The effect of the spin-orbit interaction strengths on the Faraday rotation in Pr-substituted

yttrium iron garnet and in praseodymium trifluoride

The effect of the spin–orbit interaction strengths on the Faraday rotation in Pr-substituted yttrium iron garnet and in praseodymium trifluoride

Jiehui Yang†‡, You Xu†§‖ and Maurice Guillot¶

† Department of Physics, Nanjing University, Nanjing 210008, People's Republic of China
‡ Department of Physics, Luoyang Teacher's College, Luoyang 471022, People's Republic of China⁺
§ China Centre for Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China
‖ State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
¶ Laboratoire des Champs Magnétiques Intenses, Centre National Recherche Scientifique, Max-Planck-Institut für Festkoperforschung, BP 166, 38042 Grenoble, France

Abstract. The effect of the spin–orbit interaction of both the ground and excited configurations on the Faraday rotation of the trivalent Pr ion in praseodymium-substituted yttrium iron garnet and praseodymium trifluoride is analysed. It is found that the influence of the spin–orbit coupling strength of the ground configuration on the Faraday rotation is large; however, the MO rotation does not scale linearly with the spin–orbit coupling. It is surprising that the influence of the spin–orbit coupling strength of the excited configuration on the Faraday rotation is small except when the light frequency is near an MO resonance frequency. It is demonstrated that the spin–orbit interactions of both the ground and excited configurations are not always needed to produce a net Faraday rotation. The underlying physical reasons for the differences between our theoretical results and those obtained by other authors and between the different results obtained for Pr:YIG and PrF$_3$, respectively, are discussed.

1. Introduction

The magneto-optical (MO) effects have received much attention over the last decades because they represent simultaneously a large field for fundamental research activities and a promising technological tool (Schoenes 1992, Reim and Schoenes 1990). Numerous experimental studies have been performed to determine the microscopic parameters able to tune the Kerr spectra, initially on transition metals and rare earth alloys (Buschow and van Engen 1981, Buschow *et al* 1983) and later on artificial multilayers of suitable metals (Buschow 1988, Weller *et al* 1991, Bennet *et al* 1990, Zeper *et al* 1989). However, theoretical analyses able to support this tuning type of activity are rather scarce and the role of different fundamental microscopic interactions like the spin–orbit coupling is not clear although it has been established, for quite some time, that both spin–orbit coupling and Zeeman coupling (usually through superexchange splitting) are needed to produce a non-zero MO effect (Hulme 1932, Argyres 1955). In addition, Hulme

⁺ Address for correspondence.

(1932) and Liu *et al* (1991) pointed out that it was the spin–orbit coupling in excited (final) states which must be responsible for the MO effects.

To our knowledge, Misemer (1988) was the first who investigated quantitatively the influence of the spin–orbit coupling strength and of the exchange splitting on the MO effects in MnBi, using a non-self-consistent model band structure. He arrived at the following main conclusion: the MO coefficient grows approximately linearly with increasing strength of the spin–orbit coupling. Oppeneer *et al* (1992) analysed the role of some fundamental parameters (spin–orbit coupling, exchange interaction, lattice parameters, . . .) in the MO effects in Ni metal. The main features issued from this work are: (i) the Kerr effect is basically brought about by the spin–orbit coupling; (ii) the Kerr rotation scales linearly by the spin–orbit coupling strength. However, both of them did not explicate whether it was the spin–orbit coupling in initial states or that in final states which played an important role in the MO effects.

As far as the MO properties of insulators are concerned, we have to emphasize the large enhancement of the Faraday rotation of the bismuth-substituted yttrium iron garnet (Bi:YIG). Because this giant effect is unambiguously associated with the presence of the diamagnetic Bi^{3+} ion, which has a large spin–orbit coupling constant, an appreciable number of works exist where the amazing behaviour is attributed to an increase of the spin–orbit coupling of Fe^{3+} ions resulting from the formation of a molecular orbital (mixing of the 3d Fe^{3+} orbital with the 6p Bi^{3+} one through 2p orbitals of the O^{2-} ions) (Kahn *et al* 1969, Scott *et al* 1975, Shinagawa 1982, Simsa *et al* 1984). More recently, Dionne and Allen (1993, 1994) have proposed that a large excited-state splitting induced by the large bismuth spin–orbit coupling is responsible for the Faraday rotation enhancement. However all these works lacked quantitative analysis. The origin of the large MO enhancement induced by the Bi ions in Bi:YIG is still not clear.

We present, in this paper, a quantitative analysis of the role of the spin–orbit coupling of the ground and excited configurations in the MO properties of the magnetic insulators. Our study will be performed on the high Faraday rotation induced by the presence of trivalent Pr^{3+} ions in ferrimagnetic praseodymium-substituted yttrium iron garnet (Pr:YIG), and paramagnetic praseodymium trifluoride (PrF_3). The structural properties of the two materials are different since the Pr^{3+} ion site symmetry is D_2 in the garnet and C_2 in the trifluoride, respectively. The best justification of our choice is that the values of Faraday rotation measured in the visible and in the infrared ranges are among the highest found in the literature though the magnetic moment of the Pr^{3+} ion is relatively weak. Furthermore, the two compounds offer all guarantees about the chemical stability and control of the valencies of the constituents.

The purposes of this work are: (1) to compare our results with the theoretical results obtained by Oppeneer *et al* (1992) and Misemer (1988) and to determine whether the MO effect in the two materials is basically brought about by the spin–orbit coupling and scales linearly with the spin–orbit coupling strength as is the case with the conductors (Ni, and MnBi); (2) to determine whether there is any difference between the influence of the spin–orbit coupling of the ground configuration on the MO effect and that of the spin–orbit coupling of the excited configuration, and to determine whether a large excited-state splitting induced by the excited configuration spin–orbit coupling can be the origin of the large Faraday rotation of Bi:YIG. This paper is divided into six sections. First, the notations and the definitions of the main quantities used in the paper are expressed in section 2. In section 3, a theoretical approach to the MO effects is recalled to pay special attention to the origin of the paramagnetic Faraday rotation. The influence of the spin–orbit coupling interaction of both the ground and excited configurations of the Pr^{3+} ion on the Faraday rotation in Pr:YIG (section 4) and in PrF_3

(section 5) is analysed. Finally, the main conclusions issuing from this work are summarized in section 6.

2. Notation and definition

Zero energy: taken as the ^{3}H$_4$ multiplet energy of the 4f^2 configuration of the free Pr^{3+} ion; according to this choice, the average energy of the ^{3}H term of the ground configuration is 2446 cm^{-1}.

λ_g (λ_e): ratio of a chosen spin–orbit interaction strength to the spin–orbit interaction strength from the book of Martin *et al* (1978) of the free Pr^{3+} ion ground 4f^2 (excited 4f5d) configuration. In other words, λ_g (λ_e) is equal to 1 when the spin–orbit (SO) coupling constant is equal to the values taken from the book of Martin *et al* (1978) and is equal to 0 when no spin–orbit interaction is taken into account for the 4f^2 (4f5d) configuration.

ΔE_c: Energy gap between the lowest two crystal-field (CF)–SO split 4f^2 levels.

ΔE_g: Energy difference between the lowest two CF–SO split and superexchange interaction mixed (or split) 4f^2 levels. In the definition of ΔE_g, ρ_1, ρ_2 and $\Delta\rho$, the superexchange interaction will be replaced by the external magnetic field, if paramagnetic materials are considered.

ρ_1, ρ_2: Occupation probability of the lowest two CF–SO split and superexchange interaction mixed (or split) 4f^2 levels.

$\Delta\rho$: Difference of the occupation probabilities of the lowest two CF–SO split and superexchange interaction mixed (or split) 4f^2 levels.

B_{ng}: Matrix element of the electric dipole transition from the $|g\rangle$ level of the ground configuration to the $|n\rangle$ level of the excited one.

ω_{ng}: Resonance frequency corresponding to the $|g\rangle \Rightarrow |n\rangle$ transition.

3. Theoretical approach to the MO effects

In this section, some fundamental basis needed for the calculation of the MO effects induced by the Pr^{3+} ions in the considered materials are outlined. From the observed data, it was concluded that the single-ion model allows a good approximate description of both magnetic and MO properties (Leycuras *et al* 1982, 1984a). Furthermore according to our previous works, the theoretical calculations based on the quantum theory have shown that the contribution to the MO effects of the Pr^{3+} ions results mainly from intra-ionic electric dipole transitions between the different perturbation split levels of the ground and excited configurations (Xu and Duan 1992, Yang *et al* 1997). Our calculations are based on these assumptions.

3.1. Calculation method of the MO effects

According to the strength of the different interactions, the perturbation calculation is carried out under the following order of priorities: $H_{SO} + H_{CF}$ and $H_{exch} + H_{ext}$; here H_{SO}, H_{CF}, H_{exch} and H_{ext} are the spin–orbit coupling, crystal field interaction, superexchange interaction and external magnetic field Hamiltonians, respectively. At first, the splitting of the ground term (^{3}H) of the 4f^2 configuration induced by the spin–orbit and crystal field interactions is calculated by solving the following secular equation:

$$||\langle J J_z|H_{SO} + H_{CF}|J' J_z'\rangle - E\delta_{JJ'}\delta_{J_z J_z'}|| = 0 \tag{1}$$

where the bra and ket include all the states of the ground term multiplets. It is noticeable that in equation (1) the influence of the higher-lying terms on the splitting of the ground term is

neglected. The correction of H_{exch} and H_{ext} to higher order perturbation can be deduced by solving the following secular equation:

$$||\langle i|H_{SO} + H_{CF} + H_{exch} + H_{ext}|j\rangle - E\delta_{ij}|| = 0 \tag{2}$$

where $|i\rangle$ and $\langle i|H_{SO} + H_{CF}|i\rangle$ are the eigenwave functions and eigenenergies obtained by solving equation (1). Because the occupation probabilities of high-lying CF–SO split levels are small, usually only some low-lying levels need to be included in equation (2). The number of the levels, which should be considered, is related to the value of λ_g.

In Pr:YIG, the superexchange interaction acting on the Pr^{3+} ion is expressed as (Néel 1948):

$$H_{exch} = 2\mu_B H_{exch} S_z \tag{3}$$

where H_{exch} is the exchange field which is proportional to the resultant spontaneous magnetization of the two iron sublattices M_{YIG}:

$$H_{exch} = n_0(1 + \gamma T)M_{YIG}. \tag{4}$$

The values of M_{YIG} used in this work are those deduced from nuclear magnetic resonance experiments by Gonano *et al* (1967).

In PrF_3, the Hamiltonian of the external field is simply written as:

$$H_{ext} = \mu_B H_{ext}(2S_z + L_z). \tag{5}$$

Because for the splitting of the lowest parity-allowed excited 4f5d configuration the mixing of different terms induced by the crystal field is important, all the multiplets whose spin angular momentum number is identical to that of the ground term have then to be included in the calculation. Therefore the splitting of the excited 4f5d configuration by the crystal field must be calculated by solving the secular equation:

$$||\langle LJJ_z|H_0 + H_{SO} + H_{CF}|L'J'J_z'\rangle - E\delta_{LL'}\delta_{JJ'}\delta_{J_zJ_z'}|| = 0. \tag{6}$$

For each nonequivalent magnetic site, the specific Faraday rotation induced by all the electric dipole transitions is given, according to Shen (1964) and Crossley *et al* (1969), by

$$\Theta_F = \frac{\pi N(\bar{n}^2 + 2)^2 e^2}{9c\bar{n}\hbar} \frac{8\pi}{3}(\langle r\rangle_{4f5d})^2 \sum_{ng} B_{ng} \frac{\omega^2(\omega_{ng}^2 - \omega^2 - \Gamma_{ng}^2)}{(\omega_{ng}^2 - \omega^2 + \Gamma_{ng}^2)^2 + 4\omega^2\Gamma_{ng}^2} \rho_g \tag{7}$$

where

$$\frac{8\pi}{3}(\langle r\rangle_{4f5d})^2 B_{ng} = |\langle n|V_-|g\rangle|^2 - |\langle n|V_+|g\rangle|^2. \tag{8}$$

It is important to notice that every term in the right-hand side of equation (7) is composed of the following three factors besides some constants: occupation probability ρ_g, transition matrix element B_{ng} and frequency factor. When $|(\omega_{ng}^2 - \omega^2)| \gg \Gamma_{ng}^2$, the last one is reduced to: $\omega^2/(\omega_{ng}^2 - \omega^2)$.

3.2. Origin of the paramagnetic Faraday rotation

In the following, the Faraday rotation $\Theta_F(ng)$ induced by the electric dipole transition from one state $|g\rangle$ to the excited one $|n\rangle$ is written as

$$\Theta_F(ng) = \frac{\pi N(\bar{n}^2 + 2)^2 e^2}{9c\bar{n}\hbar}(8\pi/3)(\langle r\rangle_{4f5d})^2 \frac{\omega^2}{(\omega_{ng}^2 - \omega^2)} B_{ng} \tag{9}$$

assuming that the occupation probability of the state $|g\rangle$ is equal to one.

In our discussion, two important assumptions will be made: (i) the light frequency is far from all the resonance frequencies; (ii) only the 'paramagnetic' Faraday rotation is analysed. The first approximation is widely justified because most of our calculations and most experiments have been performed at 633 nm wavelength. The second one means that the Zeeman effect of the excited configuration is neglected and has been detailed in our paper (Yang *et al* 1997) where we have shown that the 'diamagnetic' Faraday rotation is much smaller than the 'paramagnetic' one when the light frequency is not near an MO resonance frequency. The analysis of equation (9) has to be conducted according to the nature of the levels involved in the transitions and four cases have to be distinguished.

(1) There exist two nondegenerate CF–SO split levels of the ground configuration and a nondegenerate CF–SO split level of the excited configuration. The matrix element associated with each of the two electric dipole transitions is then always equal to zero. However, when the two nondegenerate CF–SO split levels of the ground configuration are authorized to be mixed by a superexchange interaction (external magnetic field), then two CF–SO split and superexchange interaction (external magnetic field) mixed levels are created (in the following they are denoted as $|g_1\rangle$ and $|g_2\rangle$). The matrix elements associated with the *two* transitions *may* be not equal to zero; furthermore the following relation is always true: $B_{ng1} = -B_{ng2}$, the total Faraday rotation being the sum of the two contributions. Because the energy gap between the $|g_1\rangle$ and $|g_2\rangle$ levels is generally small, the two resonance frequencies corresponding to the $|g_1\rangle \Rightarrow |n\rangle$ and $|g_2\rangle \Rightarrow |n\rangle$ transitions are nearly equal and the absolute values of $\Theta_F(ng1)$ and $\Theta_F(ng2)$ are then nearly identical. Finally, the total Faraday rotation can be simply written, in a first reasonable approximation, as:

$$\Theta_F(ng1)\rho_{g1} + \Theta_F(ng2)\rho_{g2} \cong \Theta_F(ng1)\Delta\rho \tag{10}$$

where ρ_{g1} and ρ_{g2} are the occupation probability of $|g_1\rangle$ and $|g_2\rangle$, respectively, and $\Delta\rho = \rho_{g1} - \rho_{g2}$.

(2) There exist a double degenerate CF–SO split level of the ground configuration and a nondegenerate CF–SO split level of the excited configuration. In this case, the matrix elements corresponding to the two transitions from the two orthogonal states of the double degenerate ground level to the nondegenerate excited one *may* be different from zero. But because the two B_{ng} coefficients are always of opposite sign with identical absolute value and the occupation probabilities of the two orthogonal states are equal, the total Faraday rotation is rigorously equal to zero. It is worth noting that many choices are offered for the two orthogonal states of a double degenerate level, but our above conclusion is independent of the choice. When the degeneracy of the ground configuration level is lifted by the Zeeman effect, the occupation probabilities of the two sublevels are now different. Then a net total Faraday rotation will be produced.

(3) There exist two nondegenerate CF–SO split levels of the ground configuration and a double degenerate CF–SO split level of the excited configuration whose two orthogonal states are denoted as $|n_1\rangle$ and $|n_2\rangle$. As far as the two transitions from any nondegenerate CF–SO split level $|g\rangle$ to $|n_1\rangle$ and $|n_2\rangle$ states are concerned, the sum, $B_{n1g} + B_{n2g}$, of the matrix elements is always equal to zero.

If the two nondegenerate CF–SO split levels of the ground configuration are mixed by the Zeeman effect, the mixed $|g_1\rangle$ and $|g_2\rangle$ levels are obtained (see case 1). Now the sum $B_{n1g1} + B_{n2g1}$ *may* be different from zero. In this case, the two quantities $B_{n1g1} + B_{n2g1}$ and $B_{n1g2} + B_{n2g2}$ have always the same amplitude but are of opposite sign. Now we arrive at a conclusion similar to that of situation (1): the electric dipole transitions have a net contribution to the Faraday rotation through the difference of the occupation probabilities of the $|g_1\rangle$ and $|g_2\rangle$ levels.

(4) There exists a double degenerate CF–SO split level for both the ground configuration and excited configuration. The orthogonal states of the levels are denoted as $|g'\rangle$ and $|g''\rangle$, $|n_1\rangle$ and $|n_2\rangle$, respectively. Now it *may* happen that the sums $B_{n1g'} + B_{n2g'}$ and $B_{n1g''} + B_{n2g''}$ are not equal to zero. Under this hypothesis, the two sums have the same amplitude but are of opposite sign. But as the occupation probabilities of $|g'\rangle$ and $|g''\rangle$ states are the same, there is no net Faraday rotation. It is only when the degeneracy of the ground level can be lifted by the Zeeman effect that a nonzero Faraday rotation is induced.

The discussions given above can be extended to triple degenerate CF–SO split levels and to levels with higher degeneracy. They will be of capital interest to understand the influence of the spin–orbit coupling interaction on the Faraday rotation of the two materials.

4. Effect of the spin–orbit coupling on the Faraday rotation in Pr:YIG

As some other light rare earth ions (Ce, Nd), the Pr^{3+} ions enhance strongly the MO properties of the iron garnets in the visible and infrared ranges when they substitute for the Y^{3+} ions in the dodecahedral $\{24c\}$ positions. A detailed theoretical calculation of both magnetic and MO properties of Pr:YIG has been recently published (Yang *et al* 1997) and the capability of the quantum theory approach has been underlined. The same quantum theory will be used in this paper. It should be pointed out that in this work, all the used parameters have identical values to those used previously in the paper by Yang *et al* (1997).

4.1. Role of the spin–orbit coupling of the ground configuration

In this subsection, the spin–orbit coupling constant of the 4f5d configuration will taken to be the value given by Martin *et al* (1978); this means λ_e is equal to 1.

4.1.1. $0 < \lambda_g \leqslant 1$. When λ_g is equal to 1, the three multiplets of the ground term (^{3}H) are split into 33 non-degenerate levels by the crystal field, the energies and wave functions of them being deduced from equation (1). The energies are: -1140.95, -1123.70, -448.32, -82.36, 105.38, 145.54, ..., 5657.3 cm^{-1}. The lowest two levels are strongly mixed with each other by the superexchange interaction, but they cannot be mixed with the third, fourth, fifth and sixth CF–SO split levels. Although their mixings with the two singlets located at 178.4 and 1683.81 cm^{-1} are permitted by the selection rules, these singlets lie so high that the mixings can be reasonably neglected. The third and fourth levels can be mixed with each other by the superexchange interaction, but the mixing is weak because of the characteristic of their wave functions. The CF–SO split and superexchange interaction mixed 4f^2 levels have contributions to the Faraday rotation.

It should be noted that the crystal field mixes the three multiplets and that because these multiplets 'repulse each other', the energies of the lowest nine CF–SO split levels, whose main components are those of the lowest multiplet, decrease. However the decrease is not uniform (it is smaller for low-lying levels than for high-lying levels) and, consequently, the energy gaps between different low-lying CF–SO split levels are reduced.

It is clear that the energy gaps between the different multiplets of the ground term follow the variation of the spin–orbit coupling strength of the ground configuration and that the 'repulsion' between the different multiplets becomes stronger when the energy differences between different multiplets decrease. In particular, the energy difference (denoted as ΔE_c) between the lowest two CF–SO split 4f^2 levels decreases when λ_g decreases as illustrated by the second column of table 1. Numerical calculations have confirmed that the decreasing of the energy gaps between other low-lying CF–SO split 4f^2 levels is also not negligible. Now the

Table 1. Pr^{3+} ion in Pr:YIG: energy gaps (in cm^{-1}) ΔE_c and ΔE_g, occupation probabilities ρ_1, ρ_2 and $\Delta\rho$, matrix elements $B_{1,1}$ and $B_{2,1}$ when $\lambda_e = 1$ (see sections 2 and 4.1). Note that only room temperature values of ΔE_g, ρ_1, ρ_2, $\Delta\rho$, $B_{1,1}$, $B_{2,1}$ are listed and that the $B_{1,1}$ and $B_{2,1}$ values have been multiplied by 1000.

λ_g	ΔE_c	ΔE_g	ρ_1	ρ_2	$\Delta\rho$	$B_{1,1}$	$B_{2,1}$
0.1	1.7214	52.057	0.3338	0.2587	0.0751	−18.10	−18.55
0.2	4.5583	50.474	0.4413	0.3446	0.0967	−17.67	−18.38
0.25	5.9698	49.756	0.4738	0.3714	0.1024	−17.39	−18.21
0.3	7.2971	49.062	0.5081	0.3997	0.1084	−17.01	−18.04
0.5	11.577	46.903	0.5571	0.4429	0.1143	−15.80	−17.19
1	17.247	44.244	0.5539	0.4461	0.1079	−13.75	−15.50
2	21.194	42.481	0.5518	0.4482	0.1036	−11.98	−13.86
4	23.387	41.474	0.5506	0.4494	0.1012	−10.84	−12.74

mixing of the lowest two CF–SO split 4f^2 levels induced by the exchange field becomes stronger when ΔE_C decreases. As a result, the energy difference between the lowest two CF–SO and superexchange interaction mixed levels (ΔE_g) increases when λ_g decreases as shown in the third column of table 1. It should be noted that because the value of the exchange field H_{exch} is dependent on temperature, the values of ΔE_g, occupation probability and B_{ng} depend on temperature; but for simplicity in table 1 and in the remainder of this section (4) only room temperature values are given. This result has been obtained by solving equation (2), using equation (3) and setting H_{ext} to zero (we only discuss the spontaneous Faraday rotation). This increasing of ΔE_g is of primary importance since it leads to the enhancement of the difference ($\Delta\rho$) of the occupation probabilities of these lowest two levels. However, when the spin–orbit coupling strength is very small (λ_g near zero), the energy gaps between the lowest two CF–SO split levels and the higher-lying CF–SO split levels are strongly reduced, so the number of important CF–SO and superexchange interaction split levels cannot be limited to two. For example, when $\lambda_g = 0.1$, the occupation probability of the third CF–SO split level is more than 35% of the occupation probabilities of the lowest two CF–SO split and superexchange interaction mixed levels. Consequently the occupation probabilities of the lowest two levels are rapidly decreasing when λ_g diminishes and then $\Delta\rho$ becomes smaller as shown in table 1. In summary, there exist two opposite effects concerning $\Delta\rho$ associated with the decrease of λ_g. The competition of these two effects leads to a maximum when λ_g is about 0.5 as reported in table 1, where the corresponding ρ_1 and ρ_2 values are also given. When λ_g decreases from 1 to about 0.5, only a small increase of $\Delta\rho$ should be noted but when λ_g varies from about 0.5 to 0.1, a rapid decrease of $\Delta\rho$ is obtained (table 1).

However, it is worth noting that, according to equation (7), the Faraday rotation depends not only on $\Delta\rho$ but also on the B_{ng} coefficients. More precisely, at 633 nm wavelength, the Faraday rotation originates mainly from the transitions from the CF–SO split and superexchange interaction mixed 4f^2 levels to the lowest two CF–SO split 4f5d levels whose energies are equal to 23 055 and 23 700 cm^{-1} respectively (Yang *et al* 1997). It should be noted that in the case $\lambda_g = 1$, the lowest six CF–SO split levels are found to be divided into three pairs. For example, the lowest two levels compose a pair. The two levels within one pair are strongly mixed with each other but only very weakly mixed with other levels by the superexchange interaction. Therefore, the coefficients $B_{1,1}$ and $B_{1,2}$ have opposite sign and very close absolute values ($B_{1,1} = -13.75 \times 10^{-3}$, $B_{1,2} = 13.75 \times 10^{-3}$). The coefficients $B_{2,1}$ and $B_{2,2}$ have the same nature ($B_{2,1} = -15.50 \times 10^{-3}$, $B_{2,2} = 15.50 \times 10^{-3}$). When λ_g is equal to other values (but not close to 0), the main features of the energy schema keep unchanged. In table 1 the values of $B_{1,1}$ and $B_{2,1}$ are listed (we recall that for $\lambda_g > 0.3$ only the occupation probabilities of the lowest two CF–SO split and superexchange interaction mixed 4f^2 levels are important).
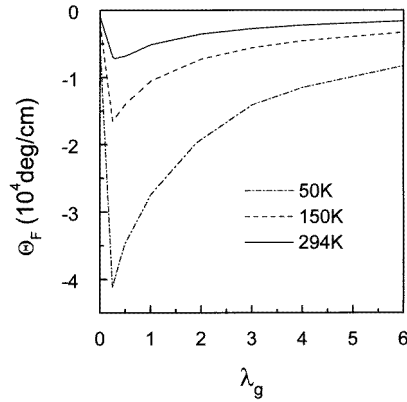
Figure 1. Contribution of the Pr^{3+} ion to the Faraday rotation in $PrY_2Fe_5O_{12}$ at 633 nm wavelength versus λ_g (relative spin–orbit coupling strength of the *ground* configuration). The relative spin–orbit coupling strength λ_e of the *excited* configuration is set to 1.

As shown in table 1, the absolute values of $B_{1,1}$ and $B_{2,1}$ increase monotonically as λ_g decreases, but this increase is very small for $\lambda_g < 0.3$. As, on the other hand, $\Delta\rho$ varies much rapidly with a maximum when λ_g is about 0.5, the Faraday rotation, at 633 nm wavelength, depends strongly on λ_g and presents a maximum when λ_g is about 0.3 as shown in figure 1. When $\lambda_g < 0.3$, the probabilities of the third and fourth levels are important but their difference is very small. Therefore the net contribution of the third and fourth levels to the MO effect is very small and the MO effect is mainly contributed by the lowest two levels. Now because $\Delta\rho$ (the difference of the occupation probabilities of the lowest two levels) rapidly decreases as λ_g varies from 0.3 to 0, the amplitude of the Faraday rotation decreases as λ_g decreases from 0.3 to 0.1. Furthermore, it should be noted that as this maximum originates from the $\Delta\rho$ and $B_{n,g}$ behaviours only, they are wavelength independent as long as the ω experimental value is far from resonance frequencies (ω_{ng}) (see equation (7)).

At the end of this subsection, it should be pointed out that: (i) whatever λ_g is, all the CF–SO split 4f5d levels have been included in our calculations; (ii) when λ_g was smaller than 0.5, not only the contribution to the Faraday rotation of the lowest two CF–SO split and superexchange interaction mixed $4f^2$ levels but also the higher-lying levels have been considered.

4.1.2. $\lambda_g = 0$. When the spin–orbit coupling of the ground $4f^2$ configuration does not exist, the orbital degeneracy of the ground term, ^3H, is completely lifted by the crystal field of D_2 symmetry but the spin degeneracy keeps unchanged. Then 11 spin triplet degenerate levels are obtained: their energies are 1076.64, 1078.57, 1807.63, 1859.80, 2278.55, ..., 3740.64 cm^{-1}. Under the superexchange perturbation, each of the CF split levels is split into three sublevels: the energy of the first one is equal to the original level one, the energies of the two others are symmetrically located above and below the first energy. It is worth noting that although the energy gap between the lowest two crystal field split levels is very small, no mixing by the superexchange interaction is authorized. All the coefficients $B_{n,g}$ associated with a transition from a sublevel whose energy is not changed by the superexchange interaction to any CF–SO split 4f5d level is equal to zero. So the net contribution of a CF split level to the Faraday rotation is proportional to the difference of the occupation probabilities of the two sublevels whose energies are not the same as that of the original CF level and is proportional to the corresponding $B_{n,g}$.

At 294 K, the ρ difference of the two sublevels issued from the lowest CF split level is 0.0422 whereas the same ρ difference is 0.0418 for the sublevels issued from the second CF split level. The sum (0.084) of these two differences is only a little larger than the $\Delta\rho$ value (0.0751) reported in table 1 for $\lambda_g = 0.1$, but as all the $B_{n,g}$ coefficients obtained for $\lambda_g = 0$ are much smaller than those corresponding to $\lambda_g = 0.1$, hence the amplitude of the Faraday rotation continues to decrease as λ_g varies from 0.1 to 0. However the Faraday rotation is still important (-920 deg cm^{-1} at 294 K) when $\lambda_g = 0$. It should be noticed that whatever the wavelength is, except in the near vicinity of the resonance frequencies, all our conclusions of this section are valid.

4.1.3. $\lambda_g > 1$. When λ_g is larger than 1, the occupation probabilities of the third and fourth CF–SO split and superexchange interaction mixed 4f^2 levels are very small; only the lowest two levels have a strong influence on the Faraday rotation. As shown in table 1, when λ_g increases from 1 to 4, the relative decrease of $\Delta\rho$ is very weak (below 7%); furthermore, $B_{1,1}$, $B_{1,2}$, $B_{2,1}$ and $B_{2,2}$ which are the most important $B_{n,g}$ coefficients also decrease with λ_g. Furthermore, as λ_g increases, the energies of the lowest two split 4f^2 levels decrease. Consequently the resonance frequencies increase and the frequency factor in equation (7) decreases. Finally, a slow and monotonic decrease of the Faraday rotation is then observed as shown in figure 1.

In ferrimagnetic Pr:YIG, the superexchange interaction between the iron and Pr sublattices acts on the electron spin of the Pr^{3+} ions. Light, however, is not directly coupled to the spin but only through the spin–orbit interaction. So light 'feels' magnetic ordering through the spin–orbit interaction. Therefore the spin–orbit interaction of the ground configuration has a great influence on the Faraday rotation. However, in contrast to the theoretical results obtained by Oppeneer *et al* (1992) and Misemer (1988) in Ni and MnBi, the Faraday rotation does not scale linearly with the strength of the spin–orbit coupling and has a maximum value when λ_g is about 0.3. This difference might be due to the following reasons: in ferromagnetic metals the exchange interaction is much larger than the superexchange interaction acting on the Pr^{3+} ions in Pr:YIG (for example, the exchange splitting in MnBi was chosen to be 2.18 eV (Misemer 1988)), while the spin–orbit interaction is smaller than that in the Pr^{3+} ions. From figure 1 it can be seen that the nearly linear dependence of the Faraday rotation on the spin–orbit interaction strength holds when λ_g is very small. So in this range of λ_g our result is in accord with the results of Oppeneer *et al* (1992) and Misemer (1988). The dependence becomes more complex when the spin–orbit interaction becomes close to or exceeds the superexchange interaction. We think that in the calculations of MnBi and Ni, if the variation range of the spin–orbit coupling strength is large enough, a complex rotation might also be obtained.
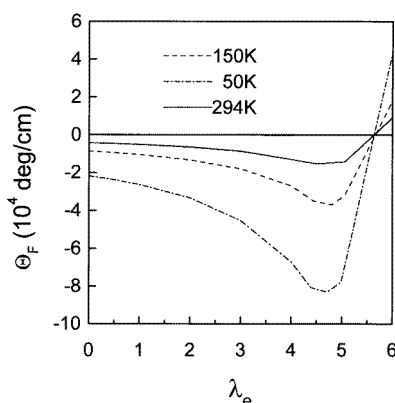
4.2. Role of the spin–orbit coupling of the excited configuration

In this subsection, λ_g is always set to 1. The degeneracy of the five spin triplet terms (^{3}H, ^{3}F, ^{3}G, ^{3}D and ^{3}P) of the 4f5d configuration is completely lifted by the crystal field. When λ_e is equal to 1, the five terms are split into 105 non-degenerate levels. Including the mixing between all the multiplets, the energies of these CF–SO split levels were determined in the 23 055–97 536 cm^{-1} range by solving equation (6) (Yang *et al* 1997). However, because of the selection rules only four levels, whose energies are 23 055, 23 700, 34 169 and 37 228 cm^{-1} respectively, yield a large contribution to the Faraday rotation below 6.0 eV photon energy (207 nm wavelength) but at 633 nm wavelength the most important contributions to the Faraday rotation originate from the lowest two levels (located at 23 055 and 23 700 cm^{-1}) (Yang *et al* 1997).

Table 2. Pr^{3+} ion in Pr:YIG: energies (in cm^{-1}) of the lowest two CF–SO split levels of the *excited* configuration, matrix elements $B_{1,1}$ and $B_{2,1}$ when $\lambda_g = 1$ (see sections 2 and 4.2). Note that the $B_{1,1}$ and $B_{2,1}$ values are calculated at room temperature and have been multiplied by 1000.

λ_e	E_{n1}	E_{n2}	$B_{1,1}$	$B_{2,1}$
0	25 620	25 720	[a]	[a]
0.5	24 733	24 742	−13.45	−14.86
1	23 055	23 701	−13.68	−15.48
2	21 141	21 655	−13.81	−15.88
4	16 978	17 312	−13.78	−15.69
6	12 560	12 774	−13.73	−15.13

[a] See comments in section 4.2.

Figure 2. Contribution of the Pr^{3+} ion to the Faraday rotation in $PrY_2Fe_5O_{12}$ at 633 nm wavelength versus λ_e (relative spin–orbit coupling strength of the *excited* configuration). The relative spin–orbit coupling strength λ_g of the *ground* configuration is set to 1.

When λ_e is larger (smaller) than 1, the energies of the low-lying multiplets of every term will decrease (increase). Therefore the energies of the lowest two CF–SO split 4f5d levels decrease as λ_e increases as shown through the following data: when $\lambda_e = 6$, the lowest two levels are located at 12 560 and 12 774 cm^{-1}, respectively, while the same levels are situated at 25 620 and 25 720 cm^{-1}, respectively, when $\lambda_e = 0$. In table 2, the energies of the lowest two levels when λ_e varies from 0 to 6 are listed. Consequently the smallest two resonance frequencies become smaller as λ_e increases.

The coefficients B_{ng} corresponding to the transitions from the lowest CF–SO split and superexchange interaction mixed $4f^2$ level (obtained for $\lambda_g = 1$) to the lowest two CF–SO split 4f5d levels are reported in table 2 as well (except the case $\lambda_e = 0$). We have to pay attention to the case where $\lambda_e = 0$; now all the CF–SO split 4f5d levels are triple degenerate. The matrix elements associated with the transitions from the lowest $4f^2$ level mentioned above to the two orthogonal states of the lowest 4f5d level (located at 25 620 cm^{-1}) are equal to −0.012 75 and −0.012 69, respectively; note that the same matrix element remains small as far as the transition corresponding to another orthogonal state of this 4f5d level is concerned. As furthermore the matrix elements associated with the transitions from the $4f^2$ levels to various orthogonal states of the second CF–SO split 4f5d level (located at 25 720 cm^{-1}) are negligible, we arrive at the conclusion that the B_{ng} coefficients obtained when the spin–orbit coupling interaction of the 4f5d level is absent are only a little bit smaller than the value corresponding

to $\lambda_e = 1$. This small variation of the B_{ng} coefficients is also observed when λ_e varies in the 1–6 range.

In summary, we have demonstrated that the variation of the Faraday rotation in the visible range versus λ_e will be mainly determined by the frequency factor of equation (7). Our detailed calculations have led to a slow and monotonic increase of the Faraday rotation amplitude when λ_e increases from 0 to 2 as shown in figure 2 (λ_g was set to 1). However, when λ_e is larger than 2, the absolute value of the Faraday rotation increases faster and faster, then reaches a maximum for λ_e equal about 4.7 and vanishes at $\lambda_e \cong 5.5$ where a change of the Faraday rotation sign is observed. Such a behaviour originates simply from the shift of the lowest resonance frequency. When ω_{ng} is equal to the experimental frequency (633 nm wavelength) in the $\lambda_e \cong 5.5$ range, the variation of the $\omega^2/(\omega_{ng}^2 - \omega^2)$ factor (equation (7)) becomes very strong. Both Faraday rotation evolutions reported in figures 1 and 2 have been calculated at 633 nm wavelength. However, it should be noted that the general features of figure 1 are independent of the choice of the light frequency (except very near a resonance frequency). In contrast, in figure 2, the λ_e values corresponding to the change of the sign of the Faraday rotation are strongly dependent on the choice of the light frequency. Finally, we arrive at the following conclusion: λ_e has not a determinant influence on the Faraday rotation except when the experimental frequency is near a resonance frequency.

5. Effect of the spin–orbit interaction on the Faraday rotation in PrF₃

Lighter rare earth trifluorides present, in the visible part of the spectrum, a large Faraday rotation as measured by Van Vleck and Hebb (1934) and later by Leycuras *et al* (1984b). The magnetic and MO properties of PrF₃ have been studied under a 20 kOe magnetic field applied along the *c* axis of the hexagonal structure in the 4.2–300 K temperature range; they have been found to originate from the Pr^{3+} ion behaviour only (Leycuras *et al* 1984b). Most observed magnetic and MO properties of PrF₃ have been explained on the basis of quantum theory (Xu and Duan 1992). It is worthwhile to recall that in the paper by Xu and Duan (1992) it was assumed that, in a first reasonable approximation, the environment of the Pr^{3+} ion in PrF₃ has a C_2 symmetry and that the four crystal field parameters were deduced from the point charge model; furthermore, no exchange coupling between Pr^{3+} ions has been considered. In this paper, all the used parameters are the same as those used in the paper by Xu and Duan (1992) except the SO strengths which are assumed to be variables.

5.1. Role of the spin–orbit coupling of the ground configuration

When $\lambda_g = 1$ the ground term ^3H is split into 22 levels by the crystal field and spin–orbit interactions; 11 of them are singlets, the others are double degenerate. In the case of $\lambda_g = 1$, the energy of these levels varies from -141.94 to 4492.96 cm^{-1}. The mixing of the different multiplets of the ^3H term by the crystal field was included in the calculation. It is very important that the lowest one is a singlet. The spin triplet terms of the 4f5d excited configuration are split, by both spin–orbit and crystal field interactions, into 69 levels including 33 singlets and 36 doublets, the energies being in the 60 106–73 184 cm^{-1} range. It should be noted that in this subsection, λ_e is always kept equal to 1. It is worth noting that the mixing of the different terms of the excited configuration (^3H, ^3F, ^3G, ^3D and ^3P) by the crystal field was introduced in our calculations. In figure 3, for the sake of simplicity, only the energy schema including the lowest seven CF–SO split 4f^2 levels is reported.

Now we discuss the effect of the external magnetic field on the lowest six CF–SO split 4f^2 levels. Because of the selection rules the lowest two levels cannot mixed with other levels
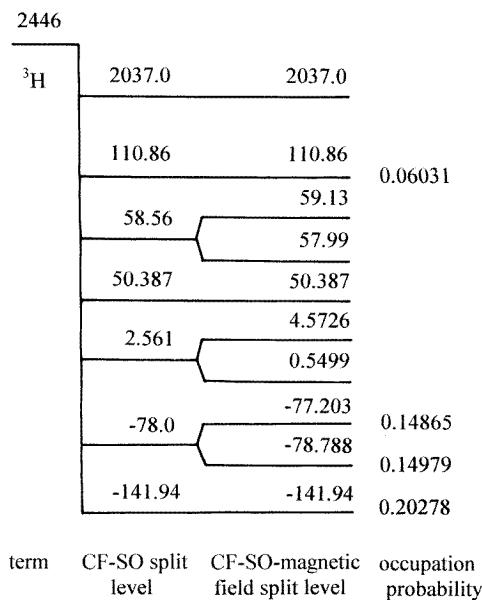
Figure 3. Pr^{3+} ion in PrF$_3$: Successive splittings of the ^{3}H term of the ground configuration when $\lambda_g = 1$. Level energies (in cm^{-1}), and room temperature occupation probabilities of some levels are reported.

by the magnetic field, while the third (fourth) one can be mixed with the fifth (sixth) one. But the energy gap between the third and fifth (the fourth and sixth) levels is larger than 55 cm^{-1}, so only the first order correction of the Zeeman effect is important. The two sublevels of each CF–SO split double degenerate level have a net contribution to the Faraday rotation, and this contribution is proportional to the difference of the occupation probabilities of the two sublevels.

When the temperature decreases from 300 K to low temperature, the difference of the occupation probabilities of the two sublevels of each doublet increases, then the amplitude of the Faraday rotation increases first. However, in the 100 K range, the occupation probability of the lowest nondegenerate level becomes very important and the absolute value of the Faraday rotation begins to decrease; finally at very low temperature, only the lowest singlet has to be considered and the Faraday rotation approaches zero. So, this energy schema explains successfully the observed fact that the Verdet constant first increases and then decreases rapidly as temperature decreases from 300 to 4.2 K (Leycuras et al 1984b).

When λ_g varies from 4 to 0.2, the energy gaps between different CF–SO split levels become smaller. However, in contrast to the high order correction of the Zeeman effect, the first order correction is insensitive to the energy gaps. Therefore the variations of the occupation probability differences between the two sublevels of the various doublets versus λ_g are small. At the same time, the values of the B_{ng} coefficients associated with these sublevels almost remain unchanged. As a result, the Verdet constant varies very slowly when λ_g decreases from 4 to about 0.2 as shown in figure 4.

However, when λ_g is very small the situation is quite different. Now we focus our attention to the situation of $\lambda_g = 0$. In this case, the ^{3}H term is split into three triple and four sixfold degenerate levels by the crystal field. The lowest three levels are shown in figure 5. Particular attention has to be paid to the lowest CF split level which is split into three sublevels by
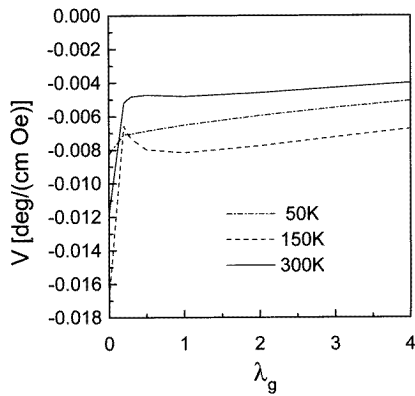
Figure 4. Variation of the Verdet constant of PrF$_3$ at 633 nm wavelength versus λ_g (relative spin–orbit coupling strength of the *ground* configuration). The relative spin–orbit coupling strength λ_e of the *excited* configuration is set to 1.
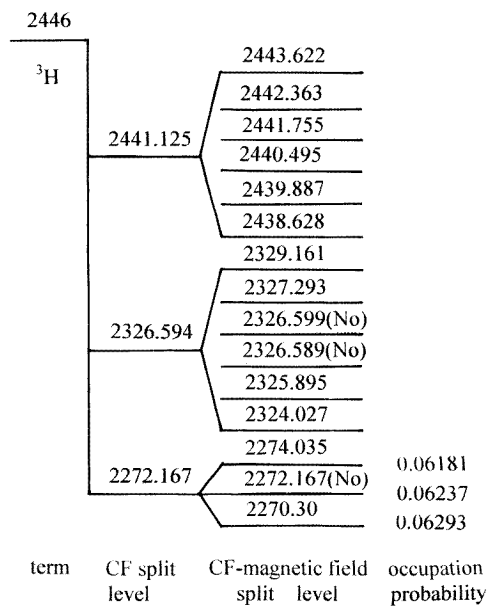

Figure 5. Same as figure 3 but for $\lambda_g = 0$. For the sake of simplicity, only the lowest three CF split levels are given. The sublevels marked by 'No' do not contribute to the Faraday rotation.

the magnetic field. The first and the third sublevels have negative and positive contribution, respectively, while the intermediate sublevel (whose energy is unchanged under the magnetic field) has a zero contribution. So now ($\lambda_g = 0$), the sublevel which does not contribute to the Faraday rotation is not the lowest one, then the magnitude of the Faraday rotation increases rapidly when λ_g approaches zero, especially at very low temperature. From above analysis we know that a spin–orbit coupling interaction of the ground configuration is not needed to produce a very important Faraday rotation contrary to the widespread opinion.

5.2. Role of the spin–orbit coupling of the excited configuration

The role of the spin–orbit coupling of the excited configuration in the MO effects induced by the Pr^{3+} ions in PrF_3 is very similar to that in Pr:YIG. The calculated Verdet constant of PrF_3 versus the relative spin–orbit coupling strength of the excited configuration is shown in figure 6 when λ_e varies from 0 to 4 (assuming $\lambda_g = 1$). It can be seen that the magnitude of the Verdet constant increases slowly and monotonically as λ_e increases. To complete our analysis, the room temperature Verdet constant (at 633 nm wavelength) in the case of $\lambda_g = \lambda_e = 0$ is calculated and the result is -12.14 deg cm^{-1} kOe^{-1}. In the cases of $\lambda_g = \lambda_e = 1$ and $\lambda_g = 0, \lambda_e = 1$ the corresponding values are -4.81 and -11.92 deg cm^{-1} kOe^{-1}, respectively. These results show that when both the spin–orbit interactions of the ground and excited configurations are absent, the Faraday rotation is about 3.5 times larger than that in the normal situation ($\lambda_g = \lambda_e = 1$). But this great difference is mainly brought about by the spin–orbit interaction of the ground configuration as shown by the fact that the Verdet constant value in the case of $\lambda_g = 0, \lambda_e = 1$ is close to the value (-12.14 deg cm^{-1} kOe^{-1}) corresponding to the case of $\lambda_g = \lambda_e = 0$.
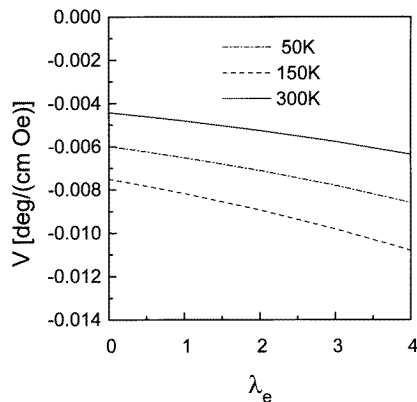
Figure 6. Variation of the Verdet constant of PrF_3 at 633 nm wavelength versus λ_e (relative spin–orbit coupling strength of the *excited* configuration). The relative spin–orbit coupling strength λ_g of the *ground* configuration is set to 1.

From the results reported above it can be seen that the effect of the spin–orbit interaction of the excited configuration on the MO effects in PrF_3 is very similar to that for Pr:YIG. However, the effect of the spin–orbit interaction of the ground configuration on the MO effects in PrF_3 is quite different from that for Pr:YIG. For PrF_3, when the spin–orbit coupling of the ground configuration is absent, the magnitude of the Faraday rotation is much larger than that exists when λ_g is equal to 1. Two reasons are responsible for this difference. First, in paramagnetic PrF_3 the external magnetic field, which is responsible for the magnetic ordering, acts directly on both the spin and orbital momenta. We have found that when we let an exchange field (but no magnetic field) act on the Pr^{3+} ions in PrF_3 (other conditions are kept unchanged), a change of the sign of the Faraday rotation takes place as λ_g decreases from 0.3 to 0. The magnitude of the Faraday rotation when $\lambda_g = 0$ is not a maximum but it is still comparable with the magnitude when $\lambda_g = 1$. Second, the difference between the site symmetries of the Pr^{3+} ions in PrF_3 and Pr:YIG is also important. It has been found by us that for Ce-substituted yttrium aluminium garnet, which has the same crystal structure as Pr:YIG but is paramagnetic, the variation of the Faraday rotation as λ_g decreases from 1 to 0 is different from that for PrF_3 but similar to that for Pr:YIG.

6. Conclusion

In this paper, the role of the spin–orbit interaction in the MO effects in the two magnetic insulators, where the Pr^{3+} ions are magneto-optically active, has been studied extensively. It has been proved that the effect of the spin–orbit coupling on the MO effects in the two materials is quite different from those shown by Oppeneer *et al* (1992) in Fe, Co, Ni, and Misemer (1988) in MnBi. From our calculations, the following main conclusions are derived: (1) The influence of the strength of the spin–orbit interaction of the excited configuration on the Faraday rotation is very small except when the experimental frequency is near a resonance frequency. Therefore, different from Dionne *et al* (1993, 1994), we think that it is not the excited-state splitting induced by the large bismuth spin–orbit coupling, but the ground-state splitting induced by the bismuth spin–orbit coupling that should be responsible for the Faraday rotation enhancement in the Bi-substituted YIG. (2) The spin–orbit interaction of the ground configuration has a great influence on the MO effects. However, in contrast to the theoretical results obtained for MnBi (Misemer 1988) and for Ni (Oppeneer *et al* 1992), the Faraday rotation in Pr:YIG does not scale linearly with the strength of the spin–orbit coupling. It varies in a complex way as λ_g changes and has a maximum value when λ_g is about 0.3. The difference may be due to the following reasons: in ferromagnetic metals the exchange interaction is much larger than the superexchange interaction between the Pr and iron sublattices in Pr:YIG, while the spin–orbit interaction is smaller than that in the Pr^{3+} ions. (3) The variation of the Faraday rotation in PrF₃ with λ_g is quite different from that in Pr:YIG. For PrF₃, when λ_g is zero, the magnitude of the Verdet constant is much larger than that exists when λ_g is 1. Both the differences between the magnetic structures and between the crystal structures of the two materials are responsible for this difference. (4) Both the spin–orbit interactions of the ground and excited configurations are not always needed to produce a Faraday rotation.

Acknowledgments

References

Argyres P N 1955 *Phys. Rev.* **97** 334
Bennet W R, Schwarzacher W and Egelhoff W F 1990 *Phys. Rev. Lett.* **93** 3169
Buschow K H J 1988 *Ferromagnetic Materials* vol 4, ed K H J Buschow and E P Wohlfarth (Amsterdam: North-Holland) p 493
Buschow K H J and van Engen P G 1981 *J. Magn. Magn. Mater.* **25** 90
Buschow K H J, van Engen P G and Jongebreur R 1983 *J. Magn. Magn. Mater.* **38** 1
Crossley W A, Cooper E W, Page J L and van Stapele R P 1969 *Phys. Rev.* **181** 896
Dionne G F and Allen G 1993 *J. Appl. Phys.* **73** 6127
——1994 *J. Appl. Phys.* **75** 6372
Gonano R L, Hunt E and Meyer H 1967 *Phys. Rev.* **156** 521
Hulme H R 1932 *Proc. R. Soc.* A **135** 237
Kahn F L, Pershan P S and Pemeika J P 1969 *Phys. Rev.* **186** 891
Kittel C 1951 *Phys. Rev.* **83** 208
Leycuras C, Le Gall H, Desvignes J M, Guillot M and Marchand A 1982 *J. Appl. Phys.* **53** 8181
Leycuras C, Le Gall H, Guillot M and Marchand A 1984a *J. Appl. Phys.* **55** 2158
——1984b *J. Appl. Phys.* **55** 2161
Liu G Q, Zuo W D, and Le Z Q 1991 *J. Appl. Phys.* **69** 1591

Martin W C, Zalubas R and Hagan I 1978 *Atomic Energy Level. The Rare Earth Elements* (Washington, DC: National Bureau of Standards)

Misemer D K 1988 *J. Magn. Magn. Mater.* **72** 267

Néel L 1948 *Ann. Phys., Paris* **3** 127

Oppeneer P M, Sticht J, Maurer T and Kubler J 1992 *Z. Phys.* B **88** 309

Reim W and Schoenes J 1990 *Ferromagnetic Materials* vol 5, ed E P Wohlfarth (Amsterdam: North-Holland) p 133

Schoenes J 1992 *Materials Science and Technology* vol 3, ed R W Cahn, P Haase and E J Kramer (Weinheim: Chemie)

Scott G B, Lacklison D E, Ralph H I and Page J L 1975 *Phys. Rev.* B **12** 2562

Shen Y R 1964 *Phys. Rev.* **133** A511

Shinagawa K 1982 *J. Magn. Soc. Japan* **6** 247

Simsa Z, Le Gall H, Simsova J, Kolacek J and Le Paillier-Malecot 1984 *IEEE Trans. Magn.* **20** 1001

Van Vleck J H and Hebb M H 1934 *Phys. Rev.* **46** 17

Weller D, Reim W, Sporl K and Brandle H 1991 *J. Magn. Magn. Mater.* **93** 183

Xu You and Duan Mingqian 1992 *Phys. Rev.* **46** 11 636

Yang Jiehui, Xu You, Zhang Fang and Guillot M 1997 *Phys. Rev.* **56** 11 119

Zeper W B, Greidanus F J A M, Gareia P F and Fincher C R 1989 *J. Appl. Phys.* **65** 4971