MÖSSBAUER SPECTRA OF ^{57}Fe IN $BaFe_4Sn_2O_{11}$

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Abstract

Mössbauer measurements of ^{57}Fe in $BaFe_4Sn_2O_{11}$ from 4.2 to 860 K are reported. The results provide evidence that the magnetism might be of the spin glass type below 77 K.

INTRODUCTION

The structure of the insulating ternary oxide $BaFe_4Sn_2O_{11}$ is of hexagonal R-type ([1]), with unit cell parameters a = 5.9624 A° and c = 13.7468 A°. The unit cell contains two formula units, and neutron diffraction data were found to be consistent with the hypothesis that six Fe^{3+} and four Sn^{4+} cations occupy the special octahedral positions 4e, 6g, while two Fe^{3+} cations occupy quasi-tetrahedral 4f sites of the P6/mmc space group. Recent investigations ([2]) of the structural and magnetic properties of the $BaFe_4Sn_xTi_{2-x}O_{11}$ family have shown that samples with $x < 0.2$ behave as re-entrant spin glasses, while those with $x > 0.2$ reveal characteristics of cluster type spin glasses (SG). These observations were established on the basis of cusps in low field ac susceptibility measurements. However the SG properties of $BaFe_4Sn_2O_{11}$ have not been clearly shown either by magnetic or Mossbauer measurements ([2]).

In this report we discuss ^{57}Fe Mössbauer spectra of $BaFe_4Sn_2O_{11}$ in the temperature region from 4.2 to 860 K. Mössbauer spectroscopy is a microscopic method and can contribute complementary data to the structural and magnetic properties on a local scale.

EXPERIMENTAL PROCEDURE

The high temperature solution method was used for the preparation of $BaFe_4Sn_2O_{11}$ samples in the form of plate-like crystals 2 mm long and 0.2 mm thick.

The flux environment of $PbCl_2 \cdot 6B_2O_3$ was kept constant at 80 wt %. The chemicals used were at least 99.5% pure. Samples were melted in a platinum crucible of 10 or 20 ml capacity. The furnace with crucible was heated to an initial temperature of about 1320° C. The soaking time and cooling rate were two hours and 15° C/h, respectively. The matrix containing the crystals was disintegrated with dilute HNO_3. Crystals were magnetic and could be separated from the disintegrated matrix by the use of a permanent magnet. The composition of the crystals was determined by chemical analysis, by a microanalyzer, and checked by their X-ray diffraction patterns.

Thin absorbers for Mössbauer measurements were first prepared by carefully grinding the single crystals. However, the Mössbauer spectra of an absorber prepared in this way were observed in the paramagnetic state as asymmetrical doublets (Fig. 1a). In order to determine the reason for these asymmetrical spectra, we made measurements at various angles between the plane of the absorber and the γ — ray beam. A strong angular dependence of the relative intensities of resonance lines was noted, indicating preferential orientation of the crystallites.

In order to assure random orientations of crystallites, it was necessary to prepare thin absorbers for Mössbauer measurements by grinding the single crystals with sugar. The finely powdered mixture was uniformly spread in an appropriate holder and as such used for all Mössbauer measurements in the temperature region 4.2 to 860 K (Figures 1b, 2, 3), using an Elscint constant acceleration spectrometer. The source was ^{57}Co in a Rh matrix. The velocity scales were calibrated by spectra of metallic iron, which was also used as a reference for the isomer shift parameter. Mössbauer spectra were analysed by a least squares computer program assuming Lorentzian line shapes.

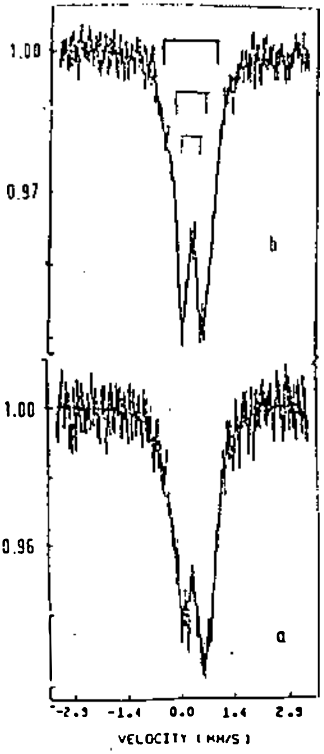

Fig. 1. Mössbauer spectra of ^{57}Fe in $BaFe_4Sn_2O_{11}$ at room temperature: a) non-randomly, and b) randomly oriented sample.

RESULTS AND DISCUSSION

The spectra measured in the paramagnetic state taken at 80 to 860 K reveal similar shapes (Figs 1b, 2), displaying the quadrupole interaction between the nuclear quadrupole moment of iron and the electric field gradient tensors at iron sites. Computer fits of these spectra gave (Table I) the quadrupole splitting, isomer shift and relative occupation of iron ions at octahedral (6g, 4e) and quasi-tetrahedral (4f) sites. The latter deviate from predicted ones (1), probably because in analysing the Mössbauer spectra equal recoiless fractions were uncritically taken for granted. The quasi-tetrahedral iron ions repre-

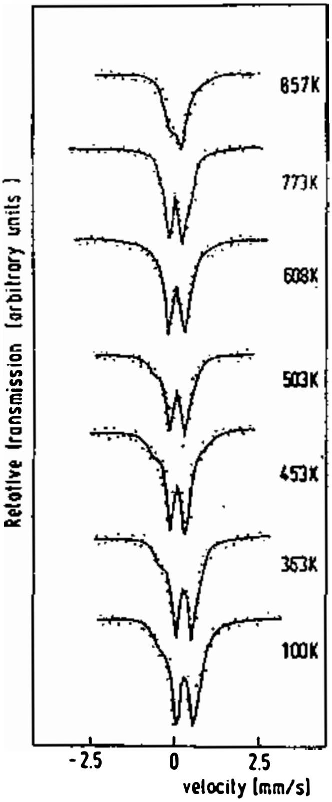

Fig. 2. Mössbauer spectra of ^{57}Fe in $BaFe_4Sn_2O_{11}$ in the paramagnetic state at various temperatures, taken with a source of ^{57}Co in a Rh matrix.

Table 1: Hyperfine parameters of ^{57}Fe in $BaFe_4Sn_2O_{11}$ at room temperature

Possition	IS/Fe mm/s	QS mm/s	site occupation %	
			Mössbauer data	diffr. date (1)
6g	0.35	0.46	57	55
4e	0.36	0.76	28	20
4f	0.23	1.33	15	25

IS-isomer shift ± 0.01, QS-quadrupole splitting ± 0.01

sent the unique feature in the hexagonal R structure due to their oscillations between two equivalent quasi-tetrahedral positions. Appreciably increased mean square displacements of these ions are expected, giving rise to pronounced reduction of the recoil-free fraction relative to the 6g, 4e, octahedral sites. However, the hyperfine parameters assigned to individual ion sites (Table 1) are characteristic of $3d^5$ configurations, corresponding to iron ions in nonequivalent crystallographic sites of the $BaFe_4Sn_2O_{11}$ structure. The relatively high value of the quadrupole splitting parameter for the 4f iron site further indicates the great distortion of this site from cubic symmetry.

Below 78 K, in the short temperature interval of 1 – 2 K, the ^{57}Fe spectra dramatically change into a structureless „triangular" pattern, indicating that some magnetic ordering process (Fig. 3) has commenced. As the temperature is decreased, the area of

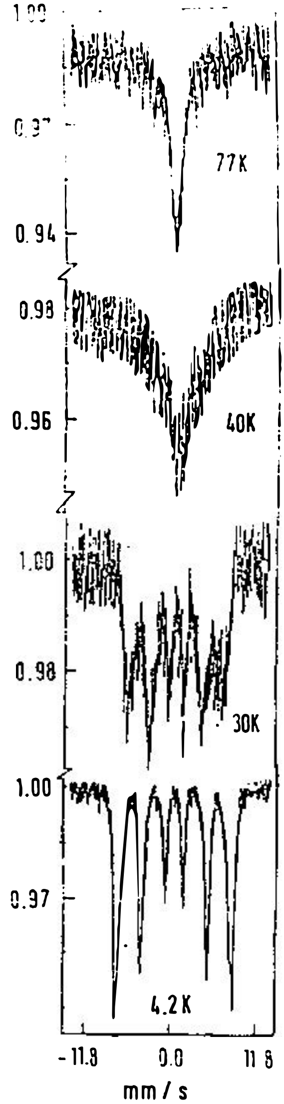

Fig. 3. Mössbauer spectra of ^{57}Fe in $BaFe_4Sn_2O_{11}$ in the magnetic ordered region at various temperatures.

this „triangular" component increases. The broadened patterns, without structure, dominate until 30 K, when hyperfine structure appears as the sextet pattern with broad asymmetrical resonance lines. This change of spectral shape in the transition temperature region is different from that usually observed in various ferrites (4), which have been interpreted either in terms of ionic spin relaxation or non-collinear structure or superferromagnetism. However, in superferromagnetism the interactions between the clusters might lead to anisotropic relaxations, and also cause transitional spectra over a significant temperature range. But the frequencies of superferromagnetic fluctuations are known to decrease with decreasing temperature, and therefore the intensity of doublets should have to descrease at the expense of magnetically ordered spectra in the cooling process. This was not found in the case of $BaFe_4Sn_2O_{11}$, where a broad unresolved shape persists from 77 to 30 K. In this temperature region the behaviour of ^{119}Sn spectra (3) were also in agreement with the behaviour of ^{57}Fe spectra. It is interesting to note the strong similarity of the spectra studied here with those of isostructural $BaFe_4Ti_2O_{11}$, which is known to experience re-entrant spin glass properties (2). There is thus some evidence that spectra of ^{57}Fe in $BaFe_4Sn_2O_{11}$ in the transition temperature region (Fig. 3) indicate slowly relaxing clusters. $BaFe_4Sn_2O_{11}$ can thus be considered magnetically as spin glass type with small ferrimagnetically ordered clusters, with weak or no exchange couplings between them. The spin freezing can be attained either by the iron spins in all or some sublattices having either transverse or longitudinal spin components. Recently, much effort has been expended in order to provide detailed information on the nature of the spin glass freezing process, either in metallic (5) or insulating materials (6).

CONCLUSIONS

Although the prediction for random freezing of the spins in our sample requires additional experimental proof, it nevertheless could not be ruled out from the behaviour of the Mössbauer spectra below 77 K (Fig. 3). The previously reported (2) Mössbauer spectra in $BaFe_4Sn_2O_{11}$ differ from ours in the transition temperature region. Since the spectra at 4.2 K seem essentially similar, the reason for these discrepancies might be due to the different methods of samples preparation. It should be noted that spin glass properties are very sensitive (5) to the sample preparation, the type and amount of impurities and the degree of disorder.

Acknowledgements

We are grateful for financial support from the Research Community of Slovenia, and the Natural Science and Engineering Research Council of Canada.

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