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Mössbauer and magnetic studies of Sn⁴⁺-substituted Ni–Zn ferrites

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Abstract. In this work we make Mössbauer and magnetization studies of Sn⁴⁺-substituted Ni_{1-y}Zn_yFe₂O₄ ($y = 0.3, 0.4$) ferrite. In this range Mössbauer spectra are not relaxed and may be used to gain insight into the Sn⁴⁺ distribution process. It is found that $H_{\text{eff}}(\text{B})$ remains almost unchanged and $H_{\text{eff}}(\text{A})$ decreases as the concentration of Sn⁴⁺ ions increases in the lattice. It is evident that Sn⁴⁺ ions occupy only the octahedral B sites. The magnetization shows a non-linear behaviour with increase in the proportion of Sn⁴⁺ ions.

1. Introduction

The present work reports the results of Mössbauer and magnetization studies of Sn⁴⁺-substituted Ni_{1-y}Zn_yFe₂O₄ ($y = 0.3, 0.4$) ferrites. In this range the Mössbauer spectra are not relaxed and may be used to gain insight into the Sn⁴⁺ distribution process. The concentrations of Sn⁴⁺ are kept very low (Ni_{1-y+x}Zn_yFe_{2-2x}Sn_xO₄, $x = 0.00-0.04$; $y = 0.3, 0.4$) unlike in previous studies [1–8]. Ti⁴⁺ substitution in this concentration range revealed an anomalous behaviour in the magnetization [9, 10]. Hence substitution of other ions, e.g. Sn⁴⁺ in the present case, in this concentration range warrants detailed study. The present activity is part of a programme to study the effects of introducing non-magnetic tetravalent cations into Ni–Zn ferrites.

2. Experimental details

For the present study the ferrite samples were prepared in an oxidizing atmosphere using the solution technique. The x-ray diffraction studies were performed using a Siefert x-ray diffractometer with Cu as the target. The x-ray diffraction pattern of the samples confirmed the presence of the single spinel phase. The magnetization measurements were made on a 150A Vibrating Sample Magnetometer (supplied by Princeton Applied Research Corporation, USA). The Mössbauer spectra of the samples were recorded using an ND-62 multichannel analyser. A 25 mCi ⁵⁷Co-in-Rh source (obtained from E I du Pont, USA) was used.

3. Study of Mössbauer hyperfine parameters

Mössbauer spectra of all the samples, $\text{Ni}_{1-y+x}\text{Zn}_y\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ ($y = 0.3, 0.4$ and $x = 0.000, 0.002, 0.004, 0.008, 0.012, 0.024, 0.04$), were recorded at room and liquid nitrogen temperature. They showed a well defined Zeeman pattern consisting of two separate sextets, due to Fe^{3+} ions at the A and B sites. Two typical Mössbauer spectra of $\text{Ni}_{0.7+x}\text{Zn}_{0.3}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.04$) at 295 and 77 K are shown in figure 1. The Mössbauer spectra were fitted using a computer program which is based upon the method developed by Law and Bailey [11]. The program also gives the error matrix [12] from which the standard error in the fitted parameters can be calculated. All the computations were done on a DEC-1090 computer.

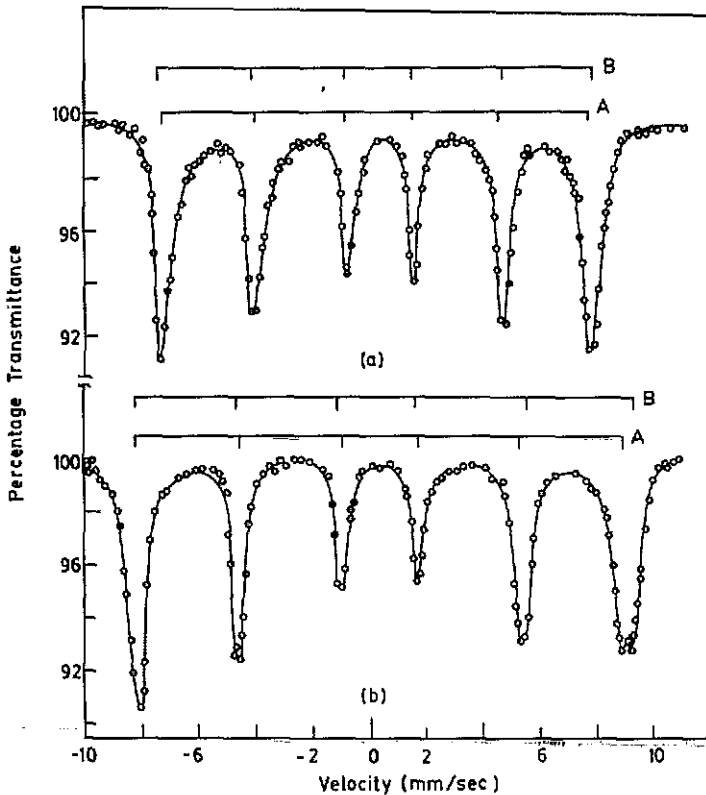


Figure 1. Mössbauer spectra of $\text{Ni}_{0.7+x}\text{Zn}_{0.3}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.04$) at (a) 295 and (b) 77 K.

The isomer shift of Fe^{3+} ions (with respect to sodium nitroprusside) at the tetrahedral site, $IS(A)$, and at the octahedral site, $IS(B)$, in the Sn^{4+} -substituted $\text{Ni}_{1-y}\text{Zn}_y\text{Fe}_2\text{O}_4$ system showed no significant change with changes in Sn^{4+} concentration. The weighted average value of the isomer shift in $\text{Ni}_{0.7+x}\text{Zn}_{0.3}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ at the A and B sites at 295 K are 0.509 ± 0.002 and $0.633 \pm 0.002 \text{ mm s}^{-1}$, respectively. At 77 K, the weighted average value of the isomer shift at the A and B sites were 0.690 ± 0.002 and $0.875 \pm 0.002 \text{ mm s}^{-1}$, respectively. In the Sn^{4+} -substituted $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite system the isomer shift of Fe^{3+} ions at the A and B sites also did not show any significant change with change in Sn^{4+} concentration.

The invariance of the isomer shift with respect to Sn⁴⁺ concentration indicates that the s-electron density at the Fe³⁺ nucleus is not affected by Sn⁴⁺ substitution. The values of the isomer shift at the A and B sites show that the iron is in the Fe³⁺ state [13]. The result $IS(A) < IS(B)$ is in agreement with the results of other workers [14, 15]. This is interpreted as being due to the large bond separation of Fe³⁺-O²⁻ for the octahedral ions compared with that for the tetrahedral ions. As the orbitals of the Fe³⁺ and O²⁻ ions overlap less, the covalency effect is smaller, and hence the isomer shift is large at the octahedral site. It is also found that the isomer shift at 77 K is larger than its value at 295 K. This increased value for the isomer shift at 77 K is due to the thermal red shift between the source at 295 K and the absorber at 77 K [16, 17].

In none of the spectra was quadrupole splitting observed within the experimental error for both the A and B sites. Zero quadrupole splitting in such ferrites may be explained by the presence of chemical disorder. This will produce an electric field gradient of varying magnitudes, directions, sign and symmetry, and a resulting distribution in the quadrupole shift. Because of the overall cubic symmetry of the spinel ferrite and the randomness of chemical disorder, there will be equal probability for small quadrupole splittings of opposite signs. Hence the centres of the Zeeman lines will not change, and consequently there will be no net observable quadrupole splitting.

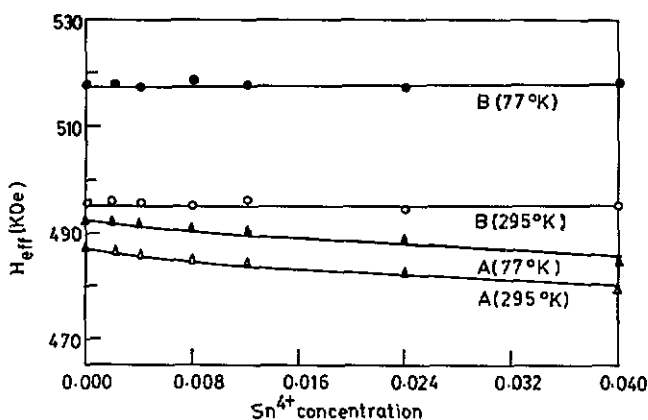


Figure 2. The variation of hyperfine field with Sn⁴⁺ concentration in Ni_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O₄ ferrite at 295 and 77 K. In this and subsequent figures, the height of the symbol represents the error bar.

In Sn⁴⁺-substituted Ni_{0.7}Zn_{0.3}Fe₂O₄ ferrite, at 295 K, the variation of H_{eff} at the A and B sites with Sn⁴⁺ concentration is shown in figure 2 and it is also tabulated in table 1. From the figure as well as the table, it can be observed that there is no significant change in $H_{\text{eff}}(B)$ which remains almost constant at a value of 495 ± 1 kOe. $H_{\text{eff}}(A)$, on the other hand, decreases from 487 ± 1 to 480 ± 1 kOe as the concentration of Sn⁴⁺ increases from $x = 0.00$ to $x = 0.04$. At 77 K similar behaviour for $H_{\text{eff}}(A)$ and $H_{\text{eff}}(B)$ with a change in Sn⁴⁺ concentration is also observed (figure 2). Here $H_{\text{eff}}(B)$ remains almost constant at 518 ± 1 kOe whereas $H_{\text{eff}}(A)$ decreases from 492 ± 1 to 485 ± 1 kOe, as the concentration of Sn⁴⁺ ions increases from $x = 0.00$ to $x = 0.04$. In Sn⁴⁺-substituted Ni_{0.6}Zn_{0.4}Fe₂O₄ ferrite we also obtain a similar variation in H_{eff} at both the A and B sites. At 295 K, $H_{\text{eff}}(B)$ remains almost constant at 446 ± 1 kOe

whereas $H_{\text{eff}}(\text{A})$ decreases from 480 ± 1 to 475 ± 1 kOe, as the concentration of Sn^{4+} ions increases from $x = 0.00$ to $x = 0.04$. At 77 K, $H_{\text{eff}}(\text{B})$ remains constant at a value of 518 ± 1 kOe and $H_{\text{eff}}(\text{A})$ decreases from 506 ± 1 to 500 ± 1 kOe as the concentration of Sn^{4+} increases from $x = 0.00$ to $x = 0.04$. For a zero concentration of Sn^{4+} the values of H_{eff} at the two sublattices at 295 and 77 K are in excellent agreement with the values reported in the literature [18]. It can also be observed that for the $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite, at 295 K, $H_{\text{eff}}(\text{A})$ is greater than $H_{\text{eff}}(\text{B})$ whereas at 77 K, $H_{\text{eff}}(\text{B})$ is greater than $H_{\text{eff}}(\text{A})$. These observations are consistent with the results reported by Daniels and Rosenwaig [18]. They studied the hyperfine field in the $\text{Ni}_{1-y}\text{Zn}_y\text{Fe}_2\text{O}_4$ ($0 < y < 1$) system and explained this anomaly as resulting from the balance between the macroscopic effect of magnetization and the microscopic effect of intersublattice magnetic bonds per Fe^{3+} ion.

Table 1. Variation of hyperfine field in $\text{Ni}_{0.7+x}\text{Zn}_{0.3}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ at A and B sites at 295 K.

x	H_{eff} (kOe) ^a	
	A site	B site
0.000	487	495
0.002	487	495
0.004	486	494
0.008	486	495
0.012	485	496
0.024	483	494
0.040	480	495

^a The error in the hyperfine field is ± 1 kOe.

The variation in the effective hyperfine field at the two sublattices could be understood on the basis of Néel's molecular field theory [19] and the supertransferred hyperfine field, H_{STHF} [20]. H_{eff} at a lattice site is primarily due to the core polarization of its site ion. But its variation is due to that of the supertransferred hyperfine field. In both systems it is found that $H_{\text{eff}}(\text{B})$ remains almost constant whereas $H_{\text{eff}}(\text{A})$ decreases with an increase in the Sn^{4+} concentration. We attribute this to the fact that all the Sn^{4+} ions occupy only the B site. We give our arguments in favour of these conclusions later.

The supertransferred hyperfine field at Fe^{3+} ion at the A site is due to spin transfer from the d-orbitals of the nearest-neighbour cations (i.e. those belonging to the B sublattice) through the ligand anions to the s-orbitals of the Fe_A^{3+} ion under consideration. Thus the supertransferred field at the A site will depend on the magnetic moment of the B site. All the non-magnetic Sn^{4+} ions occupy the B site thereby reducing the magnetization M_B ; this, in turn, reduces the supertransferred hyperfine field at the A site. Similarly, it can be argued that the supertransferred hyperfine field at the B site should remain constant as the magnetization M_A does not change, as the Sn^{4+} ions only enter at the B site.

In figure 3 we show the variation of the full width at half maximum (FWHM) of the Mössbauer absorption peak with Sn^{4+} concentration for the Sn^{4+} -substituted $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite. At 295 K, Γ_B remains almost constant at a value of 0.775 ± 0.003 mm s⁻¹, whereas at 77 K, it drops to 0.610 ± 0.004 mm s⁻¹ and remains almost constant at that value as the concentration of Sn^{4+} increases from $x = 0.00$ to $x = 0.04$.

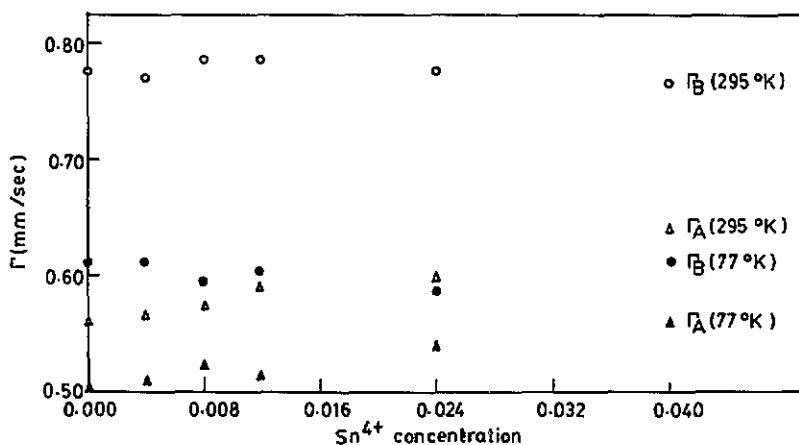


Figure 3. Variation of FWHM with Sn⁴⁺ concentration in Ni_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O₄ ferrite at 295 and 77 K.

The FWHM of the tetrahedral component of spectrum, Γ_A , at 295 K, increases from 0.561 ± 0.004 to 0.641 ± 0.003 mm s⁻¹ as the concentration of Sn⁴⁺ ions increases from $x = 0.00$ to $x = 0.04$. Γ_A at 77 K is 0.501 ± 0.003 mm s⁻¹ for the zero concentration of Sn⁴⁺ and it increases up to 0.561 ± 0.003 mm s⁻¹ for $x = 0.04$. The values of Γ_A and Γ_B at 295 and 77 K of our samples with zero concentration of Sn⁴⁺ are consistent with the values reported by Daniels and Rosencwaig [18].

If two or more cations are present in one or both of the sublattices then there will be a distribution of the values of $\langle S_z \rangle$ which results in a distribution of the values of hyperfine field at the nucleus. This, as well as the quadrupole broadening discussed earlier, contributes to the line broadening of the Mössbauer absorption peaks. The increase in the value of Γ_A with Sn⁴⁺ concentration shows that the width of the distribution of $\langle S_z \rangle$ at the B site increases as all the Sn⁴⁺ ions enter at the B site. With the decrease in temperature, the width of the distribution of $\langle S_z \rangle$ is narrowed and hence a decrease in the line broadening at 77 K.

Our studies on Ti⁴⁺-substituted Ni-Zn ferrites also show that the isomer shift remains almost unchanged with Ti⁴⁺ concentration in Ni_{1-y+x}Zn_yTi_xFe_{2-2x}O₄ ($y = 0.3, 0.4$ and $0.00 < x < 0.08$). The weighted average value of isomer shift in Ni_{0.7+x}Zn_{0.3}Ti_xFe_{2-2x}O₄ ($0.00 < x < 0.08$) at A and B sites at 295 K are 0.533 ± 0.002 and 0.615 ± 0.002 mm s⁻¹ respectively. At 77 K, the weighted average values of the isomer shift at the A and B sites are 0.719 ± 0.002 and 0.840 ± 0.002 mm s⁻¹ respectively. In this system too, the hyperfine field at A site, i.e. $H_{\text{eff}}(\text{A})$ decreases with an increase in Ti⁴⁺ concentration in Ni_{1-y+x}Zn_yTi_xFe_{2-2x}O₄ ($y = 0.3, 0.4$ and $0.00 < x < 0.08$) ferrite whereas $H_{\text{eff}}(\text{B})$ remains almost constant. These were attributed to the fact that all the non-magnetic Ti⁴⁺ ions enter at B sites. These appear to be the general features of the small concentration substitution of non-magnetic tetravalent ions in Ni-Zn ferrites. However, for definitive statements, studies for other similar ions, e.g. Zr⁴⁺ and Nb⁵⁺, will have to be conducted.

4. Study of magnetization

In figure 4 we have shown the variation of magnetization, obtained from VSM measurements at room temperature with Sn⁴⁺ concentration, for Sn⁴⁺-substituted

$\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite. The magnetization shows a steep fall from $2.62 \mu_B$ at the zero concentration of Sn^{4+} to $2.38 \mu_B$ at an Sn^{4+} concentration of $x = 0.004$ followed by a very slow decrease up to $x = 0.04$. For the Sn^{4+} -substituted $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite, we have found a similar variation in the magnetization at room temperature with Sn^{4+} concentration.

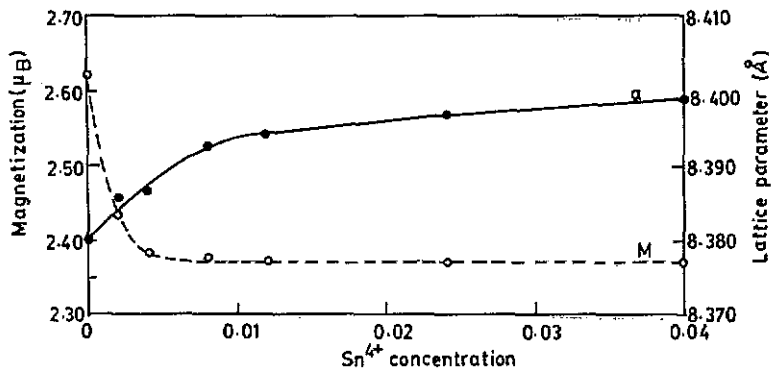


Figure 4. Variation of magnetization (M) and lattice parameter (a) with Sn^{4+} concentration in $\text{Ni}_{0.7+x}\text{Zn}_{0.3}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite at 295 K.

If we consider the Néel type of magnetic ordering then a linear fall in the magnetization is expected with an increase in the Sn^{4+} concentration as all the Sn^{4+} ions enter at the B site only. But in both the systems the magnetization curve only shows non-linear behaviour. This anomalous behaviour of the magnetization suggests the development of a canted spin structure [10].

A correlation between the lattice parameter and exchange constants can be seen in the work of Shiga [21]. Again, the exchange constants determine the magnetic structure and hence the magnetization. This correlation between the lattice parameter and magnetization is evident from the plot of experimental data for these quantities, obtained respectively from x-ray and VSM measurements, against Sn^{4+} concentration (figure 4). For a detailed analysis of the magnetic structure it is necessary to study the system by neutron diffraction and by Mössbauer spectroscopy in an external magnetic field.

5. Conclusion

It is concluded that in Sn^{4+} -substituted $\text{Ni}_{1-y}\text{Zn}_y\text{Fe}_2\text{O}_4$ ferrite all the Sn^{4+} ions occupy the octahedral site. The anomalous change in magnetization with the introduction of Sn^{4+} ions suggests the presence of canted spin structure which needs further confirmation by studying the system by Mössbauer spectroscopy in external magnetic field and by neutron diffraction.

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