STUDY ON Fe ION DISTRIBUTION IN NATURAL CHROMITE BY MÖSSBAUER TECHNIQUE

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(Received October 1991)

ABSTRACT

Mössbauer absorption spectra in a natural chromite from Shanxi province of China were measured, covering a temperature range from 12 K to 800 K. Each spectrum at low temperature can be fitted to three doublets: the first two are attributed to tetrahedral *T*-site Fe ions and the third one to octahedral *M*-site Fe ions. Such assignment was confirmed by the detailed analyses of the temperature dependent centre shift and other parameters. As a main result, our data strongly supported the ordered distribution with Fe^{2+} in *T*-site and Fe^{3+} in *M*-site for chromite studied. No evidence for electron hopping processes was detected.

Keywords: Mössbauer spectroscopy Chromite Next nearest neighbour

1 INTRODUCTION

Natural chromites as an important ore in metallurgical industries show a very wide range of composition and crystallize in spinel structure TM_2O_4, where *T* refers to a divalent metal ion (Fe^{2+}, Al^{2+}, Mn^{2+}) in tetrahedral site, M refers to a trivalent metal ion (Fe^{3+}, Al^{3+}, Cr^{3+}) in octahedral site. A number of investigations on chromites have been carried out by the Mössbauer technique, however, the interpretation of the spectra themselves is still a controversial issue, namely, some authors interpret the spectra in terms of a disordered distribution of iron atoms over both the *T*-sites and *M*-sites[1,2], but others suggested an ordered one with Fe^{2+} in *T*-site and Fe^{3+} in *M*-site[3,4]. Based on the detailed studies of synthetic spinels such as $FeCr_2O_4$, $Fe(Cr_{2-x}Al_x)O_4$[5,6], the complex Mössbauer spectra of some natural chromites can be understood essentially by the next nearest neighbour (NNN) effect on Fe^{2+} in *T*-site and on Fe^{3+} in *M*-site, but not by a disordered distribution of iron in crystal structure. For example, the Fe^{2+} in $FeCr_2O_4$ is surrounded with twelve Cr^{3+} as NNN's,

the substituted Cr^{3+} by a small amount of Al^{3+} ions ($x=0.1$) give rise to an extra doublet besides the singlet coming from Fe^{2+} in $FeCr_2O_4$. When $x>0.25$, this singlet becomes undetectable, it means the probability of having 12 Cr surrounding the Fe^{2+} is negligible and Fe^{2+} in T-site is very sensitive to its NNN environment. Therefore the $Fe^{2+}-Fe^{3+}$ ordering model seems to be more interesting, and we have extended the Mössbauer experiments to a wide temperature range between 12 K and 800 K with an aim to show the validity of this model.

2 EXPERIMENTAL

The chromite sample from Shanxi province of China was checked for purity by X-ray diffraction. The electron microprobe method shows the samples to be magnesioferrochromite. The powder sample was pressed into a disk with natural iron 4 mg/cm^2 thickness and thermally clamped to cold head of a closed-cycle refrigerator (Displex Mode CS-202) with a temperature accuracy of ± 0.1 K. A vacuum furnace was used for performing experiments at $T>300$ K. Mössbauer spectra were recorded using a constant acceleration spectrometer (OXFORD MS-500) in transmission geometry. The source of 3.7×10^8 Bq ^{57}Co/Pd was kept at room temperature. The data were analysed by using the program MOSFUN.

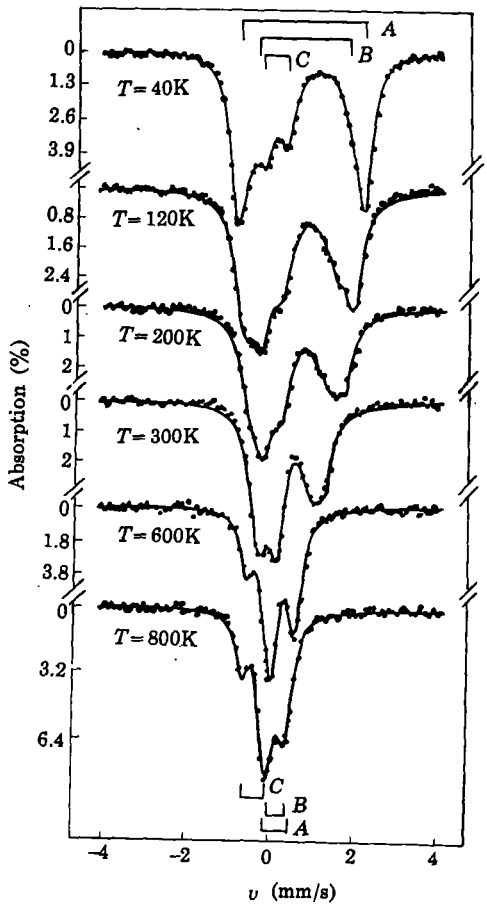

Fig.1 ^{57}Fe Mössbauer spectra of magnesio-ferrochromite sample at different temperatures

3 RESULTS AND DISCUSSION

Several Mössbauer spectra are plotted in Fig.1. The low temperature spectra consist of five resolved peaks, which can be fitted to three doublets (noted by A, B, C). The first two (A, B) are attributed to T-site Fe^{2+}, the third to M-site Fe^{3+}.

The Mössbauer spectra are in different way affected by NNN configurations, some of these configuration have a large probability and give rise to the resolved doublets (like above A, B), the others only broaden the spectra. Most Mössbauer parameters

are characterized by their temperature dependence, so experiments were carried out under a wide temperature range to make us readily to analyse the Mossbauer spectra and to illustrate the NNN influence.

3.1 Center shift (δ)

Shown in Fig.2a are the temperature dependence of the center shifts. We found three convinced evidences to support our interpretation of two ferrous doublets A, B, each of them arises from a particular NNN configurations of Al, Fe and Cr cations in *M*-site. a. At each temperature the center shifts of doublets A, B are exactly identical, especially their room temperature values (see Tab. 1) agree completely with that for *T*-site Fe^{2+} in $FeCrO_4$ and $FeAl_2O_4$[4]. b. At temperature in excess of 200 K the center shifts decrease linearly with temperature due to the second-order Doppler effect, the temperature coefficients (see Tab.1) coincide with those for Fe^{2+} in $FeCr_2O_4$ and FeV_2O_4[5]. c. A partial substitution of Rh/In and Fe for Cr in $FeCr_2S_4$ or $FeCr_2O_4$, leads to appear a "extra" doublet (like A or B in the present work)[3,7,8], its quadrupole splitting has been changed remarkably as a function of substitution concentrations, however, the center shifts remain almost constant.

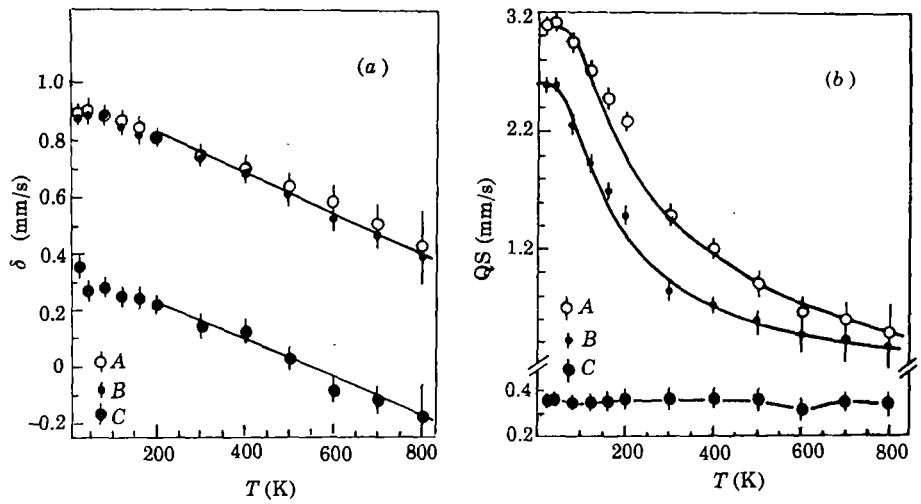

Fig.2 Temperature dependences of center shifts (a) and a quadrupole splitting (b) for magnesioferrochromite sample

As to the third doublet, its room temperature center shift is a value typical for Fe^{3+} and consistent with published data[3,4,9].

3.2 Quadrupole splitting (QS)

Temperature dependences of QS(A) and QS(B) shown in Fig.2b have a similar behaviours, and are interpreted in terms of Jahn-Teller distortions removing the degeneracy of the Eg level. Neglecting the spin-orbital interaction, the QS of *T*-site

Fe^{2+} ion as a function of temperature is expressed as:

$$QS(T) = QS(0)\ [1-\exp(-\varepsilon\ /kT)]/[1+\exp(-\varepsilon\ /kT)] \qquad (1)$$

where ε is the separation energy between $3z^2-r^2$ and x^2-y^2 levels. Thus the QS decreases with the temperature due to thermal population of excited level x^2-y^2 by the sixth electron. Fitting the experimental QS according to Eq.(1), we obtained the separation energies listed in Table 1.

Table 1

Center shift at 300 K and some parameters derived from Mossbauer spectrum analyses

δ (A)* (mm/s)	δ (B)* (mm/s)	δ (C)* (mm/s)	$d\delta$ (A)/dT (mm^{-1} deg^{-1})	$d\delta$ (B)/dT	ε (A) (cm^{-1})	ε (B) (cm^{-1})	Fe^{2+}/Fe^{3+}
0.92 (1)	0.93 (2)	0.32 (2)	-6.8×10^{-4}	-6.9×10^{-4}	215	162	0.36

* Relative to α - Fe

The Fe^{3+} ion with five d-orbitals half-filled has a spherical charge distribution, and we can take $(V_{zz})_{val} \sim 0$, therefore any observed QS arises solely from the temperature independent term $(V_{zz})_{lat}$, as it is confirmed from the bottom of Fig.2b.

3.3 High temperature spectra

Table 2

Center shifts, quadrupole splittings and line widthes (all in mm/s) obtained by three- doublet and two- doublet fits in high temperature range

	T (K)	δ (A)*	δ (B)*	δ (C)*	QS (A)	QS (B)	QS (C)	G (A)	G (B)	G (C)	χ^2
Three doublet fit	400	0.88 (2)	0.87 (4)	0.30 (6)	1.21 (7)	0.72 (7)	0.51 (6)	0.23 (7)	0.20 (6)	0.21 (4)	1.05
	500	0.81 (4)	0.79 (5)	0.20 (8)	0.91 (8)	0.59 (7)	0.51 (6)	0.21 (7)	0.19 (5)	0.19 (3)	1.12
	600	0.77 (5)	0.74 (4)	0.15 (5)	0.67 (9)	0.47 (8)	0.52 (8)	0.18 (9)	0.17 (7)	0.16 (4)	0.94
	700	0.69 (7)	0.66 (5)	0.07 (2)	0.60 (11)	0.43 (10)	0.50 (3)	0.16 (7)	0.17 (5)	0.18 (2)	1.06
	800	0.61 (8)	0.62 (7)	0.01 (2)	0.50 (12)	0.36 (14)	0.49 (4)	0.18 (9)	0.16 (9)	0.15 (2)	1.00
Two- doublet fit	400	0.87 (1)		0.30 (1)	0.92 (2)		0.50 (4)	0.28 (2)		0.17 (2)	1.07
	500	0.79 (2)		0.20 (3)	0.70 (4)		0.51 (7)	0.24 (1)		0.16 (3)	1.14
	600	0.71 (3)		0.15 (5)	0.58 (5)		0.53 (7)	0.20 (1)		0.16 (2)	0.99
	700	0.66 (1)		0.07 (2)	0.49 (2)		0.51 (4)	0.19 (1)		0.16 (2)	1.05
	800	0.57 (1)		0.01 (2)	0.41 (2)		0.51 (3)	0.19 (1)		0.14 (2)	0.99

* Relative to α - Fe

Above room temperature the difference between QS(A) and QS(B) is getting smaller that two ferrous doublets become overlapping. In this case we can analyse the Mössbauer spectra by two doublets: one ferrous and one ferric. The results obtained by two fitting approaches are presented in Table.2. The parameter errors of ferros doublet are much reduced, in comparison with those given by three-doublet fit while the parameter errors of the ferric doublet are the same for two fitting approaches. The higher is the temperature, the narrower is the line width of ferrous doublet, and two-doublet fit looks better. It seems to be unreasonable to use multiple doublets to

fit overlapping spectra for natural chromites, except some crystal and chemical reasons.

4 CONCLUSIONS

a. The experimental results strongly support an ordered distribution with Fe^{2+} in T-site and Fe^{3+} in M-site for natural chromite studied.

b. As $T > 300$ K fitting the spectra by more than three doublets seems to be not recommendable due to large errors in the Mössbauer parameters obtained.

c. Concerning the electron hopping process, no evidence was observed in present study.

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