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NEUTRON DIFFRACTION AND MOSSBAUER EFFECT STUDY ON A MIXED RARE EARTH GARNET

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ABSTRACT

A powder sample of $Y_2YbFe_5O_{12}$ was prepared using the ceramic technique. X-ray diffraction pattern showed a single phase of the garnet type structure with a lattice constant 12.323 A°. Specific heat for this composition was found to change anomously at a transition point 555±5K. Neutron diffraction and Mossbauer effect measurements were obtained over a wide range of temperature (600-4.2K) and supported the existence of a collinear ferrimagnetic spin model below the point down to 4.2K. Curie. Crystallographic, magnetic and hyperfine parameters were determined and discussed.

INTRODUCTION

Proposed fusion reactor designs require structural and electrical materials that will perform satisfactory after exposure to energetic neutrons at high temperatures. Ceramics (garnet and spinel ferrites are being considered for these applications. Rare earth iron garnets are probably the most thoroughly investigated all ferrites, because of several properties which experimental and theoretical studies find very rewarding. By substituting the various rare earth ions into the garnet lattice, one can study the effect of these ions on the macroscopic properties. The fact that all crystallographic sites are occupied and all the iron ions are trivalent (unlike the spinels) accounts for a great chemical stability of the garnets and a good reproducibility for their physical properties. Moreover, garnets are suitable materials for bubble domain technology which has potential application for computer memory and display.

The Néel collinear ferrimagnetic structure in pure $Y_3Fe_2(FeO_4)_3$ above its Curie point (550°C) and the canted spin structure at very low temperature (1.5K) in the stoichiometric $Yb_3Fe_5O_{12}$ were studied by several authors (Williams and Heaton 1968, F. Tcheou *et al* 1970). However, there is practically no data on the transmition in magnetic behaviour for the mixed garnets $Y_{3-X}Yb_XFe_5O_{12}$ which seemed interesting, since they are useful materials for the study of the behaviour of magnetic ions in insulators.

EXPERIMENTAL

The compound $Y_2YbFe_5O_{12}$ was prepared using the usual ceramic technique. Powder X-ray diffraction pattern indicated the sample had a unique crystal structure of garnet type with no evidence of impurities or separate phases. The lattice constant was determined to be a = 12.323_5A°. Infrared lattice vibrational spectrum for the prepared sample measured at 300K, showed mainly three absorption bands below 1000 cm^{-1}, (Figure 1), which arise from the lattice

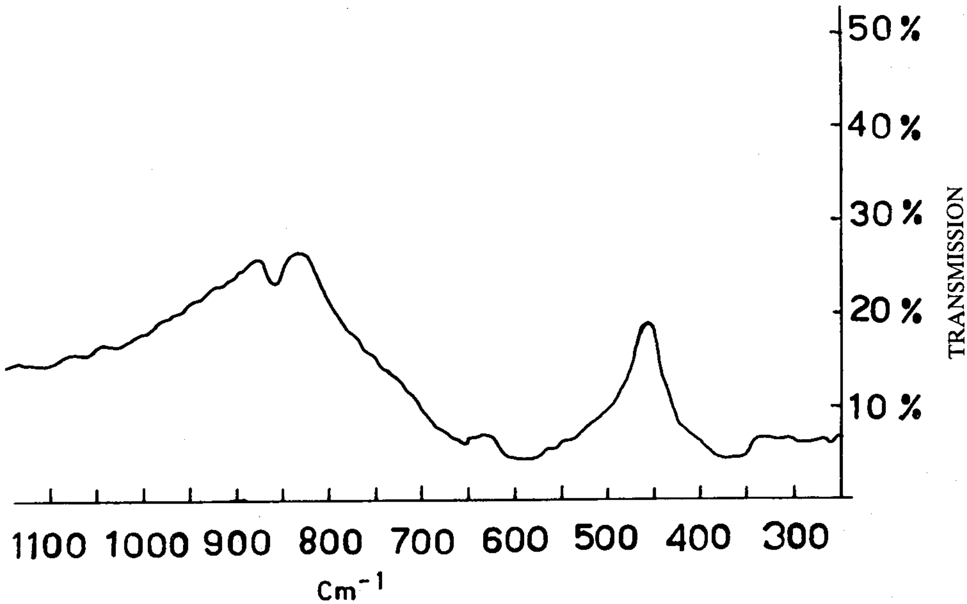

Figure 1. Infrared absorption spectrum for $Y_2YbFe_5O_{12}$ at room temperature.

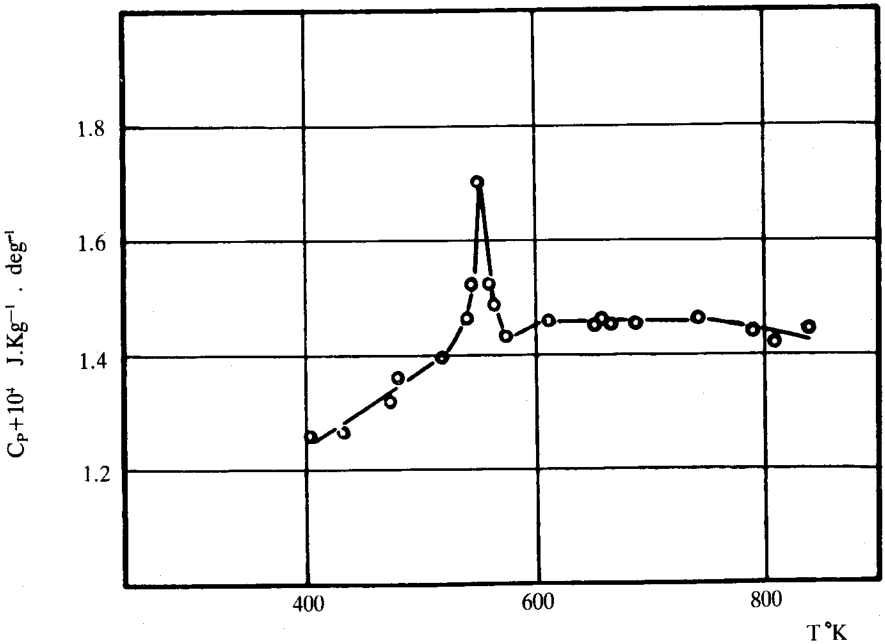

Figure 2. Specific heat anomaly for $Y_2YbFe_5O_{12}$.

vibrations of the oxide ions against the cations. Thermal conductivity, diffusivity and specifie heat measurements on this compound in the temperature range 400-1000 K (using the plane wave temperature method) were anomalously at a transition point 555±5K (Figure 2). Neutron diffraction patterns of the polycrystalline sample have been obtained at 800 and 293 K, using a neutron spectrometer placed at the ETRR, reactor of Egypt. The measurements were extended to 4.2 K using a spectrometer DN5 and a liquid helium cryostat placed at Silos reactor of CENG (with kind co-operation of Dr. Roulte) (Figure 3). ^{57}Fe Mossbauer resonant absorption spectra of the studied compound were taken at the temperature between 4.2 K and Tc, (Figures 4 and 5). The solid lines through the data points are the result of a least squares fit.

RESULTS AND DISCUSSION

Rare earth iron garnets have the most complex cubic crystal structure, the unit cell of which contains 160 atoms with eight molecules R_3^{3+} (Fe_2^{3+}) Fe_2^{3+} O_{12}. The space group is Ia3d - O_h^{10} the origin at Centre (3). Each of the 3 positive ion positions is surrounded by a different co-ordination polyhedron. For the R^{3+} ion on the so called c-site, the ployhedron is an eight cornered twelve sided figure. For the Fe^{3+} ion in position 24 or d-site the ployhedron is a tetrahedron while for the remaining Fe^{3+} ion, 16 (a) on an a-site, the figure is an octahedron. The edge lengths in any single polyhedron are not equal i.e. none of these polyhedra is regular and the oxygen lattice is very distorted. Therefore, the crystallographic parameters in the present unit cell to be determined were the variable co-ordinates of the oxygen atoms (x, y, z) placed in the general position 96(h). From neutron diffraction patterns at 800K (Figure 3) 8 distinctly separated single and five doubled nuclear reflections were found up to $2\Theta = 50°$ and taken for calculations. The atomic parameters found at least squares methods lead to a satisfactory agreement between observed and calculated squares of structure factors. The discrepancy factor R = 0.022 was achieved with the values of the oxygen parameters as follows: $x = -0.0283$, $y = 0.0553$ and $z = 0.1513$. A remarkable increase in the R factor was obtained on trying to situate some of the Yb ions on the octachedral sites normally occupied by Fe^{3+}. On the neutron diffraction patterns below the Curie point the intensities of a number of the fundamental garnet peaks increase (particularly the reflection 220) as a result of a superposition of magnetic contributions arising from aligned spins. This indicated that the magnetic unit cell has the same dimensions as that of the chemical one. Such additional scattering depends on the magnetic moments to be associated with individual lattice sites, their orientation relative to each other. Since there is no superlattice reflections observed, also no evidence of canted ordering, then the magnetic scattering of the compound $Y_2YbFe_5O_{12}$ can be analyzed with a model of ferrimagnetic ordering of rare earth and ion moments along the [111] direction and treating their magitude as parameters. The ferric ions in the two differemt sites are strongly coupled antiferromagnetically by their own mutual interactions. The moment of Yb ions is antiparallel to the resultant Fe^{3+} magnetization. This collinear structure was found to hold for the temperature interval from the Curie point to low temperatures. Using a least square procedure it was possible to obtain reasonable agreement between calculated and observed neutron intensities for total magnetic moment 4.2 μ B. AT 4.2K. The temperature dependence of the Mossbauer spectra of $Y_2YbFe_5O_{12}$ above room temperature is shown in Figure 4. At 293 K the spectrum is composed of a double sixlines Zeeman pattern corresponding to the two equivalent iron sites(a) and (b) for an octahedral - B and tetrahedral -A co-ordination with an area ratio 2:3 respectively. When temperature rises the Zeemen splitting decreases and the lines overlap each other. A complete disappearance of the magnetic structure takes place at 573 K. In contrast to other YIG ferrites a doublet instead of triplet is obtained above the Curie point,

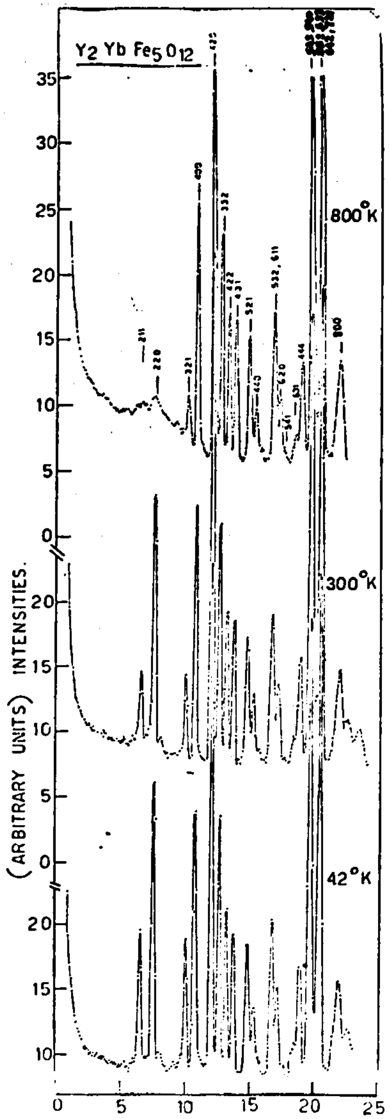

Figure 3. Neutron diffraction powder patterns of $Y_2YbFe_5O_{12}$.

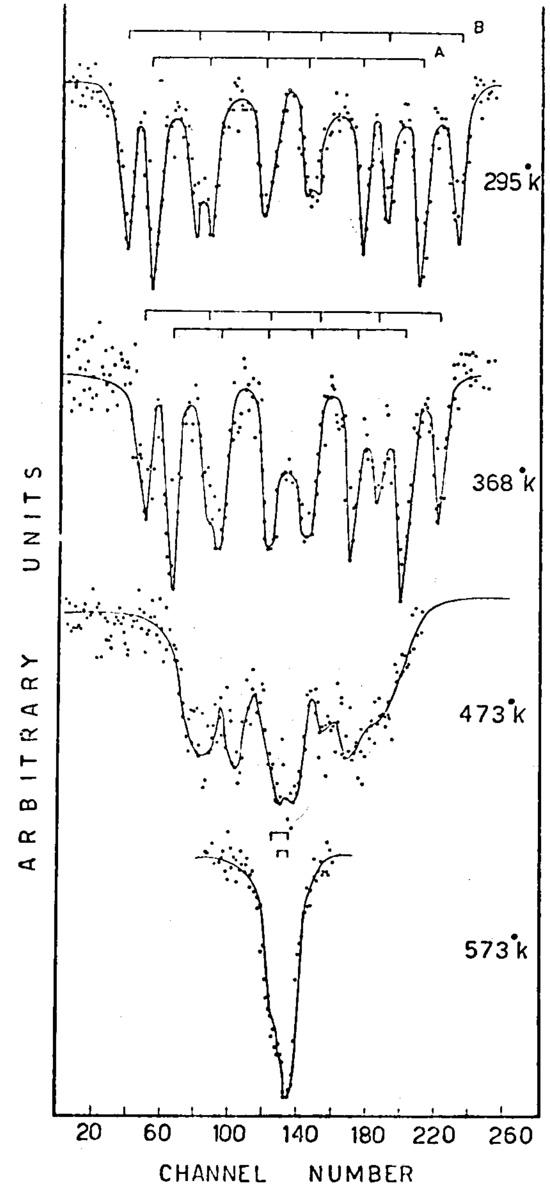

Figure 4. Mossbauer effect spectra of the mixed rare earth garnet $Y_2YbFe_5O_{12}$ in the temperature range 295 K – 573 K.

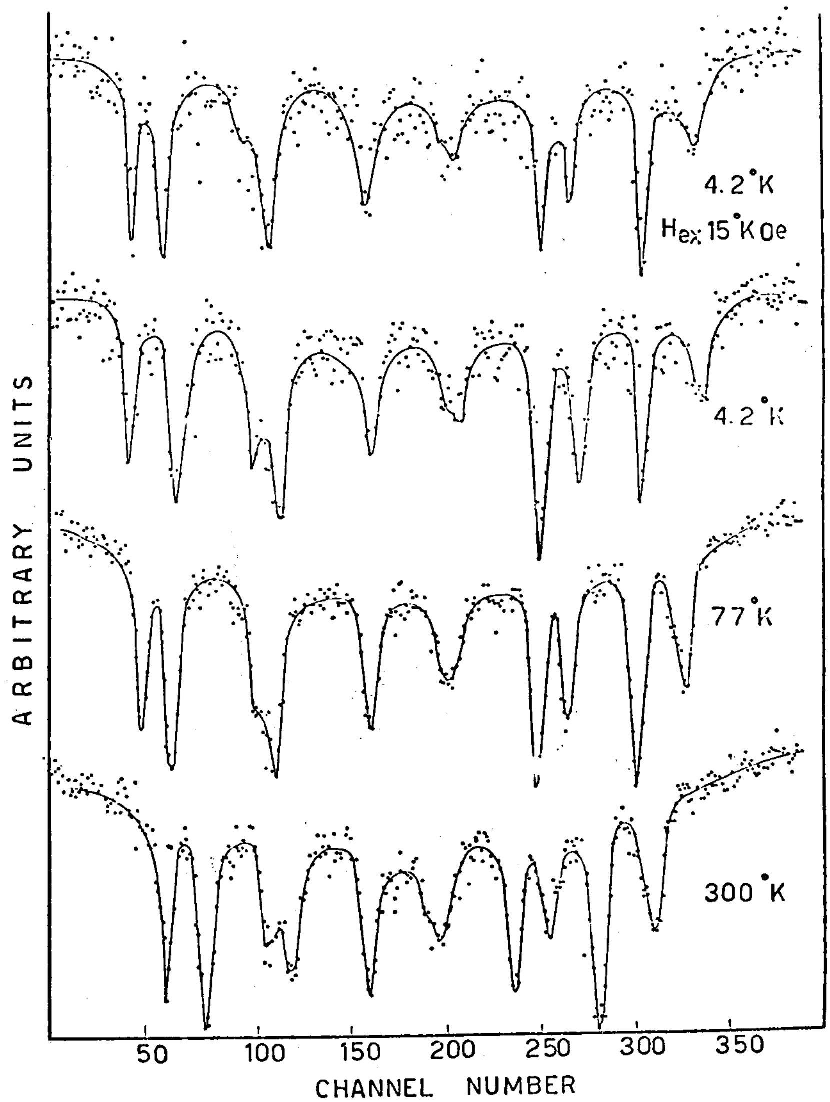

Figure 5. Mossbauer effect spetra of $Y_2YbFe_5O_{12}$ in the temperature range 300 - 4.2 K.

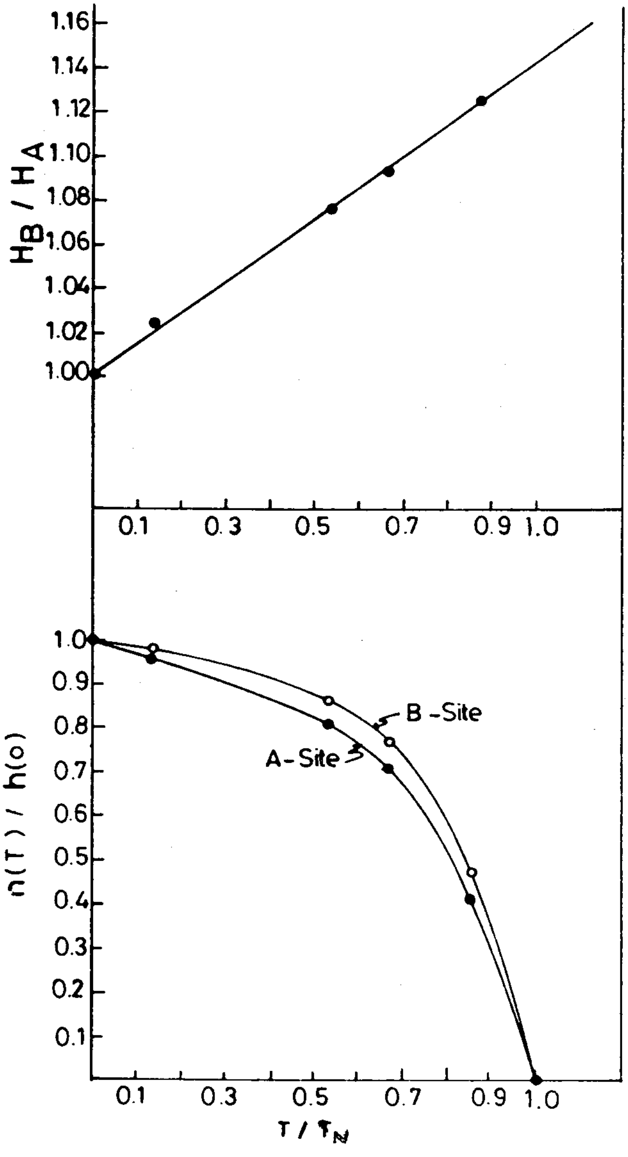

Figure 6. Reduced hyperfine field versus (a) and H_B/H_A versus T/T_C (b)

where the area of the whole spectrum is that of the two super-imposed patterns of (a) and (d) sites. The obtined quadrupole splitting values for both sites showed a slight increase from the typical values of YIG. This indicates a growth in the polyhedron deformation, which depends on the oxygen positions and the rare earth ion radius. For the spectra obtained below T_C it was assumed that: (i) the lines are of Lorentzian shape (ii) there is only one average effective magnetic field in each sublattice. The last assumption is justified by the fact that the ratio $\frac{a}{d}$ or half width of the outermost lines corresponding to the (a) and (d) sites does not exceed the value of 1.5 at all temperatures between 4.2 and 293 K (Figure 5). In such a situation it would not be reasonable to distinguish more effective fields in the octahedral sites as was done by Bokovetal (1969). Values of isomer shifts for both sites in the range characteristic of the trivalent high spin state of iron ion. Figure 6 depicts the reduced hyperfine field versus T/T_C plot, which follows Brillouin for $S = 5/2$, the ratio H_B/H_A as function of T/T_C is also given.

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دراسة الحيود النيوتروني وظاهرة موسباور لمركب الجارنت المطعم بالعناصر الأرضية النادرة

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تم تحضير عينة نقية من مسحوق مركب جارنت الأيتريوم المطعم بالايتربيوم $Y_2 Yb Fe_5 O_{12}$ واختبارها بالأشعة السينية وحساب ثابت الخلية لها (١٢٫٣٢٣ انجستروم) ومن قياس الحرارة النوعية لهذا المركب تبين أنها تتغير عند درجة انتقال ٥٥٥ درجة مطلقة . وقد أظهر نموذج الأشعة تحت الحمراء لهذا المركب ثلاثة خطوط امتصاص في مدى تردد قيمته ١٠٠٠ سم ـ١ واستخدمت لتعيين درجة حرارة ديباى الخاصة به . وتم كذلك قياس نماذج الحيود النيوتروني وأطياف موسباور في مدى حرارى واسع . أمكن من تحليلها تأكيد وجود تركيب فيريمغناطيسى تكون فيه العزوم المغناطيسية المغزلية متوازية وقد نوقشت النتائج في ظل البارمترات البللورية والمغناطيسية والفرق دقيقة التي تم الحصول عليها ..