A Mossbauer spectroscopy and X-ray diffractometry study of $Fe_{1.429-x}Ni_xAl_{1.143}Si_{0.143}O_4$ spinel ferrites

A Mössbauer spectroscopy and x-ray diffractometry study of Fe$_{1.429-x}$Ni$_x$Al$_{1.143}$Si$_{0.143}$O$_4$ spinel ferrites

Sung Ho Lee and Woong Tae Kim

Department of Physics, Kon-Kuk University, Seoul 133-701, South Korea

Abstract. The crystal structure and the magnetic properties of the Fe$_{1.429-x}$Ni$_x$Al$_{1.143}$Si$_{0.143}$O$_4$ spinel ferrites have been investigated by means of x-ray diffractometry and Mössbauer spectroscopy. The crystal structures are found to be cubic phase for $x \geqslant 0.286$ and mixed phase for $x < 0.286$. The Mössbauer spectra from cubic phases suggest that iron ions have the charge state of 3+ and that Ni^{3+} ions are present at tetrahedral sites. Line broadening of Mössbauer spectra due to the distribution of magnetic fields and a strong Al–Fe ion mixing between tetrahedral and octahedral sites have been observed.

1. Introduction

The ferrites are a class of oxides of iron group metals, many of them of technical importance, which crystallize in the spinel structure or structures closely related to it. Spinels are cubic compounds that belong to the space group $Fd3m$. Their general chemical formula is usually written as (X)[Y$_2$]Z$_4$, where X and Y denote cations, and Z denotes an anion. The parentheses represent a tetrahedral site, and the square brackets an octahedral site. The point symmetry of the tetrahedral and octahedral sites are $\bar{4}3m$ (T$_d$) and $\bar{3}m$ (D$_{3d}$), respectively. The cation arrangement in spinel-type oxides has long been a topic of interest because their magnetic, electrical and thermodynamic properties depend strongly upon the cation distribution [1–6]. Cation ordering in spinels can generally be explained by their relative site preference or interpreted in terms of electronic theory. In many spinels, however, deviations from general ordering schemes are observed, possibly as a result of cooling history and stoichiometry.

Since the first development of spinel ferrites, there has been a considerable revival of interest in the properties of magnetically disordered spinel ferrites, and the substitution of cations in spinel ferrites is known to produce changes in their magnetic, electrical and microstructural properties. The observed changes are used to obtain ferrites with desired properties. There have been many investigations of the mixed and non-stoichiometric spinel ferrites, and there have also recently been a number of Mössbauer studies of ^{57}Fe in such spinel ferrites which contain various cations or in dilute spinel ferrites [6–9].

However, as far as we know, few Mössbauer spectroscopy studies on such non-stoichiometric Si-included spinel ferrites have been carried out. In recent years we have synthesized a number of defect spinel ferrites and the existence of such a structural phase comparable with γ-Fe$_2$O$_3$ has been confirmed by Mössbauer and

x-ray diffraction studies [10, 11]. However, the defect spinel ferrites investigated in these foregoing studies are, strictly speaking, not of exact cubic structure but contain an extraneous impurity phase even though it is negligible. In the subsequent studies to these previous investigations, we were able to synthesize a pure cubic spinel phase by admixing a suitable amount of Ni ions. Furthermore, we found in these specimens that charge compensation is achieved, and we believe that this charge compensation contributes constructively to the formation of such a pure crystal structure, even though the cation-to-anion number ratio slightly deviates from 3 to 4. In this work we give the results of a Mössbauer spectroscopic and crystallographic study on the Fe_2O_3–$(Al_2O_3)_x$–$(SiO)_{1-x}$ system, in which Ni ions are substituted for Fe ions.

2. Experimental details

2.1. Sample preparation and x-ray diffraction

A system of $Fe_{1.429-x}Ni_xAl_{1.143}Si_{0.143}O_4$ ferrites has been prepared by the usual ceramic method. A mixture of the appropriate proportions of Fe_2O_3, Ni_2O_3, Al_2O_3 and SiO powders of 99.9%, 99.9%, 99.995% and 99.99% purities, respectively, was ground, pressed into pellets at 6 ton cm^{-2}, pre-heated in air at 500 °C, for 10 h and sintered at 1300 °C for 12 h. To achieve homogeneity the sintered product was pulverized, compressed and sintered at 1300 °C for 24 h again (samples A, B and C with nominal values for x of 0.143, 0.286 and 0.429, respectively). Samples A, B and C were refired at 1400 °C for 4 h (to give samples D, E and F, respectively). The final products were crushed into powder for x-ray and Mössbauer measurements. The powder x-ray diffraction pattern was obtained at room temperature using a Geiger-flex (M-3A) diffractometer with Cu Kα radiation.

2.2. Mössbauer effect measurement

Mössbauer resonance absorption spectra of the compound were taken at room temperature and 95 K, using 10 mCi Co^{57} diffused in a Pd matrix and a driving system at constant acceleration associated with a multichannel analyser working in a multiscaler time mode. The calibration of the spectrometer was carried out using the spectra of metallic iron.

3. Results and discussion

3.1. Crystallographic parameters and cation distribution

Figure 1 shows the result of x-ray diffraction measurements. Samples C, E and F have a cubic spinel crystal structure with lattice constants a of 8.194±0.0005 Å, 8.203±0.0005 Å and 8.179±0.0005 Å, respectively, without impurities or a separate phase, but the other samples show the coexistence of extraneous phases of α-$(Fe_{1-c}Al_c)_2O_3$. These extraneous phases are indicated in figures 1(a) and 1(b) with full circles, and figure 1(c) shows only the spinel phase. Thus we can conclude that a stable spinel solid solution can be attained when $x \geqslant 0.286$ and restrict our discussion to samples C, E and F. With these results, we can find distinct crystalline features in contrast with the usual cubic spinel structure. Generally cubic spinel compounds have close packing of the oxygen atoms, with a cation-to-anion number ratio
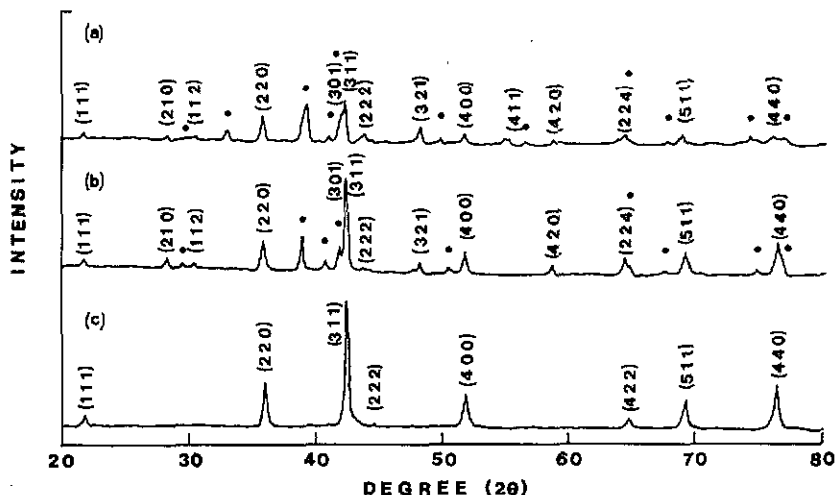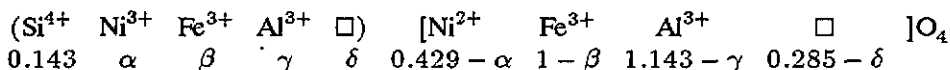
Figure 1. X-ray diffraction pattern of $Fe_{1.429-x}Ni_xAl_{1.143}Si_{0.143}O_4$ annealed at 1300 °C: curve (a), sample A ($x = 0.143$); curve (b), sample B ($x = 0.286$); curve (c), sample C ($x = 0.429$).

of 3 to 4. However, our samples with the spinel structure have a cation-to-anion number ratio of 2.714 to 4 and are expected to have incomplete filling of possible metal positions as γ-Fe_2O_3.

In the course of refinement, we consider the strong preference of Ni^{2+} ions for octahedral coordination and of Si^{4+} ions for tetrahedral coordination. Initially, it is assumed that Fe^{3+} and Al^{3+} ions are distributed over the tetrahedral and octahedral sites, and all the Si^{4+} ions are localized on the tetrahedral sites. We also consider the possibility of cation vacancies. Because the samples are non-stoichiometric, there must be cation vacancies on both the tetrahedral and the octahedral sites.
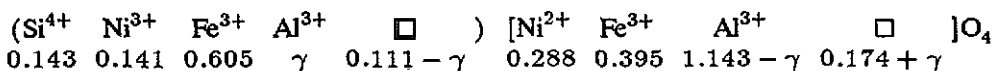
In the spinel structure, each tetrahedral site is linked with 12 octahedral sites while an octahedral site is linked with 6 tetrahedral sites through the strong superexchange interaction. So there is a combination of 12 nearest neighbours of a tetrahedral iron ion, consisting of three kinds of ion (Fe^{3+}, Al^{3+} and Ni^{2+}) distributed randomly over octahedral sites. We then, for sample C, write the cation distribution of ions over lattice sites in the form
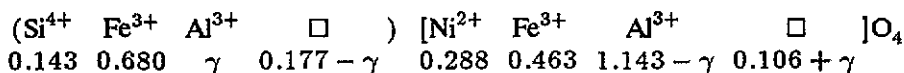
$$(Si^{4+}_{0.143} \quad Ni^{3+}_{\alpha} \quad Fe^{3+}_{\beta} \quad Al^{3+}_{\gamma} \quad \square_{\delta}) \quad [Ni^{2+}_{0.429-\alpha} \quad Fe^{3+}_{1-\beta} \quad Al^{3+}_{1.143-\gamma} \quad \square_{0.285-\delta}]O_4$$

where $\square$ is a cation vacancy on tetrahedral and octahedral sites. Although Al^{3+} ions have a strong preference for the octahedral sites, strong Al^{3+}–Fe^{3+} mixing between tetrahedral and octahedral sites has been found in several spinel ferrites [8, 12, 13]; thus we can assume tetrahedral site occupancy by Al^{3+} ions. Some Ni^{3+} ions are also expected to be in the tetrahedral sites to compensate the charge valence as the presence of Ni^{3+} ions in the $NiFe_2O_4$ spinel ferrites [14].

Since the recoil-free fractions of the tetrahedral and octahedral sites in the spinels are known to be similar [15], we assumed that relative spectral areas are proportional to relative site occupancies. On this basis and with a knowledge of the exclusive preference of cations for particular sites, it is possible to determine the cation distribution
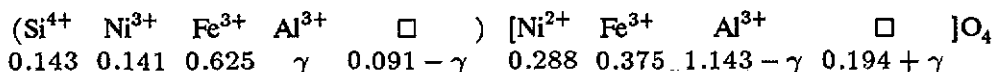
from the Mössbauer spectrum at 95 K as follows:

$$(Si^{4+} \quad Ni^{3+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad) \; [Ni^{2+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad]O_4$$

0.143 0.141 0.605 γ 0.111 $-\gamma$ 0.288 0.395 1.143 $-\gamma$ 0.174 $+\gamma$

for sample C ($x = 0.429$, sintered at 1300 °C). Similarly,

$$(Si^{4+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad) \; [Ni^{2+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad]O_4$$

0.143 0.680 γ 0.177 $-\gamma$ 0.288 0.463 1.143 $-\gamma$ 0.106 $+\gamma$

for sample E ($x = 0.286$, sintered at 1400 °C) and

$$(Si^{4+} \quad Ni^{3+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad) \; [Ni^{2+} \quad Fe^{3+} \quad Al^{3+} \quad \square \quad]O_4$$

0.143 0.141 0.625 γ 0.091 $-\gamma$ 0.288 0.375 1.143 $-\gamma$ 0.194 $+\gamma$

for sample F ($x = 0.429$, sintered at 1400 °C).

3.2. Mössbauer spectra and hyperfine interactions

The Mössbauer spectra of samples C, E and F are shown in figures 2 and 3. As expected from the result of x-ray diffraction experiments, the Mössbauer spectra for these three samples show a single spinel phase which becomes dominant with increasing content of Ni ions and increasing sintering temperature. The shape of the lines were assumed to be Lorentzian and their intensities and widths were allowed to vary freely subject only to the constraints that $I_i = I_{7-i}$ and $\Gamma_i = \Gamma_{7-i}$, where I_i is the intensity of line i and Γ_i is the width of line i. The full curves through the data points in figures 2 and 3 are the results of least-squares fits. In the spinel phase, two sextets arise from the iron ions at the tetrahedral and octahedral sites, and the Mössbauer parameters for samples C, E and F determined at room temperature and 95 K are given in table 1.

In the Mössbauer spectra, no evidence for the Fe ions which have charge states different from 3+ is found, and the observed values of isomer shift for the three samples are typical of the high-spin Fe^{3+} charge state with respect to natural iron. The smaller value of the isomer shift of the tetrahedral site is due to the larger covalency at the tetrahedral site. The increased values of the isomer shift obtained at 95 K are attributable to the thermal red shift, or transverse Doppler shift, between the source at room temperature and the absorber at 95 K.

As in other ferrites, the sextet with the large magnetic hyperfine field is due to the iron ions at the octahedral site, and the sextet with the weak field arises from iron ions at the tetrahedral sites. The weak tetrahedral-site field is primarily due to a strong covalency and therefore due to a greater degree of spin delocalization at the tetrahedral sites. However, the weak tetrahedral-site field in comparison with the octahedral-site field cannot be attributed solely to the covalency of the tetrahedral Fe^{3+} ions but is also due to an effect which will now be discussed. In a ferrimagnetic spinel, in which the intersublattice magnetic interaction is stronger than either of the intrasublattice interactions, the average nuclear magnetic field for Fe^{3+} ions in each of the two sublattices is proportional to the average magnetization of the sublattice. It has also been known that the Fe^{3+}–O^{2-}–Ni^{2+} superexchange interaction is weaker than the Fe^{3+}–O^{2-}–Fe^{3+} interaction [16] and presumably the Fe^{3+}–O^{2-}–Ni^{3+} interaction; therefore, it is clear that the averaged normalized magnetization of the tetrahedral sites is smaller than that of the octahedral sites. This arises also
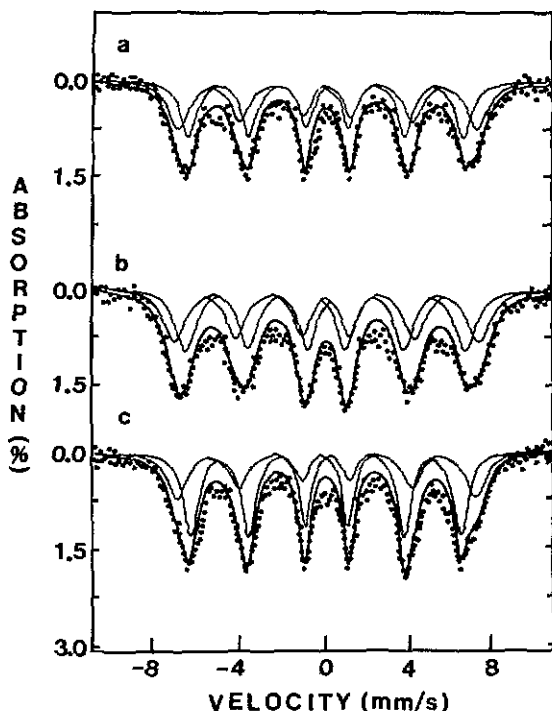
Figure 2. Mössbauer spectra of $Fe_{1.429-x}Ni_x\,Al_{1.143}Si_{0.143}\,O_4$ at room temperature: curve (a), sample C; curve (b), sample E; curve (c), sample F.

from the fact that the tetrahedral Fe^{3+} ions will have about 33% of its intersublattice bonds with magnetic cations, while the octahedral Fe^{3+} ions will have about 73% of its intersublattice magnetic bonds. The smaller averaged normalized magnetization of the tetrahedral sites at finite temperatures thus contributes to the observed weak nuclear magnetic field for this sublattice.

From table 1, it is clear that three samples show nearly the same magnetic hyperfine fields at tetrahedral sites but different values at octahedral sites. Samples C and F have the same iron content which is greater than that of sample E, but samples E and F have the same annealing temperature which is higher than that of sample C. From these facts, it is believed that the substitution of Ni ions by Fe ions occurs only in the tetrahedral sites without any replacements or migrations of the ions (samples E and F); thus the tetrahedral-site magnetization and the magnetic hyperfine fields at the octahedral sites increase. However, a comparison of sample C with sample E shows that the replacement of Ni ions in tetrahedral sites is accomplished by Fe and Al ions, i.e. cation vacancies formed by the subtraction of Ni ions are filled by Al ions which are substituted by Fe ions in the octahedral sites, and by some fraction of Fe ions. Hence the magnetic hyperfine field at octahedral sites is slightly reduced, but the small fraction of magnetic substitution at octahedral sites probably does not produce a large enough change in the total superexchange interaction because each tetrahedral Fe ion has 12 octahedral ions as its neighbours. Hence the magnetic hyperfine field at the tetrahedral sites remains unchanged. It is also easy to see that the temperature variation in the magnetic hyperfine field is larger at the tetrahedral sites than at the octahedral sites. This is similar to the study of Ni–Zn ferrite systems which
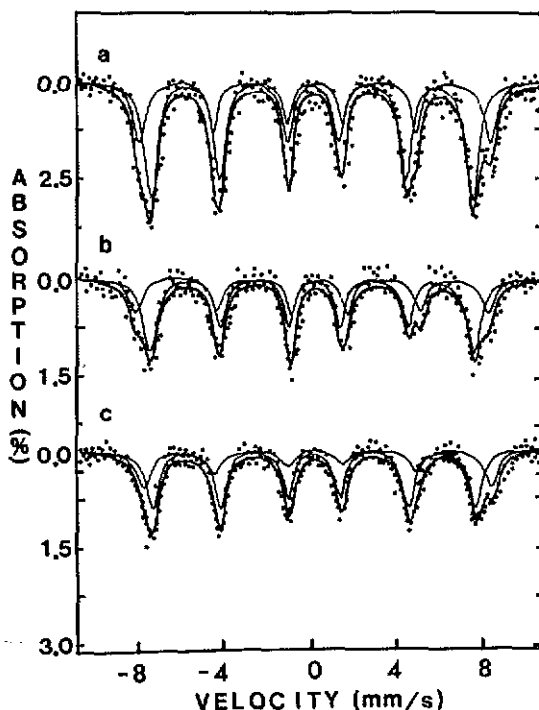
Figure 3. Mössbauer spectra of $Fe_{1.429-x}Ni_x$ $Al_{1.143}Si_{0.143}O_4$ at 95 K: curve (a), sample C; curve (b), sample E; curve (c), sample F.

Table 1. Mössbauer parameters for sample C ($x = 0.429$, sintered at 1300 °C), sample E ($x = 0.286$, sintered at 1400 °C) and sample F ($x = 0.429$, sintered at 1400 °C).

Sample	Temperature (K)	Site	Isomer Shift (mm s⁻¹)	Quadrupole splitting (mm s⁻¹)	Magnetic hyperfine field (kOe)	Full width at half-maximum[a] (mm s⁻¹)
C	Room temperature	A	0.09±0.01	−0.01±0.01	371±5[b]	0.50±0.03
C	Room temperature	B	0.15±0.01	0.01±0.01	429±5[b]	0.64±0.03
C	95	A	0.14±0.01	−0.02±0.01	475±2	0.39±0.03
C	95	B	0.29±0.02	−0.02±0.02	518±2	0.40±0.02
E	95	A	0.11±0.01	−0.01±0.01	475±3	0.40±0.02
E	95	B	0.29±0.01	−0.08±0.01	515±2	0.40±0.02
F	95	A	0.07±0.01	−0.01±0.01	476±3	0.39±0.03
F	95	B	0.21±0.01	0.03±0.01	511±2	0.42±0.02

[a] Measured from the first line of the spectra.
[b] Averaged value.

have a canted spin structure [17], and our sample lies in a border region between the random-canted ferrimagnet and the spin glass [9] or between the ferrimagnetic order and the localized canted state [6] in the magnetic phase diagram. So we presume the existence of the canted spin structure which can be verified by other experiments.

In a spinel structure exhibiting no chemical disorder, the tetrahedral sites have cubic point symmetry and thus experience no electric field gradient but the octahedral sites have trigonal symmetry, i.e. the point symmetries of the octahedral and tetra-

hedral sites require that the electric field gradient tensor exists, is axially symmetric along the [111] crystallographic direction at the octahedral sites and disappears at the tetrahedral sites. So one can expect the quadrupole splitting observed for many Fe^{3+}-containing spinels to be due exclusively to the octahedral Fe ions, both for the spinels with Fe ions exclusively at the octahedral sites and for the spinels with Fe ions simultaneously present at the tetrahedral and octahedral sites [12].

The observed values of quadrupole splitting for sample E at 95 K show good agreement with these facts, but the other samples show contradictions to the above explanation, i.e. nearly zero values of quadrupole splitting are observed from both tetrahedral and octahedral sites. In our case, there are several different ions and vacancies at tetrahedral (Si^{4+}, Ni^{3+}, Fe^{3+}, Al^{3+}, □) and octahedral (Al^{3+}, Ni^{2+}, Fe^{3+}, □) sites. So, we can expect chemical disorder. Generally, in mixed spinels, one has to take into account the effective charge which results from the valencies of the ions and then their distribution between these two sites, and thus both the point symmetry of a given site and its charge symmetry. When chemical disorder is expected, it is reasonable to suppose that electric field gradients are present at both tetrahedral and octahedral sites. The chemical disorder will produce a wide distribution of electric field gradients of various magnitudes, directions, signs and symmetries. Thus, it is conceivable that the overall cubic symmetry of the spinel ferrites and no net quadrupole splitting of Zeeman line are observable.

Besides zero quadrupole splitting, we also find line broadening at room temperature. In the case of mixed spinels, in which two or more cation species are present in tetrahedral and/or octahedral sites, there will be a distribution of values for $\langle S_z \rangle$, which will, in turn, result in a distribution of the magnetic field at the nucleus [17, 18]. This will itself be evidenced by the broadening of the individual lines of the Mössbauer spectrum in the same way as the quadrupole interaction inhomogeneity is. However, in magnetically ordered systems, the broadening of individual lines in the Mössbauer spectrum which is due to the distribution of $\langle S_z \rangle$ is temperature dependent, but line broadening which is due to the distribution of the electric field gradient is temperature independent. Consequently, in this case, the line broadening of Mössbauer spectra at room temperature is believed to be caused by the distribution of the magnetic hyperfine fields on both tetrahedral and octahedral sites.

4. Conclusions

The system $Fe_{1.429-x}Ni_xAl_{1.143}Si_{0.143}O_4$ has been studied as a function of composition and temperature. Although spinel compounds including Si ions are rarely found under ordinary pressure, a stable spinel phase including Si ions and cation vacancies is obtained, which becomes dominant with increasing Ni content and increasing sintering temperature. An analysis of Mössbauer spectra shows that Fe ions have only a high-spin state of value 3+ and Ni^{3+} ions are present at the tetrahedral sites. Al–Fe ion mixing between tetrahedral and octahedral sites is expected, although Al^{3+} ions have a strong preference for the octahedral sites, and a stronger mixing of Al–Fe ions is found as the sintering temperature decreases. The line broadening observed at room temperature is interpreted as due to the distribution of the magnetic hyperfine fields caused by various cation distributions. From the temperature dependence of the magnetic hyperfine fields and magnetic phase diagram suggested by Coey, sample C is expected to have a canted spin structure. However, it will be necessary to obtain

Mössbauer spectra in an applied magnetic field to estimate the cation distribution more quantitatively, and to establish the presence of the canted spin structure.

Acknowledgment

References

[1]   Verwey E J W and Heilmann E L 1947 *J. Chem. Phys.* **15** 174
[2]   Donald S M 1957 *J. Phys. Chem. Solids* **3** 311
[3]   Navrotsky A and Kleppa O J 1967 *J. Inorg. Nucl. Chem.* **29** 2701
[4]   Sawatzky G A, Van der Woude F and Morrish A H 1969 *Phys. Rev.* **187** 747
[5]   Srivastava C M, Srinivasan G and Nanadikar N G 1979 *Phys. Rev.* B **14** 2041
[6]   Dormann J L and Nogues M 1990 *J. Phys.: Condens. Matter* **2** 1223
[7]   Fiorani D, Viticoli S, Dormann J L, Tholence J L and Murani A P 1984 *Phys. Rev.* B **30** 2776
[8]   Srivastava J K, Le Dang K and Veillet P 1986 *J. Phys. C: Solid State Phys.* **19** 599
[9]   Coey J M D 1987 *Can. J. Phys.* **65** 1210
[10] Lee S H and Chae K P 1990 *Phys. Rev.* B **41** 1722
[11] Lee S H, Kim W T and Jung J D 1990 *Sae Mulli* **30** 589
[12] Stadnik Z M and Zarek W 1986 *Phys. Rev.* B **34** 1820
[13] Lyubutin I S, Dmitrieva T V and Chalabov R I 1990 *Sov. Phys.–JETP* **70** 526
[14] Van Uitert L G 1955 *J. Chem. Phys.* **23** 1883
[15] Sawatzky G A, Van der Woude F and Morrish A H 1969 *Phys. Rev.* **183** 383
[16] Geller S, Williams H, Sherwood R C and Espinosa G P 1962 *J. Phys. Chem. Solids* **23** 1525
[17] Daniels J M and Rosencwaig A 1970 *Can. J. Phys.* **48** 381
[18] Leung L K, Evans B J and Morrish A H 1973 *Phys. Rev.* B **8** 29