text{MgSiO}_3$ .

#### EXPERIMENTAL METHODS

Mixtures of a desired composition were prepared from the following reagent-grade chemicals: silicic acid,  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NiO}$ ,  $\text{CoCO}_3$ , and  $\text{Cr}_2\text{O}_3$ . These were mixed in an agate mortar, pressed into pellets, placed in a platinum container and heated in air. The nickel and cobalt diopsides were heated at 1275°C for six days and the enstatites at 1400°C for seven days. Each sample was removed from the furnace, reground, and repelletized twice during the heating. Ureyite was prepared according to the method of Frondel and Klein (1965) in which a slight excess of soda and silica are added to the stoichiometric mixture. This mixture was heated at 1100°C for 48 hours and slow-cooled to 500°C before removing from the furnace.

We found that with several of the cobalt-substituted diopsides the pellet was partially melted at 1275°C and that when lower temperatures were used the reaction did not go to completion. In order to prepare a more reactive starting mixture gels were made using Ludox<sup>1</sup> and the appropriate nitrates. Aliquots were mixed volumetrically and placed in an oven at 70°C. After setting, the gel was heated to 120°C to dehydrate it and to 650°C to decompose the nitrates. With these mixtures a single phase cobalt-substituted diopside could be prepared by heating at 1240°C for four days.

Phase identification was carried out primarily by X-ray diffraction powder techniques since the phases present in the products were often too fine-grained to be distinguished by optical microscopy. All specimens were single-phase material.

Cell parameters were determined by a least squares computer refinement (Evans *et al.*, 1963) of data from 15 to 28 unambiguously indexed reflections. The diffractometer was calibrated with a high-purity silicon standard ( $a = 5.4301 \text{ \AA}$ ).

<sup>1</sup> E. I. duPont de Nemours' ammonia-stabilized silica sol. Major impurities ~0.1 percent Al and ~0.05 percent Na.

Spectra were measured on a Beckman DK-2A spectrophotometer equipped with a diffuse reflectance attachment utilizing a BaSO<sub>4</sub>-coated integrating sphere. Specimens were ground to fine powder and their spectra measured using synthetic CaMgSi<sub>2</sub>O<sub>6</sub> in the reference beam. Spectra were measured on most specimens at 78°K using a specially designed liquid nitrogen dewar. The powders were packed into a brass block which was in direct contact with the liquid nitrogen. A diffuse reflectance measurement gives the absorption spectrum directly. No mathematical transformations are necessary.

The main difficulty with using diffuse reflectance methods on anisotropic crystals is that the polarization dependence of the absorption is lost. Unfortunately it does not appear feasible to prepare single crystals of sufficient size for measurement.

The precision of the reported band frequencies is limited by the difficulty in determining the peak position of the broad bands and by the pen-drive mechanism of the instrument itself. Expected accuracies are in the order of  $\pm 100$  cm<sup>-1</sup> above 10,000 cm<sup>-1</sup> and  $\pm 50$  cm<sup>-1</sup> below this value. All tabular data have been rounded to these limits.

## RESULTS

*Unit-cell parameters and X-ray data.* Table 1 is a list of the metasilicates which were prepared for optical spectra measurement along with their cell parameters. Ureyite was not included since indexed powder data and cell parameters have already been determined by Frondel and Klein (1965). The nickel diopside parameters of Gjessing (1941) are also listed. Recently, careful determinations of the cell parameters of synthetic diopside and low-clinoenstatite have been made (Rutstein and Yund, 1968 and Stephenson *et al.*, 1966) and these are included for comparison.

With our experimental procedure we were unable to prepare single-phase clinoenstatite with more than about 5 percent of Ni<sup>2+</sup> or about 15 percent of Co<sup>2+</sup> substituted for Mg<sup>2+</sup>. Campbell and Roeder (1968) report a 13 percent substitution of Ni<sup>2+</sup> for Mg<sup>2+</sup> at 1400°C. We believe that hydrothermal synthesis or much longer heatings could extend our solubility limits somewhat.

In Table 1 we see an expansion of the structure as large amounts of Co<sup>2+</sup> are substituted for Mg<sup>2+</sup> and a contraction as Ni<sup>2+</sup> is substituted for Mg<sup>2+</sup>. Biggar (1969) also noted that Ni<sup>2+</sup> compounds generally have smaller cell volumes than their Mg<sup>2+</sup> analogs although Ni<sup>2+</sup> was, for many years, thought to be larger than Mg<sup>2+</sup>. Shannon and Prewitt (1969) in their recent study of effective ionic radii list values for Ni<sup>2+</sup>, Mg<sup>2+</sup> and Co<sup>2+</sup> in six-fold coordinated oxides as 0.700, .720 and .735 Å respectively. These values are consistent with the cell parameter variation

TABLE 1. CELL PARAMETERS OF NICKEL AND COBALT PYROXENES

Composition	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta$
$\text{Ca}(\text{Mg}_{.8}\text{Ni}_{.2})\text{Si}_2\text{O}_6$	9.748 (4)	8.912 (4)	5.238 (2)	$105^\circ 48' \pm 3'$
$\text{Ca}(\text{Mg}_{.5}\text{Ni}_{.5})\text{Si}_2\text{O}_6$	9.747 (4)	8.913 (3)	5.237 (2)	$105^\circ 46' \pm 3'$
$\text{Ca}(\text{Mg}_{.2}\text{Ni}_{.8})\text{Si}_2\text{O}_6$	9.746 (5)	8.908 (3)	5.234 (3)	$105^\circ 46' \pm 4'$
$\text{CaNiSi}_2\text{O}_6$	9.739 (5)	8.902 (4)	5.228 (3)	$105^\circ 46' \pm 4'$
$\text{Ca}(\text{Mg}_{.8}\text{CO}_{.2})\text{Si}_2\text{O}_6$	9.765 (5)	8.938 (4)	5.251 (3)	$105^\circ 45' \pm 3'$
$\text{Ca}(\text{Mg}_{.5}\text{Co}_{.5})\text{Si}_2\text{O}_6^a$	9.769 (4)	8.940 (3)	5.248 (3)	$105^\circ 46' \pm 4'$
$\text{Ca}(\text{Mg}_{.2}\text{Co}_{.8})\text{Si}_2\text{O}_6^a$	9.780 (6)	8.950 (4)	5.249 (4)	$105^\circ 44' \pm 4'$
$\text{CaCoSi}_2\text{O}_6$	9.773 (6)	8.945 (5)	5.252 (4)	$105^\circ 45' \pm 4'$
$\text{Mg}_{.95}\text{Ni}_{.05}\text{SiO}_3$	9.618 (4)	8.819 (3)	5.175 (3)	$108^\circ 17' \pm 3'$
$\text{Mg}_{.95}\text{Co}_{.05}\text{SiO}_3$	9.615 (6)	8.829 (5)	5.175 (5)	$108^\circ 16' \pm 5'$
$\text{Mg}_{.90}\text{Co}_{.10}\text{SiO}_3$	9.616 (6)	8.832 (4)	5.174 (5)	$108^\circ 16' \pm 5'$
$\text{Mg}_{.85}\text{Co}_{.15}\text{SiO}_3$	9.623 (6)	8.833 (5)	5.175 (4)	$108^\circ 22' \pm 5'$
$\text{CaMgSi}_2\text{O}_6^b$	9.752 (2)	8.926 (2)	5.248 (2)	$105^\circ 50'$
$\text{MgSiO}_3^c$	9.6065 (11)	8.8146 (7)	5.1688 (6)	$108^\circ 20' \pm 1/2'$
$\text{CaNiSi}_2\text{O}_6^d$	9.67	8.88	5.25	$105^\circ 50'$

<sup>a</sup> Starting mixtures prepared by dehydrating a gel (see text).

<sup>b</sup> Rutstein and Yund (1968).

<sup>c</sup> Stephenson, Sclar and Smith (1966).

<sup>d</sup> Gjessing (1941).

in Table 1. The irregular variation of  $a$  and  $b$  for the Co-diopsides may be due to the effects of small amounts of impurities, especially Na and Al from the gel starting materials.

*Chromium-containing pyroxenes.* Ureyite,  $\text{NaCrSi}_2\text{O}_6$  has the diopside structure, space group  $C2/c$  with the  $\text{Cr}^{3+}$  on the more regular  $M_1$  site (Clark, Appleman and Papike, 1969). The powder is deep green and the reflectance spectrum is shown in Fig. 1. The two strong absorption bands at 15, 600, and 22,000  $\text{cm}^{-1}$  are characteristic of  $\text{Cr}^{3+}$  in 6-fold coordination (Poole, 1964).

The ground states of  $\text{Cr}^{3+}$ ,  $d^3$  configuration, and of  $\text{Ni}^{2+}$ ,  $d^8$  configuration, have identical symmetries. The energy levels are shown schematically in Fig. 2. Because a trivalent ion reacts strongly with the crystal field, the  ${}^4T_{1g}(P)$  level lies at high energy and is seldom observed. Complete diagrams which plot all energy levels as a function of the crystal

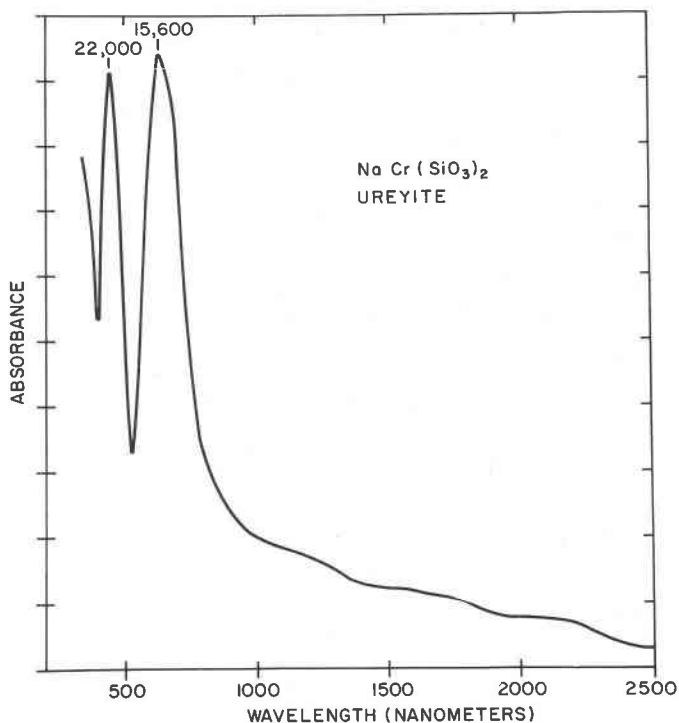


FIG. 1. Diffuse reflectance spectrum of ureyite.

field splitting parameter have been obtained by Berkes (1968) from a computer solution of the Tanabe-Sugano secular determinants.

The crystal field splitting parameter is given by  $Dq = 1/10 \nu_1$ . By analytically solving the Tanabe-Sugano matrices, an expression for the Racah parameter,  $B$  is obtained (Poole, 1964).

$$B = \frac{1}{3} \frac{(2\nu_1 - \nu_2)(\nu_2 - \nu_1)}{9\nu_1 - 5\nu_2}$$

These parameters are tabulated as compared with other chromium compounds in Table 2.

Comparison with the oxides is instructive. The  $Dq$  value is much smaller than the value for  $\text{Cr}^{3+}$  in ruby as would be expected from the interatomic distances. However,  $Dq$  for ureyite is also smaller than  $Dq$  for  $\text{Cr}_2\text{O}_3$  which is surprising in view of the nearly equal interatomic distances. The Racah parameter,  $B$ , of ureyite is much larger than  $B$  in  $\text{Cr}_2\text{O}_3$  and is even slightly larger than  $B$  of  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$ . This implies a more ionic Cr—O bond in ureyite compared with  $\text{Cr}_2\text{O}_3$ .

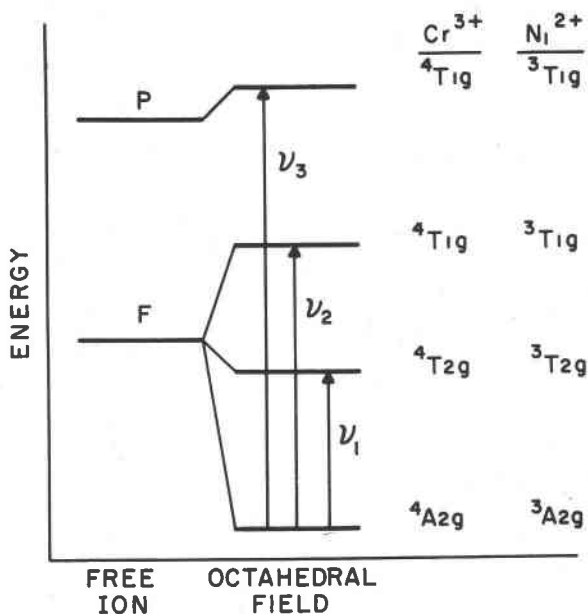


FIG. 2. Schematic energy level diagram for  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  in an octahedral crystal field. Labeling of energy levels and notation for transitions are shown.

*Nickel-containing pyroxenes.* Nickel will substitute into diopside in all proportions. The powders are yellow-green and a typical reflectance spectrum of the end member  $\text{CaNiSi}_2\text{O}_6$  is shown in Figure 3. The frequencies of the bands and their assignments are tabulated in Table 3. The agreement with Kasper (1968) is not particularly good. Spectra of all solid solutions from  $\text{CaNiSi}_2\text{O}_6$  to  $\text{CaNi}_{0.2}\text{Mg}_{0.8}\text{Si}_2\text{O}_6$  show the same features except that at low nickel concentrations an additional weak

TABLE 2. CRYSTAL FIELD PARAMETERS FOR  $\text{Cr}^{3+}$  COMPOUNDS

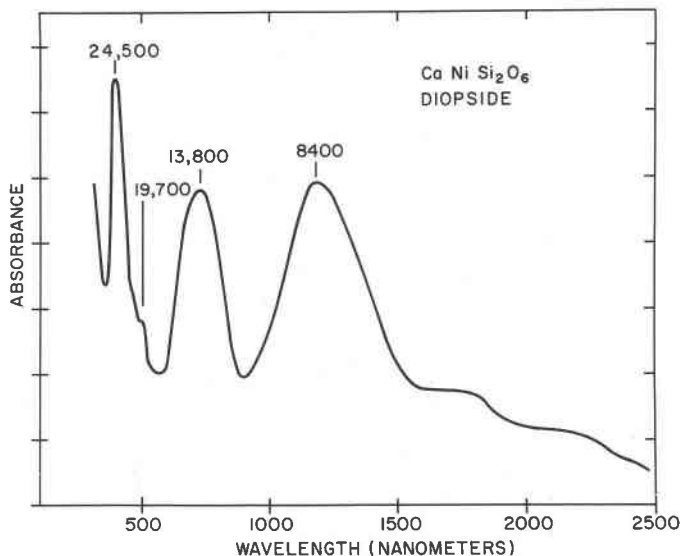
Compound	$Dq$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	M-O ( $\text{\AA}$ )
Free $\text{Cr}^{3+}$	—	918 <sup>a</sup>	—
$\text{Al}_{1.95}\text{Cr}_{0.05}\text{O}_3$	1780	664 <sup>b</sup>	1.97 (3) 1.86 (3) <sup>c</sup>
$\text{Cr}_2\text{O}_3$	1660	478 <sup>b</sup>	2.02 (3) 1.97 (3) <sup>c</sup>
$\text{NaCrSi}_2\text{O}_6$	1560	646	2.039 (2) 2.039 (2) <sup>d</sup> 1.947 (2)

<sup>a</sup> Calculated from Moore's (1952) tables.

<sup>b</sup> Poole (1964).

<sup>c</sup> Newnham and DeHaan (1962).

<sup>d</sup> Clark, Appleman, and Papike (1969).

FIG. 3. Diffuse reflectance spectrum of  $\text{CaNi}(\text{SiO}_3)_2$ .

spin-forbidden band is resolved at high frequencies. Spectra at liquid nitrogen temperature also exhibit the same features shown in Figure 3. No frequency shifts were measurable. The relative band intensities also change very little. The main effect of low temperature is to sharpen and enhance the intensity of the spin-forbidden bands. Two weak broad bands at  $5550$  and  $4400\text{ cm}^{-1}$  appear indistinctly on Figure 3. These become more distinct at low temperatures but do not change intensity. Their origin is not known.

A spectrum of  $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{SiO}_3$  with the clinoenstatite,  $P2_1/c$ , structure

TABLE 3. BAND FREQUENCIES AND ASSIGNMENTS FOR NICKEL-CONTAINING PYROXENES. ALL FREQUENCIES ARE IN  $\text{CM}^{-1}$ 

Band	$\text{CaMg}_{1-x}\text{Ni}_x\text{Si}_2\text{O}_6$			$\text{Mg}_{1-x}\text{Ni}_x\text{SiO}_3$		Assignment
	$x=1.0$	0.20	0.10 (Kasper 1968)	$x=0.05$	$x=0.05$ (Kasper 1968)	
$\nu_1$	8,400	8,400	7,800	6,900	6,650	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
$\nu_2$	13,800	13,500	12,800	12,700	12,600	$\rightarrow {}^3T_{1g}(F)$
—	19,700	19,800	—	—	—	$\rightarrow {}^1T_{2g}(D)$
—	21,200	21,300	20,800	21,900	21,500	$\rightarrow {}^1T_{1g}(G)$
$\nu_3$	24,500	24,500	23,700	24,500	24,500	$\rightarrow {}^3T_{1g}(P)$
—	—	30,000	—	—	—	$\rightarrow {}^1T_{2g}, {}^1E_g(G)$

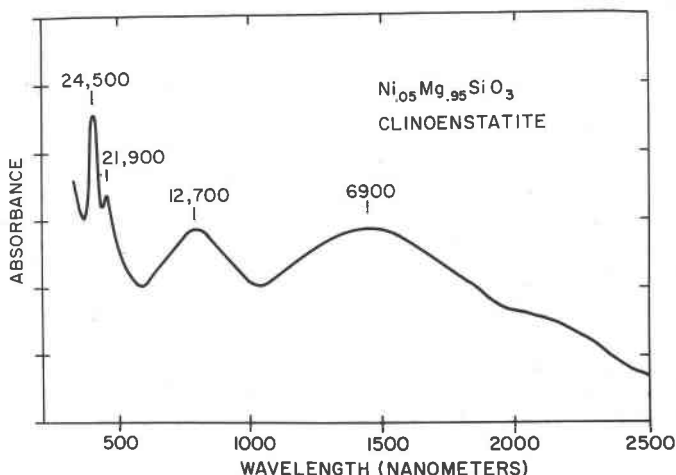


FIG. 4. Diffuse reflectance spectrum of  $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{SiO}_3$ .

is shown in Figure 4. The powder is yellow. The frequencies of the bands are tabulated in Table 3. Except for the large frequency shifts, the general appearance of the spectrum is much like that of  $\text{Ni}^{2+}$  in the diopside structure. The agreement with Kaspar's (1968) spectrum is very good. The band at  $21,900\text{ cm}^{-1}$  seems to be more intense than the corresponding band in diopside. The  $12,700$  and  $6900\text{ cm}^{-1}$  bands in Ni-clinoenstatite have larger half widths than the corresponding bands in Ni-diopside. Cooling the powder to  $78^\circ\text{K}$  has little effect on the spectrum. No additional bands or frequency shifts were observed. The weak bands at low frequencies appear as a broad shoulder in Figure 4, but are resolved into two weak bands at  $5220$  and  $4460\text{ cm}^{-1}$  in the  $78^\circ\text{K}$  spectrum.

The spectra of the nickel-containing pyroxenes are very similar to those expected from  $\text{Ni}^{2+}$  in octahedral coordination. No additional splittings or bands were observed. Crystal field parameters can be calculated from the band frequencies (using the notation defined by Fig. 2) by

$$Dq = \frac{1}{10} \nu_1$$

$$B = \frac{1}{3} \frac{(\nu_3 - 2\nu_1)(\nu_3 - \nu_1)}{(5\nu_3 - 9\nu_1)}$$

The values obtained are listed in Table 4. The Racah parameter,  $C$  does not appear in the matrices for the spin-allowed bands and was not calculated. It affects only the positions of the singlet levels. There is no conclusive explanation for the enhancement of intensity in the  ${}^1T_{2g}$  band in



TABLE 4. CRYSTAL FIELD PARAMETERS FOR  $\text{Ni}^{2+}$  COMPOUNDS

Compound	$Dq$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$M-O$ ( $\text{\AA}$ )
Free $\text{Ni}^{2+}$	—	1030 <sup>a</sup>	—
$\text{MgO}:\text{Ni}^{2+}$	860	858 <sup>b</sup>	2.106 <sup>c</sup>
$\text{CaNiSi}_2\text{O}_6$	840	881	2.115 (2) 2.065 (2) 2.050 (2) Ave. = 2.077 <sup>d</sup>
$\text{Ni}_{.05}\text{Mg}_{.95}\text{SiO}_3$	690	1039	2.12, 2.02, 2.06, 2.05 2.33, 2.29 Ave. = 2.15  2.17, 2.02, 2.21 2.00, 1.96, 2.04 Ave. = 2.07
			M(2)
			M(1)

<sup>a</sup> Calculated from Moore's (1952) tables.

<sup>b</sup> Low (1958).

<sup>c</sup> Calculated from  $a$  of Swanson and Tatge (1953).

<sup>d</sup> Clark, Appleman, and Papike (1969) for diopside.

<sup>e</sup> Morimoto, Appleman, and Evans (1960) for the Mg-end member.

Ni-clinoenstatite. Enhancement of intensity of spin-forbidden bands has been observed in borate glasses by Berkes and White (1966) and was explained by spin-orbit coupling between closely spaced singlet and triplet levels as suggested by Liehr and Ballhausen (1959). Too few spin-forbidden bands were observed to justify a calculation of the complete energy level diagram with spin-orbit coupling as was done by Berkes and White (1966).

*Cobalt-containing pyroxenes.* Cobalt can be substituted for magnesium in diopside to give compounds with a deep pink-to-lavender color. Two typical spectra are shown in Figure 5 and the frequencies of all compounds examined are listed in Table 5. The variation in frequency with changing cobalt concentration is small and erratic. Spectra taken at liquid nitrogen temperature are nearly identical to those taken at room temperature. There is a sharpening of some bands but no systematic frequency shifts are observed. The most significant feature in the spectra is the band near  $15,000\text{ cm}^{-1}$ . The spectra of compounds with 0.5 and 0.8 fraction of  $\text{Co}^{2+}$  exhibit a sharp distinct band near  $14,400\text{ cm}^{-1}$ . Spectra of  $\text{CaMg}_{0.8}\text{Co}_{0.2}\text{Si}_2\text{O}_6$  and  $\text{CaCoSi}_2\text{O}_6$  have only a shoulder which has shifted in frequency to  $15,000\text{ cm}^{-1}$  or higher. The compounds with the distinct bands were prepared from gels while the compounds with the shoulder were prepared from oxides and carbonates. Likewise the  $7700\text{ cm}^{-1}$  band of

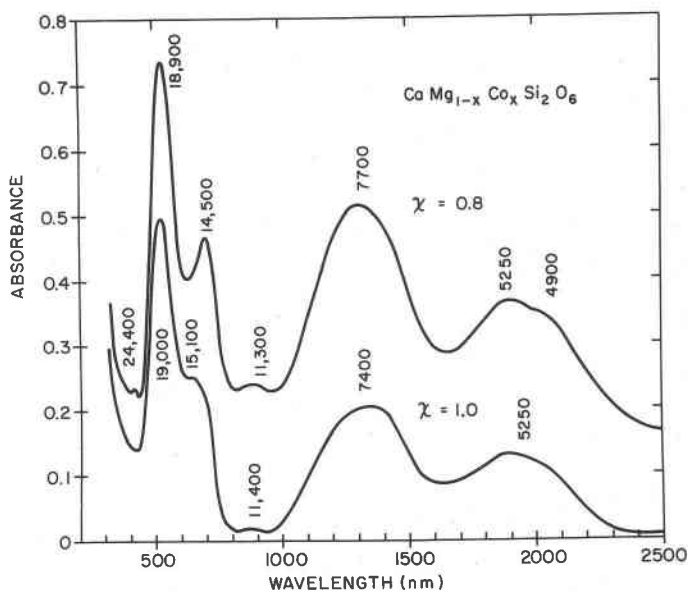


FIG. 5. Diffuse reflectance spectra of  $\text{CaMg}_x\text{Co}_{1-x}\text{Si}_2\text{O}_6$ . Bands are labeled with their frequency in  $\text{cm}^{-1}$ .

the gel-prepared material shifts significantly to  $7400\text{ cm}^{-1}$  in the oxide-prepared material. Other bands in the spectra do not seem to be sensitive to the starting materials (Table 5).

Pyroxenes with the clinoenstatite structure containing from 0.05 to 0.15 fraction  $\text{Co}^{2+}$  were prepared as pink powders. A typical spectrum is shown in Figure 6 and the frequencies are tabulated in Table 5. In

TABLE 5. BAND FREQUENCIES AND ASSIGNMENTS FOR COBALT-CONTAINING PYROXENES. ALL FREQUENCIES ARE IN  $\text{CM}^{-1}$

$\text{CaMg}_{1-x}\text{Co}_x\text{Si}_2\text{O}_6$				$\text{Mg}_{1-x}\text{Co}_x\text{Si}_2\text{O}_6$				Assignment
$x=0.2$	0.5	0.8	1.0	$x=0.05$	0.10	0.15	0.15 (78°K)	
		4,900						
5,200	5,250	5,250	5,250	6,200	6,250	6,250	6,250	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$
7,900	7,300	7,700	7,400	8,200	8,300	8,200	8,250	
—	11,500	11,300	11,400	13,100 <sup>a</sup>	13,200 <sup>a</sup>	13,100 <sup>a</sup>	13,300 <sup>a</sup>	$\rightarrow {}^2\text{E}_g(\text{G})$
15,400	14,400	14,500	15,100	15,500	15,700	15,600	15,700	$\rightarrow {}^4\text{A}_{2g}(\text{F})$
—	—	—	—	—	—	—	17,700	$\rightarrow {}^2\text{T}_{2g}{}^2\text{T}_{1g}(\text{G})$
19,000	19,000	18,900	19,000	20,200	20,200	20,200	20,500	$\rightarrow {}^4\text{T}_{1g}(\text{P})$
24,400	24,400	24,400	—	24,000	24,000	—	24,400	$\rightarrow {}^2\text{A}_{1g}(\text{G}), {}^2\text{T}_{1g}(\text{P, H})$

<sup>a</sup> May actually be  ${}^4\text{A}_{2g}(\text{F})$  of  $\text{Co}^{2+}$  on M(2) site. See text.

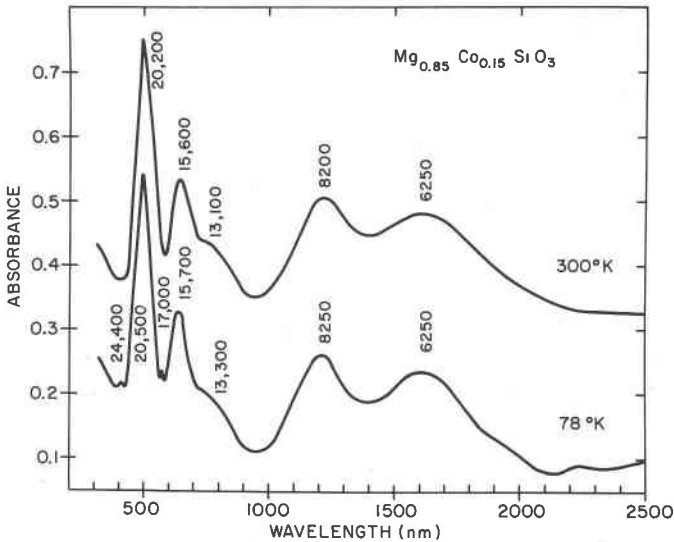


FIG. 6. Diffuse reflectance spectra of  $Mg_{1-x}Co_xSiO_3$  at room temperature and at liquid nitrogen temperature. Band frequencies are given in  $cm^{-1}$ .

general appearance the spectra are very similar to those of the diopside structures. Kasper (1968) reports the spectrum of a single cobalt-containing  $MgSiO_3$ . His frequencies are in fair agreement with our study but the assignments are markedly different. Spectra taken at liquid nitrogen temperature are sharper and several spin-forbidden bands appear (Fig. 6). The strongest band in the spectrum, near  $20,000\text{ cm}^{-1}$ , exhibits some additional splitting which is only partially resolved. Figure 7 shows this band in expanded scale.

Assignments for the  $Co^{2+}$  spectra and calculation of the crystal field parameters pose some additional difficulties. Consider first the diopside structure. It is fairly certain for crystal chemical reasons that  $Co^{2+}$  substitutes only for  $Mg^{2+}$  on the  $M1$  site. The energy level diagram for  $Co^{2+}$  is shown in Figure 8. The heavy lines are the quartet levels which account for the spin-allowed transitions. Some of the spin-forbidden doublet levels are shown as light lines. The strong band at  $19,000\text{ cm}^{-1}$  is in good agreement, in position, shape and intensity, with the  ${}^4T_{1g}(P)$  transition observed in  $MgO:Co^{2+}$  (Pappalardo, Wood, and Linares, 1961) and in  $CoO$  (Pratt and Coelho, 1959), and this assignment seems reliable. The band at  $14,500\text{ cm}^{-1}$  has three possible assignments: as a component of  ${}^4T_{1g}(P)$  split off from the main band by the distorted crystal field of the  $M(1)$  coordination polyhedron, as the  ${}^4A_{2g}(F)$  level, and as a spin-forbidden level derived from the  ${}^2G$  state with enhanced intensity and line width.

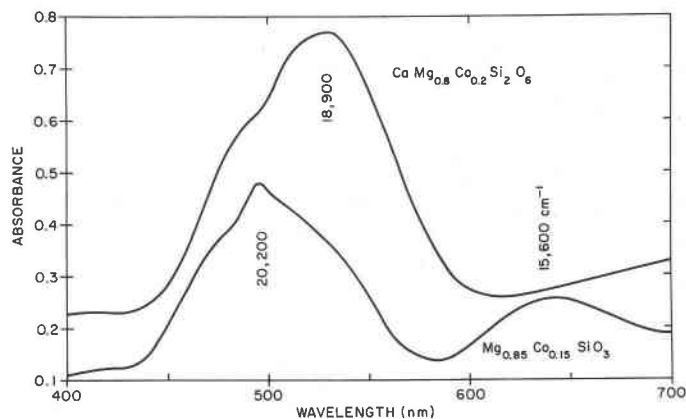


FIG. 7. Comparison of band contours of the  ${}^4T_{1g}(P)$  transition of  $\text{Co}^{2+}$  in diopside and in clinoenstatite.

It is assigned to  ${}^4A_{2g}$ . The  ${}^4A_{2g}$  level was not observed in  $\text{MgO}:\text{Co}^{2+}$  or  $\text{CoO}$ , although its calculated position is in the  $15,000\text{--}17,000\text{ cm}^{-1}$  region. Ballhausen (1962) shows that the intensity of this band is expected to be weak because it corresponds to a 2-electron jump. Its enhanced intensity in the diopside structure is possibly due to the site distortion which permits orbital mixing with other states. This leaves the lowest  ${}^4T_{2g}(F)$  level to be assigned and there are two candidate bands at  $7700$  and  $5250\text{ cm}^{-1}$ . If the  $7700\text{ cm}^{-1}$  band is  ${}^4T_{2g}(F)$ , then the  $5550$  could be assigned to the highest component of the  ${}^4T_{1g}(F)$  ground state split by the distorted crystal field. However, this choice leads to unreasonably low values for  $Dq$  ( $680\text{ cm}^{-1}$ ) for an ion on a  $\text{Mg}^{2+}$  site. If the  $5250\text{ cm}^{-1}$  band is  ${}^4T_{2g}$ ,  $Dq$  becomes  $925\text{ cm}^{-1}$ , a reasonable value, but there is no available level for the assignment of the  $7700\text{ cm}^{-1}$  band. This dilemma is resolved by assuming both bands to be components of  ${}^4T_{2g}$  and using their mean as the energy of the  ${}^4T_{2g}$  level. These assignments are listed in Table 5.

The clinoenstatite structure has two cation sites which must be considered, but the spectrum of  $\text{Co}^{2+}$  in clinoenstatite is almost identical to the spectrum of  $\text{Co}^{2+}$  in diopside. The same assignments are proposed.

It is now possible to calculate the crystal field parameters. From the Tanabe-Sugano matrices it can be shown that

$$Dq = \frac{1}{10} [\nu({}^4A_{2g}(F)) - \nu({}^4T_{2g}(F))]$$

$Dq$  values are tabulated in Table 6 using the mean of the two bands assigned to  ${}^4T_{2g}(F)$ . The Racah B parameter is related to the separation

TABLE 6. CRYSTAL FIELD PARAMETERS FOR  $\text{Co}^{2+}$  COMPOUNDS

Compound	$Dq$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$M-O$ ( $\text{\AA}$ )
Free $\text{Co}^{2+}$	—	963 <sup>a</sup>	—
$\text{MgO}:\text{Co}^{2+}$	927	845 <sup>b</sup>	2.106 <sup>c</sup>
$\text{CoO}$	888	780 <sup>d</sup>	2.130 <sup>e</sup>
$\text{CaMg}_{0.2}\text{Co}_{0.8}\text{Si}_2\text{O}_6$	802	864	Unknown
$\text{Mg}_{0.85}\text{Co}_{0.15}\text{SiO}_3$	837	936	Unknown—probably similar to $\text{MgSiO}_3$ (table 4)

<sup>a</sup> Calculated from Moore's (1952) tables.

<sup>b</sup> Pappalardo, Wood, and Linares (1961).

<sup>c</sup> Calculated from  $a$  of Swanson and Tatge (1953).

<sup>d</sup> Pratt and Coelho (1959).

<sup>e</sup> Calculated from  $a$  of Swanson *et al.* (1960).

between the excited  ${}^4T_{1g}(P)$  level and the ground state  ${}^4T_{1g}(F)$  level. Taking the difference between the roots of the Tanabe-Sugano secular equation yields the expression

$$\nu(T_{1g}(P)) = [100 Dq^2 + 180 DqB + 225 B^2]^{1/2}$$

Values for  $B$  are also tabulated in Table 6.

The only claim that can be made for the assignments and calculated parameters is that they are internally consistent insofar as the powder spectra are concerned. Figure 8 is a Tanabe-Sugano diagram for  $\text{Co}^{2+}$  taken from the compilation of Berkes (1968). The agreement for the spin-allowed transitions is good. The assignments for the spin-forbidden transitions were taken from this diagram. The position of these levels is strongly a function of the Racah  $C$  parameter. Since several levels fall close together, no attempt was made to compute revised values for  $C$ .

Two problems make the derived parameters uncertain. The first is that the splitting of the ground state is unknown. The  $B$  parameter for the pseudooctahedral field should be calculated from the separation of the mid-points of the components separated by the field distortion. This choice has been made for the excited  ${}^4T_{1g}(P)$  level. The transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  will originate from the lowest component of  ${}^4T_{1g}(F)$  and this could be as much as  $1000 \text{ cm}^{-1}$  lower than the mid-point. The agreement between the calculated  $B$ -values and the  $B$ -value for cobalt-doped  $\text{MgO}$  suggests that the ground state splitting is small, but it remains an unknown error in the parameter.  $Dq$  is determined from a frequency difference and the position of the ground state cancels out. However, the  ${}^4T_{2g}(F)$  level should separate into three components in a distorted field. Only two are definitely observed. If the lower frequency band is really

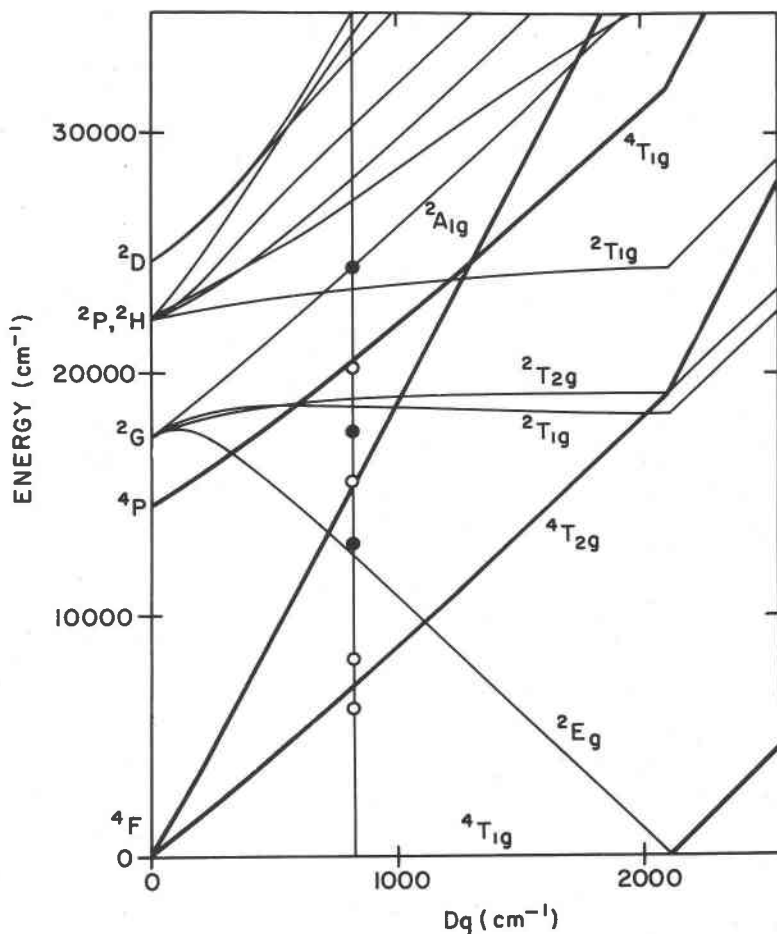


FIG. 8. Energy level diagram for  $\text{Co}^{2+}$  in an octahedral field. Racah parameters used in calculation:  $B=971 \text{ cm}^{-1}$ ,  $C=4497 \text{ cm}^{-1}$ . After Berkes (1968). Band frequencies for Colclonopyroxene shown by open circles for spin-allowed and filled circles for spin-forbidden transitions. Heavy lines are quartet levels (spin-allowed). Light lines are doublet levels (spin-forbidden).

two levels as is indicated by a slight splitting (shown in Fig. 5), then the  $Dq$  values would be raised by  $50 \text{ cm}^{-1}$ . If, on the other hand, the third component lies at very low frequencies, below the range of the instrument,  $Dq$  would be increased even more. This last possibility does not seem likely but cannot be completely ruled out. In general, the analysis of the spectra can go no further until the polarization dependence from single crystal spectra is known.

## DISCUSSION AND CONCLUSIONS

*Site populations.* The distribution of transition elements between crystallographically distinct sites in a crystal is currently of considerable interest. The transition ions  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  would be expected to substitute onto the smaller  $M1$  site in the diopside structure and this is what is indeed observed. The  $Dq$  value for each ion in the diopside structure is close to the  $Dq$  value for the pure oxide or the ion in an  $\text{MgO}$  host. The average interatomic distances of the  $M1$  site in diopside are sufficiently close to those in  $\text{MgO}$  that the comparison is valid. On the other hand, substitution on the large 8-fold Ca-site would cause a large lowering in  $Dq$ . The situation is not quite as exact as one would like. The average metal-oxygen distance in ureyite and  $\text{Cr}_2\text{O}_3$  are almost identical, yet  $Dq$  is  $100\text{ cm}^{-1}$  smaller in ureyite. The careful refinement of  $\text{CaMgSi}_2\text{O}_6$  by Clark, Appleman and Papike (1969) gives an average bond length for the  $M1$  site that is significantly smaller than the bond length in  $\text{MgO}$  which should result in a larger  $Dq$ . In reality  $Dq$  is a little smaller for Ni-diopside, which the cell parameters indicate has a nickel-oxygen distance very close to that of magnesium-oxygen. Little can be said about  $\text{CaCoSi}_2\text{O}_6$  because of the uncertainty in  $Dq$  and because of the lack of structural data. To what extent the small discrepancies are the result of site distortion is not yet known.

The crystal field parameter for  $\text{Ni}^{2+}$  in clinoenstatite is  $690\text{ cm}^{-1}$ , much smaller than  $Dq$  for either nickel diopside,  $840\text{ cm}^{-1}$ , or nickel-doped  $\text{MgO}$ ,  $860\text{ cm}^{-1}$ . This seems strong evidence the  $\text{Ni}^{2+}$  in clinoenstatite orders on the larger  $M2$  site. Further evidence is provided by the Racah  $B$  parameter which is essentially equal to the free ion value—evidence for a small interaction between  $\text{Ni}^{2+}$  and its surroundings. The relation

$$Dq = KR^{-5}$$

where  $K$  is a constant of proportionality and  $R$  is the metal-oxygen distance, can be applied.

$$Dq(M2) = Dq(\text{diopside}) \left[ \frac{R(\text{diopside})}{R(M2)} \right]^5$$

Using the values in Table 4, the expected  $Dq$  for  $\text{Ni}^{2+}$  on  $M2$  is  $706\text{ cm}^{-1}$ , in good agreement with the observed value of  $690\text{ cm}^{-1}$ . If  $\text{Ni}^{2+}$  were on the  $M1$  site, the  $Dq$  value should be approximately the same as in diopside.

$Dq$  for  $\text{Co}^{2+}$  in clinoenstatite is similar to the value in diopside, although  $B$  is somewhat larger. This provides circumstantial evidence that  $\text{Co}^{2+}$  is mainly on the  $M1$  site. The spectra do not rule out the possibility

of some  $\text{Co}^{2+}$  also on the  $M2$  site. Indeed the rather broad shoulder at  $13,100\text{ cm}^{-1}$  in Figure 6 may represent the  ${}^4A_{2g}$  transition of  $\text{Co}^{2+}$  on  $M2$ . This transition would be expected to lie at lower frequencies because of the smaller  $Dq$ .

Burns (1970) has recently made predictions of the site distribution of transition elements in various silicates based on crystal field stabilization energies, ion sizes, and site distortions. Although Burns does not specifically make predictions for the clinoenstatite structure, this structure is sufficiently similar to orthoenstatite that the same predictions should apply.  $\text{Co}^{2+}$  should occur on the  $M2$  site because of site distortion and  $\text{Ni}^{2+}$  should occur on  $M1$  because of the increased crystal field stabilization energy. Our data indicate exactly the opposite. While the site distribution of  $\text{Co}^{2+}$  could be disputed because of the uncertainty in the band assignments, the data for  $\text{Ni}^{2+}$  seem reasonable. There is no obvious explanation for the location of  $\text{Ni}^{2+}$  on the  $M2$  site when a larger stabilization energy could be realized on  $M1$ .

*Effects of site distortion.* The spectra of these transition metal pyroxenes are surprisingly simple when compared with the spectra  $\text{Fe}^{2+}$ -containing pyroxenes.  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ , both of which have orbitally symmetric,  $A_{2g}$ , ground states exhibit no additional splitting of bands. The low symmetry of the cation sites should split all triply degenerate levels into three components and the large variations in metal-oxygen distances (Table 4) should insure a large separation between these components. The splitting of the ground state  $T_{2g}$  level in  $\text{Fe}^{2+}$  with one electron outside the half-filled shell is on the order of  $4000\text{--}5000\text{ cm}^{-1}$  (Bancroft and Burns, 1967; White and Keester, 1967). The excited state  $T_{2g}(F)$  level of  $\text{Co}^{2+}$ , with two electrons outside the half-filled shell is split by  $2000\text{ cm}^{-1}$  and such evidence as we have suggests that the ground state  $T_{1g}(F)$  level has only a small splitting.  $\text{Cr}^{3+}$  in which the  $t_{2g}$  orbital is half full and  $\text{Ni}^{2+}$  with a full  $t_{2g}$  orbital, exhibit at most very small splittings which are not detectable on the diffuse reflectance spectra of powders. These ions, therefore, make very poor probes of their environment except that their spectra are sensitive to average metal-oxygen distances of the coordination polyhedron.

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