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Electron paramagnetic resonance study of iridium in forsterite

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Abstract Electron paramagnetic resonance of Ir^{2+} in forsterite is studied at Q-band frequency and room temperature. There are four equivalent spectra superimposed along the three crystallographic axes. The individual spectrum consists of four hyperfine lines of approximately equal intensity separated from each other by 42 G; one axis of the g tensor is near the c axis. Ir^{2+} is certainly substituted for Mg^{2+} . Because of the fourfold degeneracy of the EPR spectrum, it may be suggested that iridium occurs at M_1 . Taking into account that one eigenvector of the g tensor is nearly parallel to c , it seems also possible that the substitution takes place at the M_2 position. In this case, the lattice relaxation of the crystal structure around Ir^{2+} at M_2 must break the point symmetry m at M_2 .

Keywords EPR · Forsterite · Iridium

Introduction

Forsterite, Mg_2SiO_4 , is an end member of the family of olivines. Pure forsterite rarely occurs in nature, but crystals of high quality may be synthesized, for instance by the Czochralski technique (Takei et al. 1984). In forsterite, magnesium occurs at two sites, $4a$ (M_1) and $4c$ (M_2) with point symmetry -1 and m , respectively. Both sites are octahedrally co-ordinated by oxygen, and several impurities can be substituted for Mg depending on the nature of the impurity and on the crystal growth

conditions. For example, when Mg^{2+} is substituted by Fe^{3+} , the impurity is not equally distributed over the two octahedrally coordinated positions, M_1 and M_2 . It was shown that Mn^{2+} and Gd^{3+} are present only at the M_2 position (Michoulier et al. 1969, Gaite 1987). Cr^{3+} is located in the two octahedral sites in different proportions depending on the origin of the sample (Rager 1977, 1978), the substitution of Cr^{3+} for Mg^{2+} is sometimes charge balanced by the presence of Al^{3+} substituted for Si^{4+} nearby (Bershov et al. 1983). Chromium may also be present in other valence states (Cr^{2+} , Cr^{3+} , Cr^{4+}) (Tarasov et al. 1995).

Non-Kramers ions such as Ni^{2+} were also observed in forsterite, it was shown that Ni^{2+} is located at M_1 , but the EPR parameters reported for this ion in two different samples are very different (Rager et al 1988, Tarasov and Shakurov 1996), which may be explained by different lattice relaxations around the impurity, depending on the presence of other impurities and on the crystal growth conditions. Here, an EPR study of iridium in a synthetic forsterite single crystal is presented.

Experimental results and discussion

The crystal used for this study is a small part of the one previously studied by Chatelain and Weeks 1970 and later by Gaite and Rager 1997. The measurements were performed at room temperature and at Q-band frequency using a Varian spectrometer. In this sample, beside the well-known EPR signals of Mn^{2+} and Fe^{3+} , a new spectrum has been detected which is characterized by four equally spaced resonance lines of approximately the same intensity. Further, the spectrum exhibits a fourfold degeneracy, i.e. the four spectra collapse into one when the magnetic field, B , is along one of the crystal axes (Fig. 1) and coincide two by two with B in each of the three crystallographic planes. Therefore, the new spectrum should result from paramagnetic centres at M_1 . The angular dependence was studied in the three crystallographic planes. However, only in the ac plane could be the new spectrum observed for all orientations without being masked by other EPR lines, whereas in the two other planes the spectrum is often overlapped by Mn^{2+} EPR lines.

The spacing between the four lines is about 42 G. This suggests, together with their approximately equal intensity, that the four lines are due to an interaction between an electron spin, S ,

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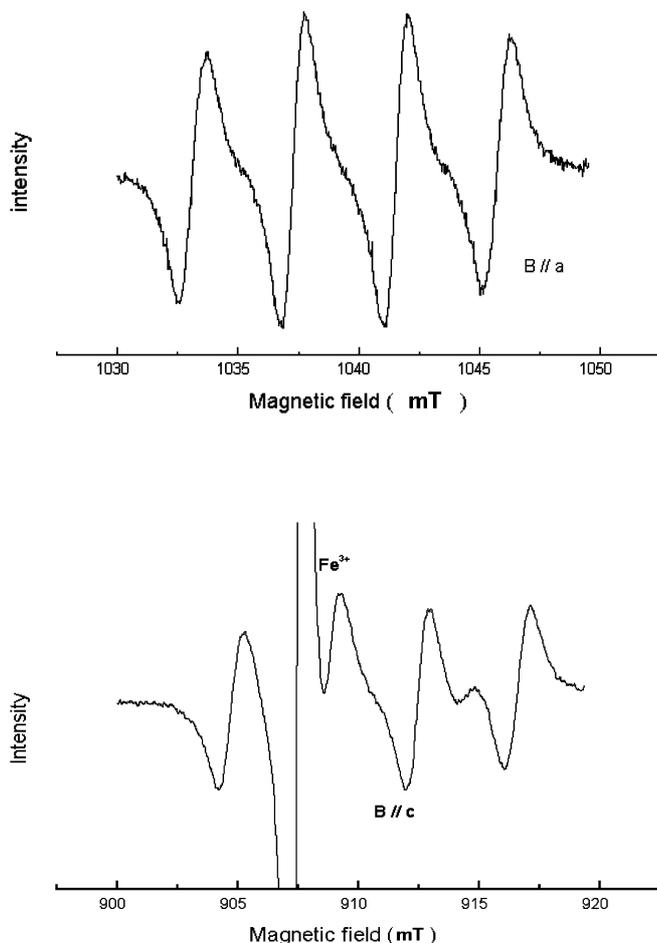


Fig. 1 EPR spectra of Ir^{2+} in forsterite at Q band frequency (34.620 GHz), the magnetic field is respectively parallel to the crystal axes a (top) and c (bottom)

Table 1 Values of the g tensor in the a, b, c reference frame

g_{ij}	x	y	z
x	2.363	0.2856	-0.0382
y		2.108	0.0137
z			2.712

Table 2 Principle values of the g tensor and their direction cosines in the a, b, c reference frame θ and ϕ stand for the spherical coordinates

g_{ii}	a	b	c	θ	ϕ
1.9207	0.546	-0.8377	0.0409	87.65	56.90
2.5444	0.8263	0.5446	0.1436	81.74	33.46
2.7169	-0.14264	-0.0446	0.9887	8.62	17.36

and a nuclear spin $I = 3/2$ in 100% abundance. There are several isotopes having 100% abundance and $I = 3/2$. However, looking at the four-line spectrum in detail, it follows that the two outer lines are wider than the two inner ones. Taking into account the value of the hyperfine structure, iridium with the isotopes ^{193}Ir

($I = 3/2$, natural abundance 62.7%) and ^{191}Ir ($I = 3/2$, natural abundance 37.3%) seems to be very likely responsible for the new spectrum. This assumption is supported by the fact that the sample was pulled from the melt in an iridium crucible. Further, crystal-chemical reasons suggest that iridium is incorporated in the forsterite matrix as Ir^{2+} . Then, the electron spin, S , might be $3/2$. However, Raizman et al. (1977), who studied Ir^{2+} in CaO and MgO , pointed out that the features of the spectrum are those expected for an ion with $S = 1/2$ and $I = 3/2$. The same was observed in the spectrum here. Therefore, we describe the EPR using an effective spin $S = 1/2$ in analogy to Co^{2+} which also has the electron configuration d^7 .

On the basis of the measurements in the three crystallographic planes, the tensors g and A of this spectrum were then calculated using the spin-Hamiltonian:

$$H = \beta B g S + I A S.$$

The g matrix components in the abc crystal frame for one of the four non-degenerated spectra are given in Table 1. The principle values of g and their orientation with respect to the crystal axes are given in Table 2. The hyperfine splitting of the EPR transitions is nearly isotropic and shown in Fig. 1. In first order, the hyperfine interaction tensor A can thus be given by a constant value $A = (39 \pm 1) 10^{-4} \text{ cm}^{-1}$. The value of A is close to that one of Ir^{2+} in CaO . This is a proof of the valence state of iridium.

From the kind of degeneracy it is concluded that Ir is located at M_1 . This is surprising, as previously it was observed that large ions such as Mn^{2+} and Gd^{3+} were located at M_2 because of the larger volume of the $M_2\text{-O}_6$ polyhedron (Michoulier et al. 1969; Gaite 1987). Looking, therefore, at the principal axes of the g tensor from Table 2, it is observed that one principal axis is at 8.6° from the c axis. This small deviation might indicate that Ir occupies the larger M_2 position where the mirror plane is perpendicular to c , a lattice relaxation consecutive to the substitution destroying the symmetry at M_2 . Such lattice relaxation breaking the point symmetry was previously observed in other cases (Gaite et al. 2001). However, such a structural distortion must be very large to induce the observed deviation of the g tensor orientations.

As a conclusion, it is certain that iridium is substituted for magnesium in only one of the positions M_1 and M_2 , and more probably in M_1 .

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