ORIGINAL PAPER

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Evaluation of ferrous and ferric Mössbauer fractions. Part II

Abstract Mössbauer fractions f are reported for various ferrous- and/or ferric-containing oxides, hydroxides, silicates, and phosphates to extend the list previously reported by De Grave and Van Alboom (1991). The f fractions were evaluated from the experimental temperature dependencies of their center shifts, assuming the Debye model for the lattice vibrations. For most Fe^{2+} sites the characteristic Mössbauer or lattice temperatures Θ_M are in the range 300–400 K, while those for Fe^{3+} sites are close to or exceed 500 K, implying significantly higher f fractions for Fe^{3+} than for Fe^{2+}, in particular at room temperature. A correlation between Θ_M and the coordination type, or, for a given valence state and coordination type, between Θ_M and the mineral type is, however, not obvious.

Keywords Mössbauer effect · Lattice temperature · Recoilless fraction

Introduction

[57]Fe Mössbauer spectroscopy remains a useful and very successful technique in geosciences and especially in mineralogy. The reasons are manifold, e.g. the straightforward determination and quantification of the oxidation state of iron, the high sensitivity of the numerical parameters defining the absorption profiles to the electronic state and to the chemical environment of the [57]Fe probe nuclei (such as the coordination number), the possibility to measure the site occupancies of iron among structurally different lattice sites in a given mineral. For quantitative phase analyses, use is made of the relative spectral areas of the Mössbauer subspectra associated with the respective phases or species. These are indeed proportional to their respective abundancies, and this proportionality is governed by the Mössbauer fraction f.

The determination of the Fe^{2+}/Fe^{3+} ratio is of uttermost importance to study, for example the oxidation state of the mantle, where direct sampling of mantle minerals has been possible from examination of ultramafic xenoliths brought to the surface in kimberlites or alkali basalts, or as inclusions in diamonds. (e.g. Luth and Canil 1993; McCammon 1997; McCammon et al. 1997). For this latter application, and for the Fe^{2+}/Fe^{3+} characterization of micron-sized crystallites in general, with sizes down to 50 μm, the Mössbauer milliprobe is a very promising variant of the traditional Mössbauer spectrometer (McCammon 1994; De Grave et al. 1999). The amount of ferric iron is also a valuable indicator for the oxygen fugacity conditions prevailing during crystallization or during later transformations (see, e.g. Oliveira et al. 2002; Eeckhout et al. 2002). [57]Fe Mössbauer spectroscopy has also been successfully applied to study weathering phenomena (e.g. da Costa and Viana 2001) and for quantitative phase analyses of the iron constituents in soils and sediments (Bowen et al. 1993). Since this latter application commonly concerns magnetic Mössbauer spectra (MS), the use of strong external magnetic fields often provides additional analytical performance (De Grave et al. 1998b). During the past 25 years, major advances in high-pressure mineral-synthesis technology have been developed so that many high-pressure silicate and oxide phases of potential geophysical significance can be synthesized (see, e.g. Woodland 1998). Such synthetic species have the crucial advantage of being free of cation substitutions (unless otherwise wanted), hence facilitating a sound interpretation of the MS and of the various fundamental physical properties that can be derived from the results of precise data analyses.

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In order to determine the Fe^{2+}/Fe^{3+} ratio for a given mineral, one needs to know the ratio f_2/f_3 of the respective f factors. Commonly, it is assumed that this ratio is close to unity. This assumption, however, is not justifiable (De Grave and Van Alboom 1991) and often results in an overestimation of the Fe^{3+} content. The calculation of the magnitude of the corrections is not an easy task and is also extremely time-consuming. It is a fairly common practice to derive the value of the Mössbauer fraction f from the second-order Doppler shift, $\delta_{SOD}(T)$, which is mathematically described in terms of the Debye model for the vibrational modes of the lattice.

The present paper reports f values for various natural and synthetic oxides, hydroxides, silicates, and phosphates as an extension of a similar list published earlier in this periodical (De Grave and Van Alboom 1991). The majority of the data have been collected in the authors' research group, but, additional data were retrieved from the literature.

Method of calculation

The temperature variations of center-shift data, $\delta(T)$, of approximately 45 compounds were used to evaluate the characteristic Mössbauer temperatures Θ_M of these compounds and from these quantities the respective Mössbauer fractions f were calculated. This procedure requires very smooth experimental temperature variations with a high number of data points extending over a broad temperature interval in order to retrieve reliable and reproducible f values. For more details about the applied method the authors refer to De Grave and Van Alboom (1991) and to Eeckhout et al. (2000). The calculated Θ_M and f values are listed in Table 1. These data are almost all totally in line with earlier results and infer that (1) the ferrous and ferric Mössbauer fractions are unequal, and (2) assuming equal values may produce significant errors (of the order of 10%) in Fe^{2+}/Fe^{3+} ratios and in the results of phase analyses.

It was observed in the course of these investigations that for Ca-pyroxenes at temperatures above 600 K, the calculated $\delta(T)$ values slightly, but consistently, exceed the experimental data (E. De Grave and S.G. Eeckhout, 2003; S.G. Eeckhout and E. De Grave, 2003). This implies that at such high temperatures $\delta_{SOD}(T)$ is not able to describe $\delta(T)$ adequately. Perkins and Hazony (1972) obtained similar results for their $\delta(T)$ curves observed for some iron halogenides, and proposed a weak temperature dependence of the form:

$$\delta_I(T) = \delta_I(0\ K) + C_{\delta,Q} \times 10^{-5}T \qquad (1)$$

to explain the mismatch between the observed and calculated $\delta(T)$ values. These authors argue that this temperature dependence is due to the thermal radial expansion of the t_{2g} and e_g wave functions. To obtain Θ_M values for these Ca-pyroxene species, Eq. (1) was used with no constraints imposed on the linear correlation coefficient, $C_{\delta,Q}$. A closer agreement between the experimental and calculated data was obtained, particularly at $T \geq 600$ K. The slope of the linear correlation between δ_I and T was found to be $\sim-4.5 \times 10^{-5}$ mm/(s.K). The as-such calculated Θ_M values are ~100 K higher than in the case that no temperature variation for δ_I was considered. This is conceivable, since the temperature dependence of δ_I also has its effect, although to a lesser extent, at relatively "low" temperatures in a way that, if the correlation is not introduced in the model, $\delta_{SOD}(T)$ has to take account of a steeper decrease of $\delta(T)$ with increasing temperature, thus yielding a lower value for Θ_M.

Results

The results reported by Chen et al. (1992) for Fe^{3+} in natural chromites are not in line with the trends obtained for many other compounds, including synthetic spinel oxides. Visual inspection of their spectra, however, reveals complicated line shapes in the velocity range of the ferric doublet, with strong overlap with the dominant low-velocity absorption of the ferrous species, resulting in δ versus T curves that are subjected to significant scatter. Moreover, only a limited number of temperatures (five) have been considered in the fits. As it has been argued by De Grave and Van Alboom (1991), a large number of precise data points are required to extract reliable and reproducible Θ_M, and hence f values. Therefore, it is believed that the numerical results of Chen et al. (1992) are seriously underestimated.

Discussion

At this point, one can, of course, argue that the Debye model for the lattice vibrations is quite simplistic and unrealistic for a complex lattice system. This is undoubtedly true and therefore the derived characteristic Mössbauer-temperature values, Θ_M, have little absolute meaning. However, significant variations observed for structurally closely related samples should be considered as reflecting real variations in the vibronic spectrum and thus in the chemical bonding. In such cases, the calculated f fractions are physically relevant and may provide valuable information about the tightness of binding. For instance, in the Mg–Fe $P2_1/c$ clinopyroxene series (see Table 1), Θ_M at M1 remains fairly constant along the $MgSiO_3$–$FeSiO_3$ join, whereas a slight decrease in Θ_M at M2 is observed at higher Fe contents. These results suggest a similar bonding strength at M1 regardless of the composition, and a slight weakening of the bonding at M2 with increasing Fe concentration (Eeckhout et al. 2000).

Conclusion and outlook

Mössbauer spectroscopy has long been a unique technique to determine the oxidation states of Fe in minerals. Wet-chemical analyses often underestimate the Fe^{2+} content as a result of oxidation during the chemical treatment. Atomic absorption spectroscopy and electron microprobe analysis cannot distinguish among the valence states of elements and the ferrous/ferric ratio can only be estimated by assuming charge balance and perfect stoichiometry. This approach seems to work satisfactorily for spinels, provided that adequate standards and correction procedures are used, but not for garnets and pyroxenes because of lower total Fe and higher

Table 1 Characteristic Mössbauer temperature Θ_M and Mössbauer fractions at 80 and 300 K, f_{80} and f_{300}, for various synthetic (S) and natural (N) compounds; q is the charge of the iron and C its co-ordination

Compound	q	C	Θ_M (K)	f_{80}	f_{300}	Ref[a]
1. Oxides and hydroxides						
Bernalite, $Fe(OH)_3$	+3	$(OH)_6$	492	0.922	0.835	1
Chromite spinels (S)						
$MgFe_{2-x}Cr_xO_4$						
$x = 0.2$	+3	O_4, O_6^b	387	0.895	0.753	2
$x = 0.4$	+3	O_4, O_6^b	496	0.923	0.837	
$x = 0.6$	+3	O_4, O_6^b	495	0.923	0.837	
$x = 0.8$	+3	O_4, O_6^b	517	0.927	0.848	
$x = 1.0$	+3	O_4, O_6^b	495	0.923	0.837	
$x = 1.2$	+3	O_4, O_6^b	543	0.931	0.861	
$x = 1.4$	+3	O_4, O_6^b	467	0.917	0.820	
$x = 1.6$	+3	O_4, O_6^b	496	0.923	0.837	
$x = 1.8$	+3	O_4, O_6^b	466	0.917	0.819	
$Mg_{1-y}Zn_yFe_{1.5}Cr_{0.5}O_4$						
$y = 0.0$	+3	O_4, O_6^b	520	0.927	0.850	2
$y = 0.1$	+3	O_4, O_6^b	539	0.931	0.859	
$y = 0.2$	+3	O_4, O_6^b	523	0.928	0.851	
$y = 0.3$	+3	O_4, O_6^b	538	0.930	0.858	
$y = 0.4$	+3	O_4, O_6^b	559	0.934	0.867	
$y = 0.5$	+3	O_4, O_6^b	572	0.935	0.872	
$y = 0.6$	+3	O_4, O_6^b	568	0.935	0.871	
$y = 0.7$	+3	O_4, O_6^b	577	0.936	0.874	
$y = 0.8$	+3	O_4, O_6^b	528	0.929	0.854	
$y = 0.9$	+3	O_4, O_6^b	517	0.927	0.848	
$y = 1.0$	+3	O_4, O_6^b	511	0.926	0.845	
Chromite spinels (N)						
$Mg_{0.69}Fe^{2+}_{0.31}Fe^{3+}_{0.06}Al_{0.48}Cr_{1.46}O_4$	+2	O_4	309	0.857	0.645	3
	+3	O_6	302	0.852	0.632	
$Mn_{0.01}Mg_{0.74}Fe^{2+}_{0.27}Fe^{3+}_{0.10}Al_{0.39}Cr_{1.50}O_4$	+2	O_4	317	0.862	0.659	3
	+3	O_6	331	0.870	0.681	
$Mn_{0.01}Mg_{0.71}Fe^{2+}_{0.28}Fe^{3+}_{0.08}Al_{0.58}Cr_{1.34}O_4$	+2	O_4	368	0.887	0.731	3
	+3	O_6	374	0.890	0.738	
2. Silicates						
Aegirine (N)						
$Na_{1.06}Ca_{0.06}Mg_{0.04}Fe_{1.01}Al_{0.06}Si_{1.91}O_6$	+3	O_6 (M1)	540	0.931	0.859	4
	+2	O_6 (M1)	380	0.892	0.745	
Mg-Fe $P2_1/c$						
clinopyroxenes (S)						
$Mg_{0.91}Fe_{0.09}SiO_3$	+2	O_6 (M1)	350	0.901	0.730	5[c]
	+2	O_6 (M2)	400	0.914	0.782	
$Mg_{0.81}Fe_{0.19}SiO_3$	+2	O_6 (M1)	345	0.898	0.720	5[c]
	+2	O_6 (M2)	340	0.897	0.715	
$Mg_{0.68}Fe_{0.32}SiO_3$	+2	O_6 (M1)	375	0.908	0.759	5[c]
	+2	O_6 (M2)	365	0.905	0.747	
$Mg_{0.53}Fe_{0.47}SiO_3$	+2	O_6 (M1)	335	0.895	0.708	5[c]
	+2	O_6 (M2)	335	0.896	0.710	
$Mg_{0.39}Fe_{0.61}SiO_3$	+2	O_6 (M1)	375	0.907	0.755	5[c]
	+2	O_6 (M2)	400	0.919	0.780	
$Mg_{0.22}Fe_{0.78}SiO_3$	+2	O_6 (M1)	340	0.896	0.710	5[c]
	+2	O_6 (M2)	325	0.892	0.695	
$Mg_{0.13}Fe_{0.87}SiO_3$	+2	O_6 (M1)	390	0.911	0.772	5[c]
	+2	O_6 (M2)	340	0.896	0.712	
$Mg_{0.09}Fe_{0.91}SiO_3$	+2	O_6 (M1)	340	0.897	0.716	5[c]
	+2	O_6 (M2)	315	0.887	0.676	
$FeSiO_3$	+2	O_6 (M1)	355	0.901	0.733	5[c]
	+2	O_6 (M2)	310	0.885	0.667	

Table 1 (Contd.)

	Hedenbergite (N)					
$Ca_{1.00}Fe^{2+}_{0.74}Mg_{0.16}Mn_{0.03}Al_{0.03}Fe^{3+}_{0.02}Si_{2.00}O_{6.00}$	+2	O_6 (M1)	330	0.869	0.680	6
	+3	O_6	440	0.911	0.801	
$Ca_{1.00}Fe^{2+}_{0.68}Mg_{0.20}Mn_{0.15}Al_{0.05}Fe^{3+}_{0.04}Si_{1.92}O_{6.00}$	+2	O_6 (M1)	370	0.888	0.734	
	+3	O_6	490	0.922	0.834	
Diopside (N)						
$Ca_{0.73}Mg_{0.96}Fe_{0.01}Si_{2.15}O_{6.00}$	+2	O_6	350	0.879	0.712	7
$Ca_{1.13}Mg_{0.77}Fe_{0.06}Si_{2.02}O_{6.00}$	+2	O_6	350	0.879	0.712	
$Ca_{1.16}Mg_{0.64}Fe_{0.30}Si_{1.93}O_{6.00}$	+2	O_6	350	0.879	0.712	
	+3	O_6	545	0.931	0.861	
Riebeckite (N)						
$Na_{0.47}K_{0.45}Fe^{2+}_{2.81}Fe^{3+}_{2.21}Mn_{0.22}Zn_{0.23}Ti_{0.18}Si_{7.80}O_{22}(OH)_2$	+2	$O_4(OH)_2$ (M1)	410	0.90	0.77	8
	+2	$O_4(OH)_2$ (M3)	390	0.90	0.76	
	+3	O_6 (M2)	520	0.93	0.85	
$Na_{1.86}Fe^{2+}_{2.65}Fe^{3+}_{2.25}Mg_{0.60}Si_{7.72}O_{22}(OH)_2$	+2	$O_4(OH)_2$ (M1)	370	0.89	0.73	8
	+2	$O_4(OH)_2$ (M3)	360	0.88	0.72	
	+2	O_6 (M4)	340	0.87	0.69	
	+3	O_6 (M2)	520	0.93	0.85	
Garnet (N)						
$Mn_{2.02}Fe_{1.02}Al_{2.04}Ca_{0.02}Si_{2.94}O_{12.00}$	+2	O_8	296	0.847	0.624	
3. Phosphates						
Anapaite (N)						
$Ca_2Fe(PO_4)_2.4H_2O$	+2	$O_2(OH_2)_4$	370	0.888	0.734	9
Strunzites (N)						
		$(OH)_2(H_2O)O_3$	474	0.919	0.824	

[a] References: *1* McCammon et al. 1995; *2* de Bakker (1994); *3* Chen et al. (1992); *4* De Grave et al. (1998a); *5* Eeckhout et al. (2000); *6* S.G. Eeckhout and E. De Grave, 2003; *7* E. De Grave and S.G. Eeckhout, 2003; *8* Van Alboom and De Grave (1996); *9* Eeckhout et al. (1999)
[b] Average for tetrahedral and octahedral sites; differences between these sites are believed to be small in spinel oxides (De Grave and Van Alboom 1991)
[c] Mössbauer fraction at 40 and 275 K

levels of SiO_2 (Canil and O'Neill 1996), nor for amphiboles where stoichiometry cannot be uniquely determined. During the past years, however, quantitative determination of iron oxidation states has been made possible using electron energy-loss near-edge structure spectroscopy (ELNES) at the Fe $L_{2,3}$ edge (van Aken et al. 1998) and at the Fe $M_{2,3}$ edge (van Aken et al. 1999). These newly developed methods, making use of a transmission electron microscope, have a high spatial resolution on a scale down to 10–100 nm. This does not imply that the application of Mössbauer spectroscopy in mineralogical sciences will become redundant in the future. On the contrary, new areas of interest where the technique can play a crucial and maybe unique role have emerged in recent years and are further being developed, such as in-field phase analyses (Klingelhöfer et al. 2002) and the exploration of the surface of Mars with miniaturized spectrometers (Klingelhöfer et al. 2001).

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