

The Magnetic Circular Dichroism of Pyrope-Almandine Garnets

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Abstract

Magnetic circular dichroism (MCD), which has been used for the study of paramagnetic ions in crystals, is now applied to minerals as a technique complementary to optical absorption. Two garnets from the pyrope-almandine series have been studied by both absorption and magnetic circular dichroism and compared. MCD spectra, being unaffected by the ultraviolet absorption edge, unambiguously demonstrate a distinct band centered at 22700 cm^{-1} (441 nm) with a half-width of 7000 cm^{-1} at 17 K . This band, which influences the color of garnet, is assigned to Ti^{3+} , but its intensity and position also permit assignment to Ti-Fe charge transfer or Mn^{3+} transitions.

Introduction

There has been a large literature on the absorption spectra of natural garnets, including papers by Clark (1957), Manning (1967a, 1967b, 1969, 1972), Moore and White (1972), White and Moore (1972), Shankland, Duba and Woronow (1974) and Runciman and Sengupta (1974). Bands have been ascribed to Fe^{2+} , Fe^{3+} , Mn^{2+} , Cr^{3+} , V^{3+} , and Ti^{3+} . There are frequent discrepancies of interpretation and a new technique should be useful in identifying band origins. Magnetic circular dichroism (MCD) is well adapted to this purpose. The background and theory of MCD have been discussed by Buckingham and Stephens (1966), Schatz and McCaffery (1969), and Stephens (1970). Applications of MCD to chemical systems, ordered and disordered systems, and color centers have recently been described and listed by Stephens (1974); it now seems desirable to extend the application of this technique to mineralogical substances with cubic or uniaxial symmetry. Information may be obtained relating to the symmetry of color centers and the electronic degeneracies of the levels concerned in optical transitions.

Experimental

The single crystals of garnet were mounted in an Oxford Instruments Company superconducting solenoid capable of reaching 8T with cooling of the crystals in exchange gas. The spectra were obtained on a Cary 61 spectropolarimeter with a range from 12500 to 54000 cm^{-1} .

The properties of an almandine garnet, specimen G23, are as follows: $a_0 = 11.52\text{ \AA}$, sp. gr. = 4.20, $n = 1.81_3$. The composition related to ideal garnets is approximately 81.9 mole percent almandine, 13.3 mole percent pyrope, 2.7 mole percent spessartine, 0.8 mole percent grossular, 1.0 mole percent andradite, and 0.3 mole percent uvarovite.

The results of the electron microprobe analysis of G23 are (expressed as weight percent of the oxides):

SiO_2	36.56	FeO	36.89
TiO_2	<0.07	MnO	1.18
Al_2O_3	21.49	MgO	3.34
Cr_2O_3	0.12	CaO	0.72

The properties of the pyrope garnet, G35, are as follows: $a_0 = 11.54\text{ \AA}$, sp. gr. = 3.72, $n = 1.75_0$. The composition related to ideal garnets is approximately 21.0 mole percent almandine, 65.3 mole percent pyrope, 0.6 mole percent spessartine, 7.5 mole percent grossular, and 5.6 mole percent andradite.

The results of the electron microprobe analysis of G35 are (expressed as weight percent of the oxides):

SiO_2	41.35	FeO	11.99
TiO_2	0.42	MnO	0.29
Al_2O_3	23.59	MgO	17.76
Cr_2O_3	<0.07	CaO	4.93

The Mössbauer spectrum of G35 indicated an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of about 6:1, whereas the amount of Fe^{3+} in G23 is less than the estimated detection limit of 0.5 weight percent. Comparison of the absorption spectrum of G35 with that of other garnets suggested

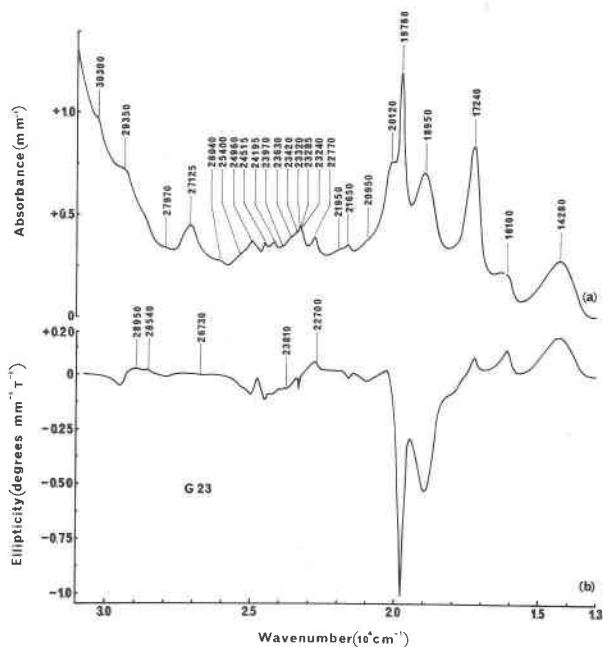


FIG. 1. Spectra of an almandine garnet: (a) absorption spectrum at 17 K, (b) MCD spectrum at 30 K and 2.65 T. The wave-numbers (in cm^{-1}) of bands distinguishable only in the MCD spectrum are marked in (b), the wave-numbers (in cm^{-1}) of other bands in (a).

that the Fe^{3+} in G35 was mainly at the octahedral site.

Absorption and MCD Spectra

The absorption and MCD spectra of the almandine garnet, G23, are shown in Figures 1(a) and 1(b) respectively. The absorption spectrum shows the three strong bands at 17240 cm^{-1} (580 nm), 18950 cm^{-1} (528 nm), and 19760 cm^{-1} (506 nm) which are so characteristic of almandine garnets in the visible spectrum. These bands were attributed by Moore and White (1972) to transitions to the triplet states of Fe^{2+} from the quintet ground state. The MCD bands are largely of the temperature-dependent *C* type with an admixture of the temperature-independent *B* type, suggesting that the Fe^{2+} ground state is degenerate or nearly so. The calculations of Runciman and Sengupta (1974) are consistent with the MCD results in this respect, as they found that the spin-orbit components of the 5A ground state are near-degenerate, with the two lowest levels having a separation of only 0.02 cm^{-1} . The sign and intensity of the MCD signal from a given transition can in theory be calculated from the formulae of Schatz and McCaffery (1969) or Stephens (1970) and so would provide additional criteria for the assignment of these bands.

The spectra of pyrope garnet G35 (Fig. 2a, b) show in a weaker form the MCD bands previously noted for almandine garnet. There is also a strong underlying absorption in the visible. If only the absorption spectrum be considered, it is not clear whether this underlying absorption is due to a "tail" of the ultraviolet absorption edge, or whether there is a distinct band, as suggested by Manning (1972); he reported a band centered at 21000 cm^{-1} with a half-width of 2700 cm^{-1} . Comparison with the MCD spectrum, which is unaffected by the ultraviolet absorption edge, shows unambiguously that much of this absorption is due to a distinct band, centered at 22700 cm^{-1} (441 nm) with a half-width of 7000 cm^{-1} at 17 K and a *C*-type MCD signal; these values of the parameters are more reliable than any extracted from the absorption spectrum alone. The improved value for the band position was used to obtain more accurate estimates of the peak band absorbance in 13 garnets of different compositions. The absorbance is not proportional to Fe^{2+} , Fe^{3+} , or Mn concentrations, or to products of these concentrations; the electron microprobe analyses suggest an assignment to Ti^{3+} , though the band intensity and position also permit

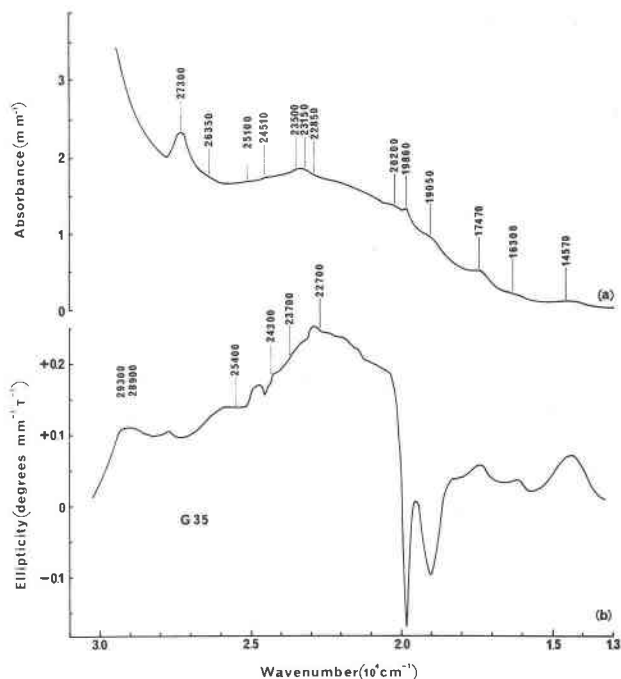


FIG. 2. Spectra of a pyrope garnet: (a) absorption spectrum at 17 K, (b) MCD spectrum at 30 K and 2.65 T. The wave-numbers (in cm^{-1}) of bands distinguishable only in the MCD spectrum are marked in (b), the wave-numbers (in cm^{-1}) of other bands in (a). (Note the difference in ordinate scales between Figures 1 and 2).

assignment to Ti-Fe charge-transfer or Mn^{3+} transitions.

The band at 22700 cm^{-1} influences the color of the garnet. When it is strong, the pyrope garnet is reddish-brown or orange in thin section, or fire-red as the band is weakened. In the case of a very weak band the color is reddish-violet or rose-colored in thin section.

MCD is useful in separating bands near the ultraviolet absorbing edge, which does not swamp the MCD in this region. Also the different relative intensities of the absorption and MCD signals for different bands assist in distinguishing overlapping bands.

Conclusion

MCD spectra can provide information complementary to that obtained by absorption spectroscopy, particularly for absorption bands near an absorption edge. For illustration the spectra of two garnets have been described. Since the spin-allowed bands in garnet are expected to occur in the range $4500\text{--}7800\text{ cm}^{-1}$, it is hoped that measurements will be made for a greater variety of crystals over a wider wavenumber range. In other crystals, diamond for example, MCD can reveal the presence of electronic degeneracy in the electronic levels of color centers. Thus MCD is likely to have a diversity of applications to many mineralogical systems.

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