FIG. 94. Polarized electronic absorption spectra of Cr-bearing actinolite [from Goldman (1977)].

in their β and γ spectra that will tend to obscure any Mn bands; however, these may be apparent in the α spectra. Figure 93 shows the spectra of a tremolite containing significant Cr^{3+}. The broad intense bands at ~ 15400 cm^{-1} and 22200 cm^{-1} are (spin-allowed) d–d transitions of Cr^{3+}, with the sharp bands at ~ 14400 cm^{-1} and ~ 14600 cm^{-1} being spin-forbidden transitions. Figure 94 shows the spectrum of an actinolite with significant Cr^{3+}. The bands at ~ 15400 cm^{-1} are definitely characteristic, particularly in the α spectrum; without the α spectrum, it is feasible that these could be confused with an Fe^{2+}–Fe^{3+} IVCT band.

MISCELLANEOUS SPECTROSCOPIC METHODS AND AMPHIBOLES

The work summarized here has generally been exploratory in nature, and thus extensive characterization of amphiboles has not yet been done. Nevertheless, such studies indicate both the potential and the drawbacks of such methods

when examining materials as complex as amphiboles.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (ESCA, electron spectroscopy for chemical analysis) may be used to examine relative core-binding energies (electron-orbital energy levels) of atoms in crystals. In principle, this technique should have wide application in studies on site-population characterization and chemical bonding in minerals, and early studies (Yin et al. 1971, Huntress & Wilson 1972) suggested that this might be the case. However, more extensive studies on a wide variety of silicate minerals (Adams et al. 1972) indicate that there are important limitations to this technique. Firstly, lines of paramagnetic ions (e.g., Fe^{2+} and Fe^{3+}) are very broad because of exchange interaction. No energy differences were observable between Fe $2P$ binding energies of Fe^{2+} (in hedenbergite) and Fe^{3+} (in epidote); in addition, there was no

TABLE 56. BINDING ENERGIES IN AMPHIBOLES, DETERMINED BY X-RAY PHOTOELECTRON SPECTROSCOPY

		Fe $2p_{1/2}$	Fe $2p_{3/2}$	Fe 3s	Mg 2s	Si 2p	C1s	O1s
Crocidolite[1]	B.E.[3]	723.4(8)	710.3(6)	92.6(6)	-	102.4(5)	284.8(4)	-
	P.W.	7.0	7.2	3.8	-	2.4	2.3	2.9
Anthophyllite[2]	B.E.[4]	-	-	-	88.4(5)	101.9(5)	-	531.1(5)
	P.W.	-	-	-	3.1	2.6	-	2.8

[1]Magnesio-riebeckite(3), Appendix A; [2]Anthophyllite(8), see Appendix F,G; [3]absolute B.E. (binding energy in eV) determined by assigning the O1s level as 530.8(7) eV; [4]absolute B.E. by assigning the C1s level as 284.6(5) eV. P.W. = peak width

significant broadening in the iron lines in crocidolite where contributions of both Fe^{2+} and Fe^{3+} occur. Diamagnetic ions (e.g., Mg^{2+}, Al^{3+}, O^{2-}) have much narrower line-widths, but the technique cannot yet detect with any certainty energy differences due to differing structural environment, although Adams et al. (1972) noted that O1s line widths are slightly narrower in minerals containing one type of oxygen (i.e., bridging or nonbridging) than in minerals containing both types of oxygen (cf. Yin et al. 1971). With increase in resolution due to improved instrumentation and the use of more sophisticated methods of numerical resolution (Mendes & de Polignac 1973), this technique may be useful in mineralogical studies. Results on amphiboles are summarized in Table 56.

Diffuse-reflectance spectroscopy

This technique is fairly similar to optical-absorption spectroscopy, the principal difference being that the experimental arrangement is in the reflection rather than the transmission geometry. Only a limited amount of data on amphiboles is available. Hunt & Salisbury (1970) presented spectra for two samples of tremolite, two of actinolite and three of hornblende, none of which were characterized in any other way; the principal features noted were the presence of overtone and combination tones of the OH stretch and "ferric and ferrous iron bands" at ~ 1300 cm^{-1} and ~ 10000 cm^{-1}, respectively. Smith & Strens (1976) presented diffuse-reflectance spectra for three samples of glaucophane (with FeO and Fe_2O_3 contents of 2.0, 3.4; 4.9, 3.2; 14.3, 1.6 wt.%, respectively). All three spectra show a broad band at ~ 17000 cm^{-1}, and the intensity of this band is strongly correlated with the Fe content (Fig. 95). Smith & Strens (1976) assigned this band to M(3)—M(2) and M(1)–M(2) charge transfer, indicating that the broad band in the reflectance spectra is a merging of the two strong bands at ~ 16300 cm^{-1} and 18100 cm^{-1} seen in the polarized-
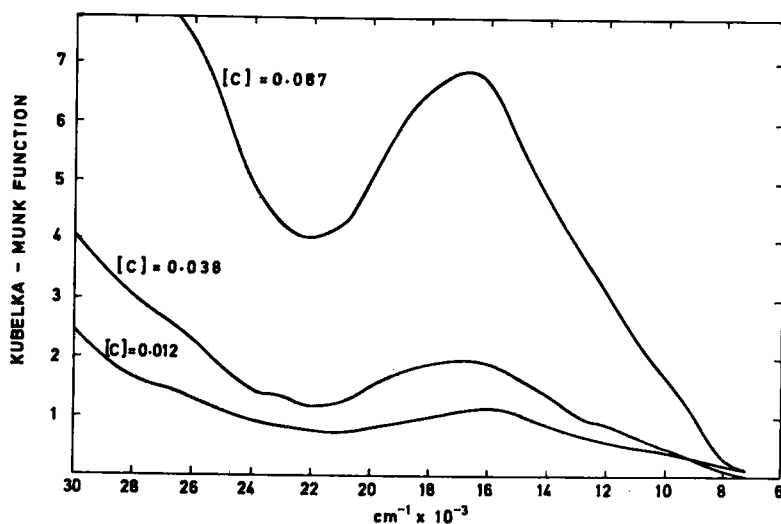

FIG. 95. Diffuse relectance spectra for three samples of glaucophane; [C] is the product of the donor (Fe^{2+}) and acceptor (Fe^{3+}) concentrations [from Smith & Strens (1976)].

transmission electronic-absorption spectra of glaucophane (Fig. 91). Additional spectra for actinolite and hornblende are given by Adams (1975).

Nuclear-magnetic-resonance spectroscopy

Nuclear-magnetic-resonance (N.M.R.) spectroscopy in mineralogy has primarily been used for the investigation of cations (isotopes) possessing a nuclear electric-quadrupole moment. Such studies have not been performed on amphiboles. However, proton-magnetic-resonance (P.M.R) studies have been used for site-population characterization in amphiboles (Kalinichenko *et al.* 1977). The principle underlying this particular use of P.M.R. spectroscopy is similar to that underlying the use of infrared absorption spectroscopy to obtain site populations. Variable occupancy of the 2M(1)+M(3) sites co-ordinating the hydroxyl provides differing magnetic environments for the protons of the hydroxyl groups. The relative intensities of the resultant lines are used to estimate the site populations exactly as in the infrared

absorption technique. Hence many of the drawbacks of the infrared absorption technique also apply to this method. Kalinichenko *et al.* (1977) examined an edenite, a pargasite and magnesio-hornblende(46); they also quoted Fe site-populations from Mössbauer data for magnesio-hornblende(46), but the source is not given. A comparison of the results for magnesio-hornblende(46) by all three methods is given in Appendix B3. The edenite contains insufficient paramagnetic cations to significantly affect the spectrum; in the pargasite, equal distribution of Fe at the M(1) and M(3) sites similar to the magnesio-hornblende(46) results. Using the standard criteria for clustering, pargasite shows clustering, whereas magnesio-hornblende(46) does not. However, with regard to this result, the work of Whittaker (1979) is pertinent. Banzaraksheev *et al.* (1978) have reported the P.M.R. spectrum of fibrous anthophyllite; it consists of a single isotropic line, suggesting $M(1) \sim M(3) \sim Mg$.

Electron-spin-resonance spectroscopy
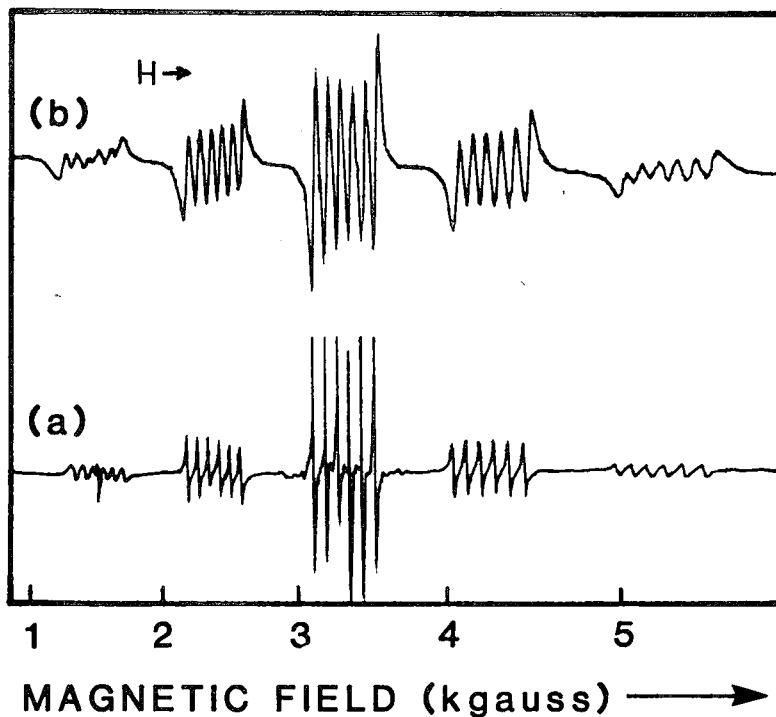
Electron-spin resonance (E.S.R.) may be

FIG. 96. Electron-spin-resonance spectra of Mn^{2+} in (a) white tremolite (0.01% Mn) and (b) pink tremolite (2.5% Mn) with the magnetic field directed along the Z magnetic axis [from Manoogian (1968a)].

used to examine paramagnetic ions (*e.g.*, Mn^{2+}, Fe^{3+}, Cr^{3+}) that are present in trace amounts in a structure. The characteristics of the resultant spectra may be used to indicate the site(s) occupied by the paramagnetic ion; when a cation occupies more than one site, the relative intensities of the superimposed spectra may be used to derive quantitative site-occupancies (Ghose *et al.* 1968, Ghose & Schindler 1969). This technique has not been used widely in minerals for site-occupancy studies, possibly because of the difficulty in arriving at a unique interpretation of the results. Certainly, in some of the common silicates where Mn^{2+} resonance has been examined, this has proved to be a problem (olivine: Chatelain & Weeks 1970, Michoulier *et al.* 1969; diopside: Vinokurov *et al.* 1964, Ghose *et al.* 1968, Ghose & Schindler 1969). Bershov *et al.* (1966) and Manoogian (1968a, b) have examined the electron-spin resonance of Mn^{2+} in tremolite (Fig. 96). Both studies indicated that Mn^{2+} is confined to one site in the tremolite samples examined [Bershov *et al.* (1966): no analysis, locality Slyudyanka; Manoogian (1968a): white tremolite 0.01% Mn, pink tremolite 2.5% Mn, no localities given]. Bershov *et al.* (1966) concluded that Mn^{2+} substitutes for Mg; that is, it occupies the M(1,2,3) sites in tremolite by analogy with the results of Vinokurov *et al.* (1964) on diopside. Manoogian (1968a) noted that his results are very similar to those of one Mn^{2+} site in diopside, but drew no conclusions from this concerning the site occupancy of Mn^{2+} in his tremolite samples. Ghose *et al.* (1968) and Ghose & Schindler (1969) advanced a persuasive argument to reverse the site assignment of the spin-Hamiltonian parameters in diopside determined by Vinokurov *et al.*

(1964). This being the case, the same reversal should apply to the site assignment in tremolite, whereby the studies of Bershov *et al.* (1966) and Manoogian (1968a) are compatible with Mn^{2+} occupancy of the M(4) site in tremolite.

Both studies fitted the experimental data to a spin Hamiltonian of the form $H = \beta g_z S_z H_z + \beta g_x S_x H_x + \beta g_y S_y H_y + 1/3\ b^0_2 O^0_2 + 1/3\ b^2_2 O^2_2 + 1/60\ b^0_4 O^0_4 + 1/60\ b^2_4 O^2_4 + 1/60\ b^4_4 O^4_4 + AS_z I_z + BS_x I_x + CS_y I_y$.

The calculated values of the spin-Hamiltonian

TABLE 57. SPIN HAMILTONIAN PARAMETERS FOR PYROXENE AND AMPHIBOLES

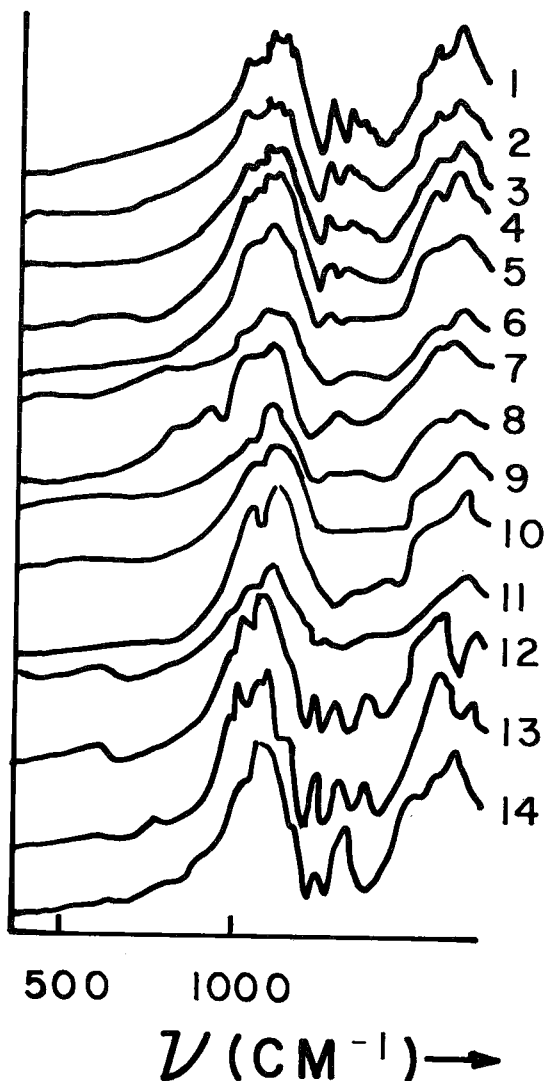|	Pink tremolite[1]	White tremolite[1]	Tremolite	Diopside[3] M1	M2
g_z	1.9980(10)	1.9951(10)	1.9990(5)	2.0015(5)	2.0017(5)
g_x	–	–	2.0000(5)	2.0013(8)	2.0016(8)
g_y	1.9971(10)	1.9930(10)	2.0030(5)	2.0008(8)	2.0016(8)
A	77.9(5)	79.9(5)	81.3	91.3(5)	84.4(5)
B	76.7(5)	79.0(5)	81.3	91.7(5)	84.4(5)
C	–	–	79.3	90.8(5)	81.9(5)
b^0_2	-448.3	-442.9	445.0	373.84	432.95
b^2_2	-234.7	-238.1	-237.4	51.26	-308.5
b^0_4	-0.96	-0.43	-0.7	-6.58	0.34
b^2_4	33.0	-19.0	-13.8	-2.93	-4.74
b^4_4	-34.6	18.2	13.1	32.47	15.88

[1]Manoogian (1968); [2]Bershov et al. (1966); [3]Vinokurov et al. (1964)

FIG. 97. Infrared absorption spectra for calcic amphiboles, numbered 1–14 in Appendix G4 [after Kukovskii & Litvin (1970)].
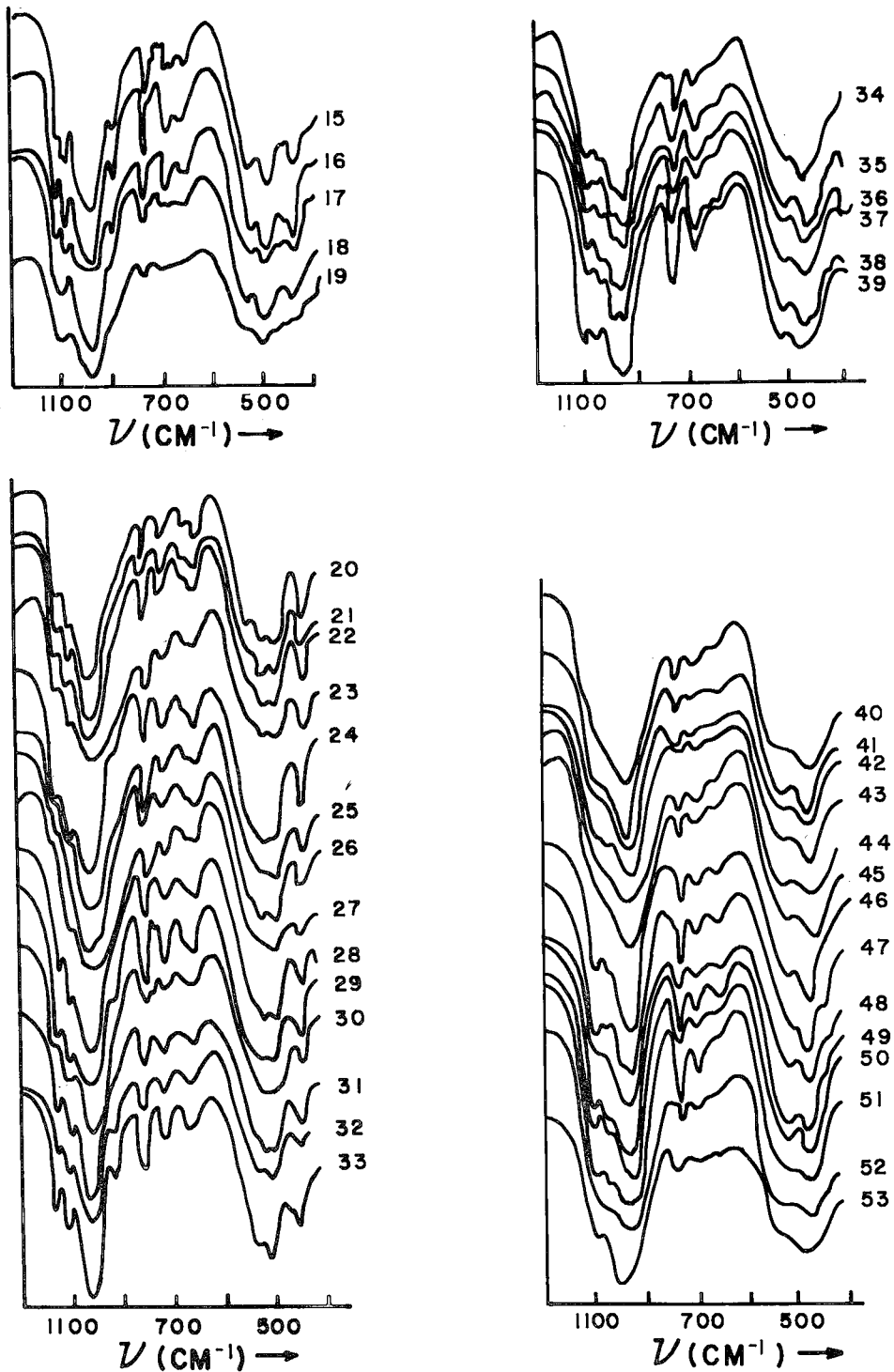
FIG. 98. Infrared spectra for amphiboles, numbered 15–53 in Appendix G4 [from Barabanov *et al.* (1974)].

parameters are shown in Table 57, where they are compared with the results of Vinokurov et al. (1964) on diopside with the site assignments reversed as suggested by Ghose & Schindler (1969). In the study of Manoogian (1968a), the resonance lines in x (magnetic axis, //Y crystallographic axis) were grouped close together, so that no accurate magnetic-field measurements of their positions could be made.

Vibrational spectroscopy

Vibrational spectroscopy encompasses infrared and Raman spectroscopy; here we distinguish these studies from those concerned solely with the principal OH-stretching band. Some work has been done on amphiboles, but as yet this has not been of great use. Kukovskii & Litvin (1970) gave infrared absorption spectra in the region 2000–400 cm^{-1} for fourteen well-characterized amphiboles, numbered *1–14* in Figure 97 and Appendix G4. Barabanov et al.

(1974) reported infrared absorption spectra in the region 1200–400 cm^{-1} for the thirty-nine amphiboles of Figure 98; detailed physical and chemical properties together with tabulated absorption data are given in Appendices G4 and G5. The intense absorptions between 1100–900 cm^{-1} are associated with Si–O vibrations; Barabanov et al. (1974) assigned the bands at ~450 cm^{-1} and ~530 cm^{-1} to Si–O–Mg and Si–O–Fe^{2+} modes, respectively, and also showed that the exact frequency of the band at ~640 cm^{-1} is linearly related to the FeO content in the cummingtonite – grunerite amphiboles (Fig. 99).

There has been little Raman spectroscopic work on amphiboles. The Raman effect requires exact translational symmetry over several unit-cells in order to produce a sharp spectrum. Perturbation of this symmetry by order–disorder causes rapid peak broadening and loss of detail in the Raman spectrum; experimental evidence to this effect can be seen by comparing the Raman spectra for actinolite and tremolite (Fig.
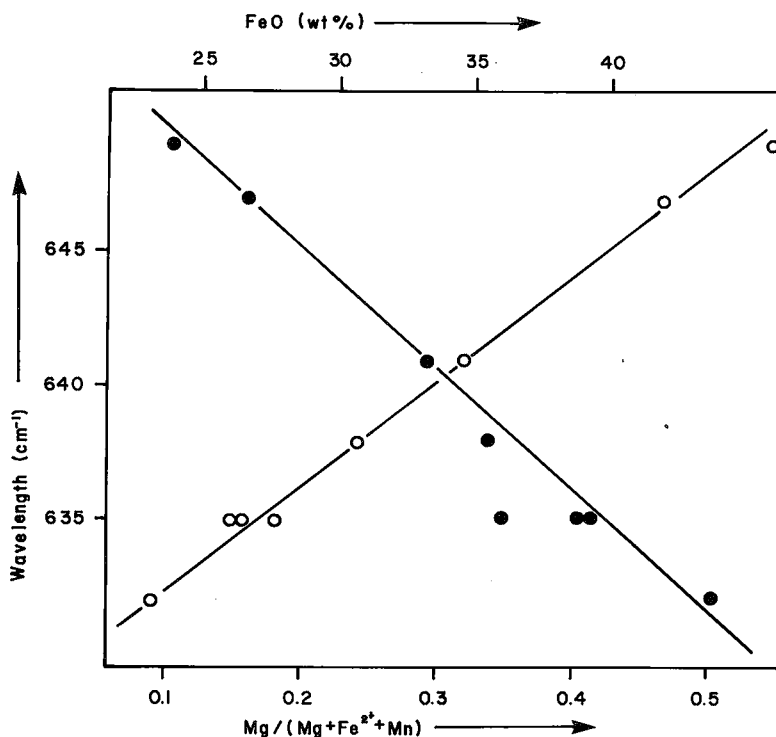

FIG. 99. Correlation between band frequency and chemical composition in the monoclinic Fe–Mg–Mn amphiboles. Solid circles show the variation of the frequency of the ~640 cm^{-1} band as a function of FeO content in wt. %; open circles show the same band-variation as a function of Mg/(Mg+Fe^{2+}+Mn) in the amphibole [after Barabanov et al. (1974)].
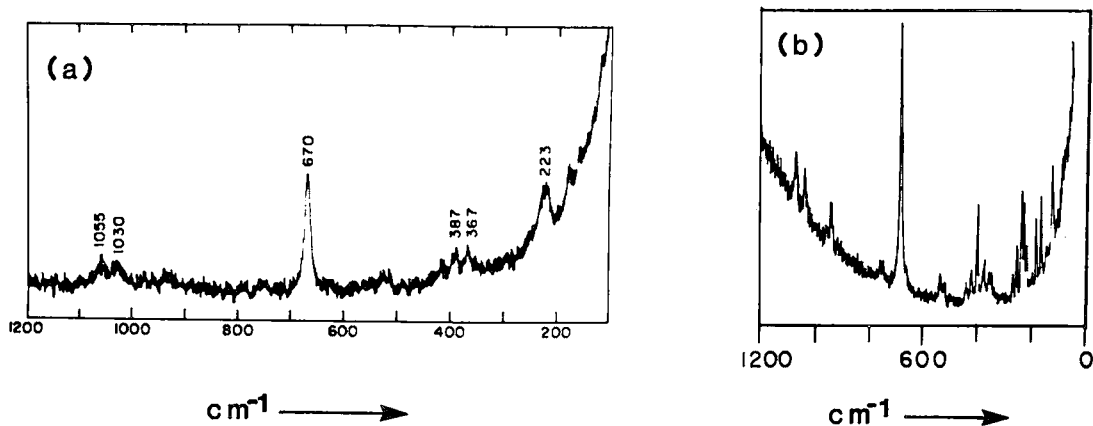
FIG. 100. Left: powder Raman spectrum of actinolite. Right: laser Raman spectrum of a crystal of tremolite [from White (1975) and Blaha & Rosasco (1978), respectively].

100). Tremolite is fairly well ordered and produces a detailed spectrum, whereas actinolite has significant cation disorder and gives a smeared weak spectrum; only a few weak bands are observed, the bridging oxygen mode at 670 cm^{-1} being the only band of appreciable intensity, with weak bands observed at 1055, 1030, 387, 367 and 223 cm^{-1}. It should be noted, however, that the laser-Raman technique is useful for the characterization of fibrous or asbestiform amphiboles where these are highly ordered (as is often the case).

Neutron-inelastic scattering

Infrared absorption studies concerning the OH group in amphiboles have concentrated on the region of the principal stretching band around $\sim$3650 cm^{-1}. There are other vibrations of the OH anion, considered as a rigid group bound in the structure, and these carry information concerning the bonding of the OH anion to other ions in the structure. However, these vibrations occur below 1000 cm^{-1}, where they are complicated by the extensive vibrational and lattice modes of the structure. Because of the differences in neutron-scattering cross-sections, the most intense peaks in neutron-inelastic-scattering spectra are those resulting from the motion of hydrogen-bearing groups. Consequently, oscillatory and translatory modes of the OH anion can be examined using this technique.

Naumann *et al.* (1966) have reported neutron-inelastic-scattering spectra for four amphiboles; the spectra are shown in Figure 101. The

principal features of each spectrum are the same. Each is characterized by a sharp primary maximum at $\sim$650 cm^{-1} and a sharp, secondary maximum at $\sim$510 cm^{-1}, although the latter is much weaker in crocidolite than in the remaining three amphiboles. In addition, there are a number of less intense broader peaks at lower frequencies. The narrow symmetrical shape and high relative intensity of the 650 cm^{-1} and 510 cm^{-1} peaks characterize the motions involved as torsional oscillations of the OH groups. The narrow, symmetrical peak-shape is indicative of very weak hydrogen bonding or none at all. The remaining peaks (below 400 cm^{-1}) can be assigned to translatory vibrations of OH groups, optical (broader, less symmetrical and less intense than the oscillatory modes) and acoustic modes (the lowest frequency modes).

CATION DISTRIBUTIONS IN AMPHIBOLES

The wide variety of cation co-ordinations in the amphiboles, together with the large structural compliance of some of the sites, result in considerable chemical complexity in these minerals. A knowledge of the site occupancies and order–disorder relationships in the amphiboles is essential to a better understanding of their crystal chemistry, phase relations, optical and electrical properties and oxidation–dehydroxylation mechanisms. Consequently, the amphiboles, more than any other mineral group, have been studied from the viewpoint of site-population characterization.

Warren (1930) considered chemical varia-