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Study of $LaFe_{12}O_{19}$ from Mössbauer spectra

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A study of lanthanum ferrite, $LaFe_{12}O_{19}$, by use of the Mössbauer effect has contributed experimental data on the temperature dependence of the internal magnetic field on the sites of the ^{57}Fe nuclei, on isomer shift and on quadrupole splitting in the region from 90 to 820K. The Curie temperature was determined at 697K. The Mössbauer spectra of lanthanum and thallium lanthanum ferrite suggest that a special Fe^{2+} sublattice is not present.

1. Introduction

Results of previous investigations using the Mössbauer technique on ferrites of the type $Me^{2+}Fe_{12}^{3+}O_{19}$ with Me standing for Ba^{2+}, Sr^{2+} or Pb^{2+} [1-3] are in accordance with the crystallographic data for magnetoplumbite type crystal lattice. Five non-equivalent lattice sites given by Adelsköld [4] are present, namely octahedral 12 K (I), 2a (III), $4f_2$ (III), tetrahedral $4f_1$ (II) and trigonal 2b (IV) in the ratio of 6:1:2:2:1.

Lanthanum ferrite, $LaFe^{2+}Fe_{11}^{3+}O_{19}$, is of interest for a study using the Mössbauer effect as it is crystallographically isomorphous with the ferrites of the mentioned type. Because it contains one additional Fe^{2+} ion per formula unit [5] (about 8% of iron content) it might provide further experimental evidence on the location of the Fe^{2+} ion. For divalent and trivalent iron ions the differences in the effective magnetic fields and in the isomer shift and quadrupole parameters should be sufficient to separate out the corresponding lines in the spectra because the uncertainty in determining the position of lines is smaller than a third of the channel width (0.03 mm sec^{-1}).

2. Experimental

Samples of lanthanum ferrite were prepared by standard ceramic techniques from a mixture of Fe_2O_3 and La_2O_3 in mole ratio 12:1. The mixture was kept at 1390°C for 72 h and then quenched to room temperature. X-ray powder analyses showed, besides lanthanum ferrite, the presence of some magnetic Fe_3O_4 which was removed by 10% H_2SO_4 dissolving magnetite stronger than magnetoplumbite. The reaction was performed in an apparatus similar to the magnetic separator described by Aharoni and Schieber [6] until the X-ray powder diffraction diagram showed the magnetoplumbite phase only. This diffraction pattern also characterized the compound on the basis of the results of the investigation of Aharoni and Schieber.

The Mössbauer spectra were measured at various temperatures from 90 to 820K. The lower temperature limit was obtained by thermal contact of the absorber with the liquid nitrogen reservoir, while higher temperatures were reached with 0.1 K accuracy by use of a vacuum furnace controlled by a Chromel-Alumel thermocouple. Absorbers were powdered samples of lanthanum ferrite with 10 mg cm^{-2} of ^{57}Fe pressed between two beryllium windows. The source containing ^{57}Co in Pd matrix was mounted on a loudspeaker-drive and kept at room temperature during the measurements. Pulses from a krypton-methane proportional counter were sent to a 256 channel analyser operated in the usual pulse height mode. The velocity scale was calibrated by use of line spectra determined in separate experiments with iron oxide Fe_2O_3 samples and with metallic iron samples as absorbers. Metallic iron was used also as a reference in the determination of the isomer shift.

The spectra were analysed in the usual way by fitting the experimental data with Lorentzian shape curves.

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3. Results

Typical Mössbauer spectra of $LaFe_{12}O_{19}$ enriched to 70% with ^{57}Fe obtained at various temperatures are given in Fig. 1. The spectra with unenriched thin absorbers containing 0.3 mg cm^{-2} ^{57}Fe do not show any significant differences which could be assigned to the presence of the Fe^{2+} ion site. The complex spectra below the Curie temperature comprise six line patterns which disappear around the Curie temperature to leave only one peak. Measured patterns have been assigned to individual iron sites by use of the quadrupole splitting values and the Mössbauer patterns established for other magnetoplumbite materials [2, 3] assuming that the configurations I, II, III, and IV are present in the ratio 6:2:3:1.

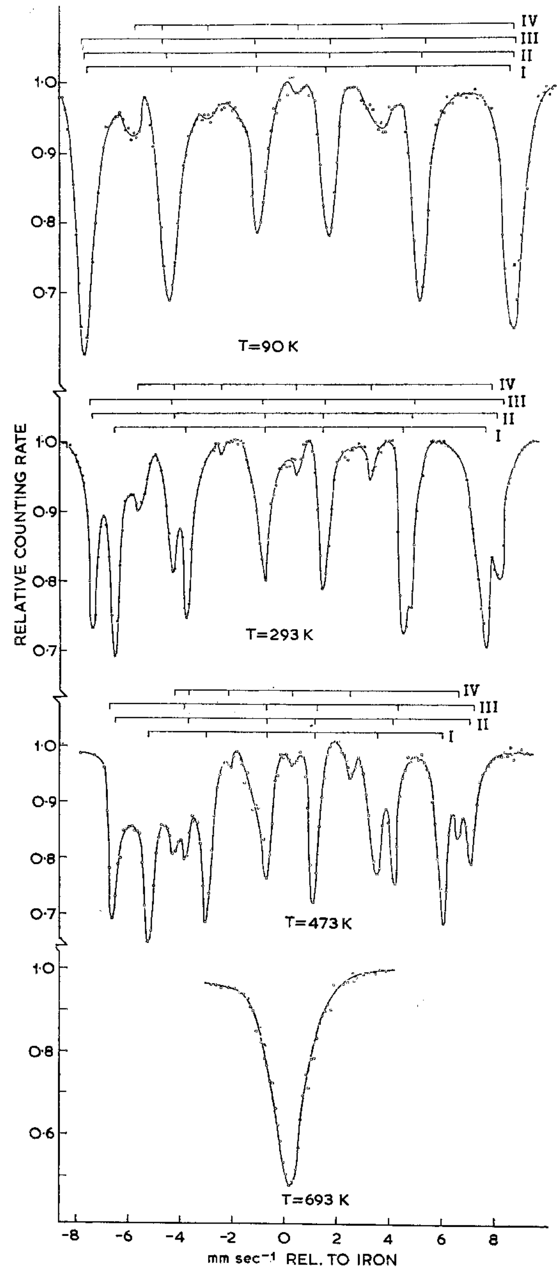

Figure 1 Mössbauer spectra of $LaFe_{12}O_{19}$ polycrystalline absorber at several temperatures taken with a source of ^{57}Co in the Pd matrix.

The six line spectra assigned to various sites are characteristic for combined electric and magnetic hyperfine coupling. In 12 K, $4f_2$, $4f_1$ iron sites, the quadrupole interaction represents a small perturbation only of the magnetic 14.4 keV energy level. For five co-ordinated 2b iron sites, the quadrupole interaction is more dominant so that the ratio of the quadrupole to the magnetic interaction is nearly 1 on the base of Kunding's [7] analysis. The gradient of the electrical field is practically parallel to the magnetic field H, with the angle θ varying between 0 and 10°.

The values of the isomer shift relative to metallic iron, and of the quadrupole coupling parameters for the iron ions in the four iron sites at various temperatures, are shown in Fig. 2. The results are characteristic for the $3d^5$ configuration corresponding to Fe^{3+} ions.

The Curie temperature was determined from the measured temperature dependence of the counting rate at zero velocity shown in Fig. 3 as 697 ± 2 K. The same value resulted from the study of the temperature dependence of the effective magnetic field intensity of different iron sublattices given in Fig. 4. The Curie temperature is also evident in Fig. 2 by an abrupt change of isomer shift induced by the transition from the ferrite to the paramagnetic state.

Additionally, thallium lanthanum ferrite $Tl_{1/2}La_{1/2}Fe_{12}O_{19}$ was studied as it contains Fe^{3+} iron ions only, and further information might be provided from the comparison of the spectra with those of La ferrite.

Samples of the TlLa ferrite were prepared by a standard ceramic technique from a mixture of Fe_2O_3, La_2O_3 and Tl_2O_3 in mole ratio of 24:1:1. The compound was identified by the X-ray analysis giving a diagram identical to the TlLa ferrite reported by Laroia [8].

Relative areas of magnetically split spectra of TlLa ferrite (Fig. 5) correspond to the site occupation 6:3:2:1 of the sites I:II:III:IV as in

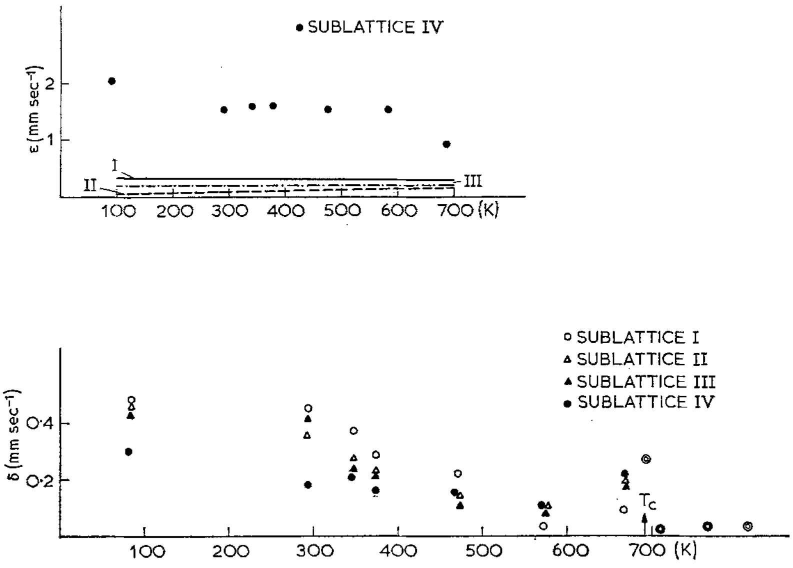

Figure 2 Temperature dependence of the isomer shifts relative to metallic iron and quadrupole couplings for ^{57}Fe in four sublattices of $LaFe_{12}O_{19}$.

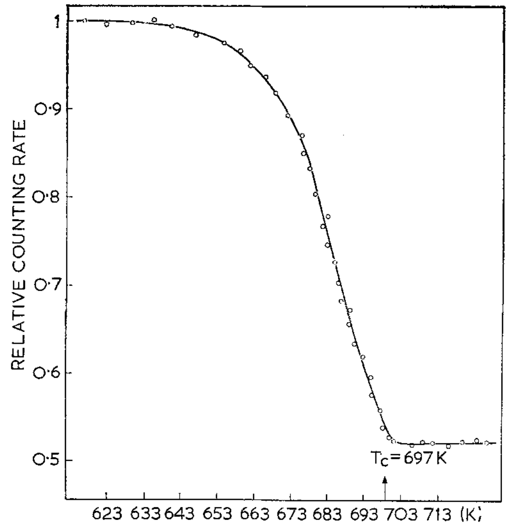

Figure 3 Temperature dependence of the relative counting rate from a stationary source.

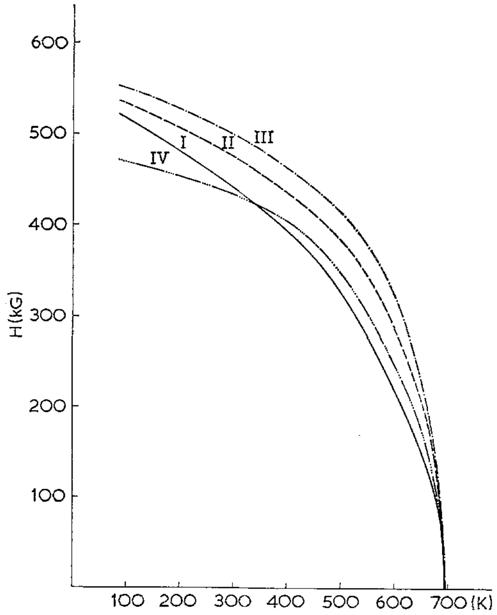

Figure 4 Temperature dependence of the effective magnetic fields at Fe nuclei on four sublattices.

La ferrite. The spectra show the same relative intensities and widths of the lines as spectra of Lanthanum ferrite. The results lead to the conclusion that within the experimental errors, iron nuclei in La ferrite show the average fields of $3d^5$ and $3d^6$ electron configurations. The averaging hyperfine fields evident from the Mössbauer spectra could originate in a fast electron exchange between Fe^{2+} and Fe^{3+} or in the process of sharing one electron by the 6

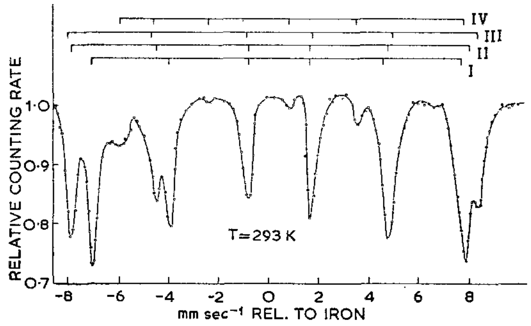

Figure 5 Mössbauer spectrum of TlLa ferrite at room temperature.

irons in I sublattice as proposed by Aharoni [6]. Further study is needed to decide on the dominating mechanism.

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