SHORT COMMUNICATIONS

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A note on the Mössbauer spectrum of ^{57}Fe in ferrocarpholite

THE mineral carpholite can be represented by the end-members manganocarpholite, $MnAl_2Si_2O_6(OH)_4$, ferrocarpholite, $FeAl_2Si_2O_6(OH)_4$, and magnesiocarpholite, $MgAl_2Si_2O_6(OH)_4$ (Mottana and Schreyer, 1977). Substitution of Fe^{3+} for Al is always below 9% and generally much lower. Following Naumova *et al.* (1975) the crystal structure of both manganocarpholite and ferrocarpholite (MacGillavry *et al.* 1956) can be described in the space group *Ccca*. It is made up from Si_2O_6 chains that link octahedral zigzag strips (Al_I, 8*e*, site symmetry 2) and beams consisting of Al_{II} (8*f*, site symmetry 2) and (Mn,Fe,Mg) octahedra (8*f*, site symmetry 2). The arrangement of the (Mn,Fe,Mg) octahedra relative to the Al_{II} octahedra is similar to that of the M2 octahedra in pyroxenes relative to their M1 octahedra, but the linkage of the beams to the Si_2O_6 chains is different.

Natural carpholites from Crete, Greece (samples K75/67 and K75/74, Seidel, 1978) have been studied by Mössbauer spectroscopy. They range in composition from $Fe_{55.0}Mg_{43.8}Mn_{1.2}$ to $Fe_{67.7}Mg_{31.6}Mn_{0.7}$ carpholites (i.e. magnesian ferrocarpholites) as calculated from the analyses using the correction scheme for Fe^{3+} and Si as proposed by Mottana and Schreyer (1977). No difference in hyperfine parameters has been observed between these two extremes and most of the measurements have been made on the more Fe-rich sample.

Mössbauer spectra were taken on absorbers with 3-5 mg Fe/cm^2 with a ^{57}Co source in Rh matrix and in the constant acceleration mode. Left-hand and right-hand sides of the spectra have been recorded separately in a 1024 channel multichannel analyser. The raw data have been fitted to sums of Lorentzian functions by a least-squares technique and the reported parameters represent averages of the two sides of the spectra.

The Mössbauer spectrum of ^{57}Fe in ferrocarpholite is characterized by a strong outer doublet with slight asymmetry, which could be due to preferred orientation, and a weak inner doublet (fig. 1). The large quadrupole splitting and isomer shift of the intense doublet (Table I) indicate that it is due to ferrous iron in an octahedral coordination, i.e. the (Mn,Fe,Mg) site. The narrow line widths of this doublet (0.28 and 0.26 mm/sec at room temperature) demonstrate that no Fe^{2+} is present in other octahedral sites and that effects of next-nearest neighbour interactions are absent. On the other hand, the weak inner doublet gives an isomer shift of 0.38 mm/sec relative to metallic iron and a

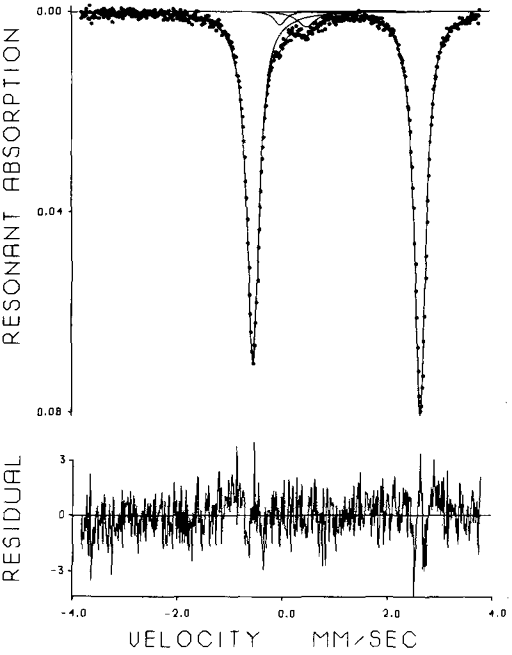

FIG. 1. ^{57}Fe Mössbauer spectrum of $Fe_{67.7}Mg_{31.6}Mn_{0.7}$ carpholite taken at room temperature. The envelope is an unconstrained least-squares fit assuming four Lorentzians (twelve line variables, one background variable), which are also indicated. The deviations of the envelope from the data (divided by the square root of the background) are plotted below the spectrum. The velocity is given relative to the ^{57}Co in Rh source. For conversion to metallic iron 0.114 mm sec^{-1} has to be added. The outer doublet is due to Fe^{2+}, the inner to Fe^{3+}, both in octahedral coordination.

quadrupole splitting of 0.55 mm/sec at room temperature, which are typical of Fe^{3+} in octahedral coordination (Annersten and Halenius, 1976), probably either the Al_I or Al_{II} position of the structure, or both. The line widths (0.26 and 0.41 mm/sec at room temperature) and the hyperfine parameters of the Fe^{3+} doublet are rather imprecise due to the strong overlap of the low-velocity component with the more intense Fe^{2+} peak. Nevertheless, the area ratio of the two doublets gives a reasonable estimate of the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio (0.96 from the spectrum at 77 K, compared to 0.90 from the raw chemical analysis and 0.97 after correction according to Mottana and Schreyer, 1977).

TABLE I. *Isomer shifts* δ *(relative to metallic iron,* ± 0.005 *mm* sec^{-1}*) and quadrupole splittings* ΔE_Q (± 0.005 *mm* sec^{-1}) *of* Fe^{2+} *in* $Fe_{67.7}Mg_{31.6}Mn_{0.7}$ *carpholite*

T(K)	δ (mm sec^{-1})	ΔE_Q (mm sec^{-1})
8	1.306	3.446
30	1.305	3.450
77	1.304	3.456
293	1.178	3.198
345	1.150	3.111
395	1.113	2.994
434	1.088	2.915
463	1.068	2.843
496	1.042	2.756
524	1.022	2.688
593	0.964	2.538
623	0.955	2.459

Both isomer shift and quadrupole splitting of the Fe^{2+} doublet exhibit a strong dependence on temperature (Table I). At high temperatures (above 77 K) the isomer shift decreases almost linearly with temperature at a rate of 7×10^{-4} mm $sec^{-1}K^{-1}$, which closely corresponds to the effect of the second-order Doppler shift (7.3×10^{-4} mm sec^{-1} K^{-1} for the 14.4 keV of the ^{57}Fe gamma rays, Hazony, 1973) at temperatures well above the Debye temperature. According to the Debye model for the temperature dependence of the isomer shift the deviation from the linear relationship between isomer shift and temperature at low temperatures can be used to estimate the Debye temperature of Fe^{2+} in its position according to the formalism proposed by Clark *et al.* (1967). Assuming isotropic vibration a value of $\theta_D = 290\pm20$ K is obtained. The quadrupole splitting attains a maximum close to 3.45 mm sec^{-1} at a temperature near 80 K. The high absolute value of ΔE_Q and the appearance of a maximum in the ΔE_Q v. temperature relationship indicates, in terms of the model proposed by Gibb (1968), that axial distortion of the (Mn,Fe,Mg) polyhedron is low.

The quadrupole splitting of Fe^{2+} in ferrocarpholite is markedly higher than that of Fe^{2+} in both the M1 and M2 sites of orthopyroxene (3.11 and 2.04 at 77 K, respectively, Burnham *et al.*, 1971) and, despite the low site symmetry, even exceeds that of Fe^{2+} in the highly symmetrical octahedral site of garnet (3.16–3.19 mm sec^{-1} at 77 K, Amthauer *et al.*, 1977) which represented the maximum ΔE_Q value reported so far for octahedrally coordinated Fe^{2+} in minerals. Thus, the geometry of the (Mn,Fe,Mg) octahedron in carpholite must closely correspond to the maximum in the ΔE_Q v. distortion relationship, which occurs at low distortions (Ingalls, 1964) where the contribution by the valence term is already high but the opposed contribution by the lattice term is still low. Such a low distortion of the (Mn,Fe,Mg) octahedron is not adequately reflected in the structure determinations for carpholite available at present (MacGillavry *et al.*, 1956; Naumova *et al.*, 1975). However, the precision of the metal-oxygen distances and oxygen-metal-oxygen angles obtained in these studies is not sufficient to compare the site geometry in this phase to that encountered in other silicates. It should be pointed out that much of the bond length and bond angle variation encountered in the structurally analogous M2 position of orthopyroxenes is due to the shared edge between this polyhedron and a SiO_4 tetrahedron. Lack of this edge-sharing in carpholite might make a more regular geometry feasible.

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Mineralogisches Institut
Universität Kiel
Kiel, Germany

F. SEIFERT

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Tritolyl phosphate—a suitable immersion oil for fluid inclusion freezing-stage studies

INFORMATION on the bulk composition and salinity of fluid inclusions in minerals can be obtained from the direct observation of various phase changes in frozen or cooled inclusions using a microscope freezing-stage (for example, see Roedder, 1963; Hollister and Burruss, 1976). Transient phases that develop on cooling such as ice, solid CO_2, CO_2-hydrate, and NaCl-hydrate are, however, often very difficult to observe because of the small size of most fluid inclusions (generally less than 100 μm). To facilitate these observations and to enhance the definition of small inclusions in transparent minerals it is normal practice to prepare high-quality, polished wafers of the host mineral. A relatively simple preparation technique has recently been published by Brumby and Shepherd (1978), but situations commonly arise where observations at low temperatures are required on inclusions in small mineral grains or fragments unamenable to routine polishing procedures. This note describes an alternative method of improving the optical quality of such material by immersing the sample in a small drop of tritolyl phosphate (tri-cresyl phosphate or phosphoric acid tri-(methyl-phenyl) ester).

Tritolyl phosphate, a readily available industrial chemical marketed under the trade names Lindol, Celluflex, and Kronitex, exists in three isomeric forms (ortho-, meta-, and para-cresyl; M. wt. = 368.36). The ortho form, tri-*o*-cresyl phosphate, has certain toxicological hazards particularly following ingestion (for details see Sax, 1975, p. 1190) and is usually excluded as much as possible from commercial tritolyl phosphate. However, it is advisable to specify 'ortho-free' when ordering this substance.

Ortho-free tritolyl phosphate is a suitable immersion oil for quartz at room temperature (Gordon, 1945). It is a colourless, odourless, and viscous oil, stable at ambient temperatures, has a refractive index of 1.55, is cheap to purchase, and, provided the usual laboratory precautions are taken, is safe to handle.[1] But the particular quality that makes it ideal for low temperature fluid inclusion studies is that *it maintains its* transparency at sub-zero temperatures (down to at least −100 °C). Other readily available oils with refractive indices in the range 1.5 to 1.6 such as clove oil, bromoform, and chlorobenzene have been tested in our laboratories but either freeze to a multigranular, crystalline aggregate or become progressively translucent on cooling. Tritolyl phosphate does not crystallize but freezes to a transparent metastable glass (the pour point of commercial-grade tritolyl phosphate is −28 °C according to the 1976 Merck Index).

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[1] Soap and water are sufficient to remove this substance from surfaces. However, tritolyl phosphate is a well-known plasticizer and any contact with vinyl plastics should be avoided.