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ESR of dislocation defects in MgF_2 crystals —with more than 130 line peaks*

Hou Bi-Hui(侯碧辉)[a)†], Zheng Ying-Guang(郑莹光)[b)], Shao Meng(邵 萌)[a)], Liu Feng-Yan(刘凤艳)[a)], and Fan Zhi-Da(范志达)[c)]

[a)] *College of Applied Sciences, Beijing University of Technology, Beijing* 100022, *China*
[b)] *Analysis and Testing Center, Jilin University, Changchun* 130023, *China*
[c)] *Research Institute of Synthetic Crystals, Beijing* 100018, *China*

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In this work, more than 130 line peaks in electron spin resonance (ESR) spectra have been discovered of the laser material MgF_2 crystal in room-temperature experiments. A sample is cut from the shoulder part of the MgF_2 crystal, and another is from the MgF_2:Co crystal. The samples were not treated by any irradiation. The same anisotropic ESR spectra of the two samples indicate that the dopant Co^{2+} introduces defects which induce the same multinuclear free radicals as in dislocations in the sample of MgF_2. These paramagnetic solid multinuclear free radicals show good stability, and their ESR spectra are found to be anisotropic. ESR signals are derived from three different types of multinuclear free radicals from a tentative simulation analysis.

When the direction of the applied magnetic field is along the [100] or [010] orientation of the crystal, the magnetic field at which the ESR signals are detected ranges from 0.2294T to 0.4654T and the width of this range is 0.2362T (corresponding to an energy band of 0.233eV); the most narrow peak in the ESR spectra has a width ΔH about 1.28×10^{-3}T. This width ΔH, equivalent to the energy difference of two neighbouring levels, is very small, only 1.85×10^{-7}eV (or 1.46×10^{-3}cm^{-1}).

This fact indicates that the ground state is highly degenerate, and splits into nearly quasi-continuous energy levels like an energy band in an applied magnetic field. It may be served as a new starting point of solid laser exciter frequency modulation.

Keywords: ESR, anisotropy, MgF_2crystal, multinuclear free radicals
PACC: 7630L,7630R, 7530G

1. Introduction

Magnesium fluoride is an ionic conductor and is also an important material for most solid lasers in use.[1,2] Since nuclear spins of alkaline-earth metals and halogen elements are not zero, in an ionic crystal of the alkaline-earth halide it is possible that some multinuclear free radicals are produced in the dislocation and negative vacancy defects. There have been investigations about irradiation or doping-induced colour centres in ionic crystals,[3−6] but the electron spin resonance (ESR) spectra they studied are not as complicated as those obtained in our study.

Magnesium fluoride is a crystal of a rutile structure (TiO_2) in D_{4h} group, in which there are two metal ions per unit cell. Each with only a rhombic symmetry is coincident with the other under a 90° rotation about the crystal c-axis, see Fig.1.[5] Each cation is surrounded by a distorted octahedron of fluorine ions: two (axial) anions are shifted along [110] orientation; four (equatorial) anions lie in the perpendicular plane in a square with one side parallel to the c-axis. The axial anions lie slightly farther from the cation than the equatorial ions. It is convenient to use the coordinate system relative to the cation sites as follows: the z-axis is along the c-axis, the x-axis is along the [110] line joining the two axial fluorine ions and the y-axis is taken to be perpendicular to the x-axis and z-axis.

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†E-mail: houbh@bjut.edu.cn

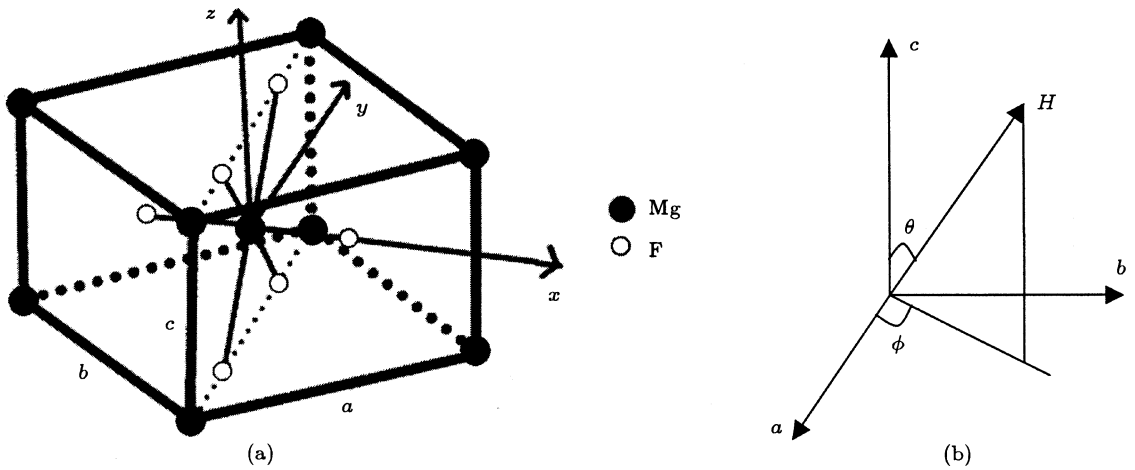


Fig.1. (a) Schematic of unit cell of MgF_2, (b) Magnetic field H relative to the c-axis and a-axis.

2. Experiment and discussion

In the experiment, sample 1 is cut from the shoulder part of the undoped MgF_2 crystal, prepared by Stockbarker–Bridgeman method with a mass 0.53978g, and sample 2 is cut from a MgF_2:Co crystal with a mass 1.63375g. The two samples have not been treated by any irradiation.

There are stable, regular and anisotropic ESR signals at room temperature from the two samples. However, there is no ESR signal from a sample cut from the part of good crystal below the shoulder part of this MgF_2 crystal. ESR experiments were carried out at room temperature using a Bruker ER2000-SRC spectrometer at X-band with an angle controller. The crystal c-axis of the sample was determined with x-ray diffraction. The ESR spectra were measured under varying θ and ϕ. Here θ and ϕ are the angles made by the magnetic field H with the c-axis and a-axis respectively as shown in Fig.1(b). Middle field was 0.3450T, and scan width was 0.2600T. Microwave frequency used was 9.7455GHz for sample 1, and 9.5910GHz for sample 2.

We found that ESR spectra from the two samples were very complicated. More than 130 line peaks have been discovered. The experimental ESR spectra of the MgF_2 and MgF_2:Co crystals are shown in Fig.2, with the magnetic field applied along the [100] or [010] orientation in the crystal. However, the ESR spectrum of the MgF_2:Co crystal was observed to be the same as that of the MgF_2 not only in Fig.2, but also in all the experimental anisotropic spectra. That is to say, the dopant Co^{2+} creates the defects that induce the same multinuclear free radicals as the dislocations do in sample 1. The magnetic field at which the ESR signals in Fig.2 are detected ranges from 0.2292T to 0.4654T and the width of this range is 0.2362T (corresponding to an energy band of 0.233eV); the most narrow peak in ESR spectra has a width ΔH is about 1.28×10^{-3}T. This width ΔH, equivalent to the energy difference of two neighbouring levels, is very small, only 1.85×10^{-7}eV or 1.46×10^{-3}cm^{-1}. This fact indicates that the ground state is highly degenerate, and splits into nearly quasi-continuous energy levels like an energy band in an applied magnetic field. Thus, we think, it may be served as a new starting point of solid laser exciter frequency modulation.

These paramagnetic solid multinuclear free radicals show good stability, and their ESR spectra are found to be anisotropic. The anisotropic ESR spectra of the MgF_2 and MgF_2:Co crystals are shown in Figs.3 and 4. And the spectrum in Fig.4(a) is seen to be the same as that in Fig.4(d). That is to say, the ESR signals from the directions [100] and [010] is equivalent in accordance with the crystal symmetry.

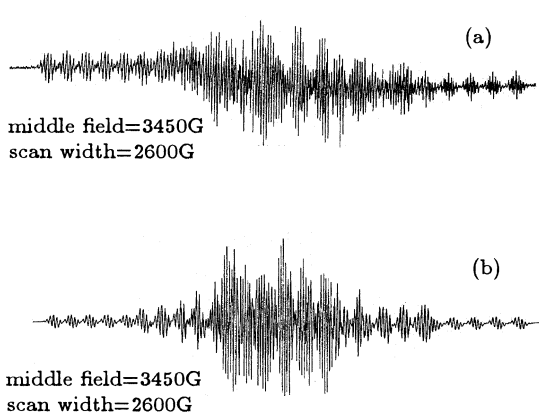


Fig.2. The ESR spectra of (a) MgF_2 crystal and (b) MgF_2:Co crystal with the field H parallel to the [100] orientation.

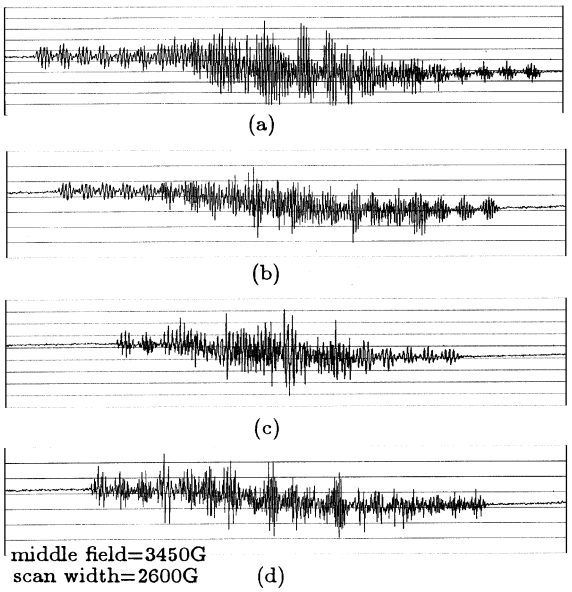


Fig.3. The anisotropic ESR spectra of MgF_2 crystal with θ=90° (a), 60° (b), 30° (c) and 0° (d).

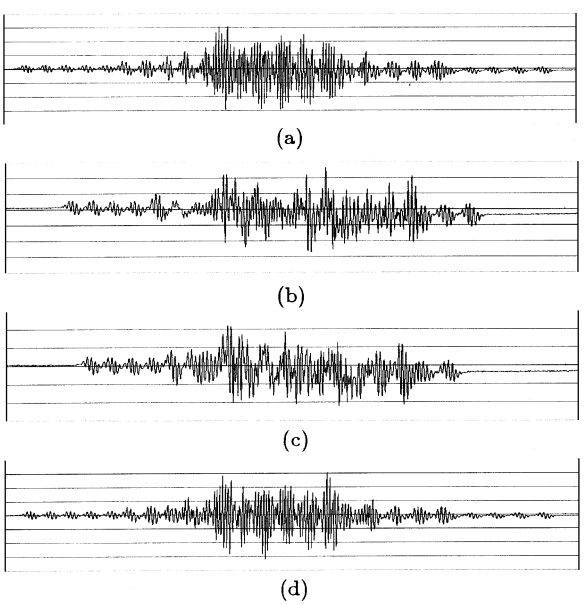


Fig.4. The anisotropic ESR spectra of MgF_2:Co crystal with θ=90°, and ϕ=0° (a), 30° (b), 60° (c) and 90° (d).

The samples were not doped with other impurity materials except Co^{2+} in sample 2 and not treated by any irradiation. There are some defects in the grown crystal of MgF_2, especially the shoulder part in which the main defect is dislocations.[7] These defects can produce some unpaired electrons, e.g. solid free radicals. Therefore, the anisotropic ESR spectra of sample 1 disclose the stable and regular defects in the shoulder part of the MgF_2 crystal.

In fact, Tinkham[8] has observed the hyperfine structured (hfs) spectrum of Co^{2+} (nuclear spin I=7/2) in Co:MgF_2, in which there can be seen 8 hfs peaks with ΔH=0.0070T only at very low temperature of 12K. In our experiment, we observed the ESR signals from MgF_2:Co single crystal, which are not from Co^{2+} at room temperature, but without the 8 hfs peaks from Co^{2+} with I=7/2.

The nuclear spin of fluorine is I=1/2, and its natural abundance is 100%. An isotope of the atom ^{24}Mg is ^{25}Mg whose nuclear spin is I=5/2 and its natural abundance is 10.13%. This may be a reason for the formation of very complicated multinuclear free radicals. Since MgF_2 is an ionic conductor, the multinuclear free radicals produced in it can move in the lattice like a fluid, so the line width ΔH is very narrow. A set of five most fundamental peaks with strength ratio of 1:4:6:4:1 with line width ΔH about 0.0016T was derived from four equivalent nuclei with I=1/2. A result was obtained from tentative simulation analysis of the ESR spectrum at θ=90°, using a model for analyzing the free radicals in liquid. The ESR signals were derived from three different types of multinuclear free radicals: R_1, R_2, R_3. And the result for the simulation spectrum is composed of a strength ratio of $R_1 : R_2 : R_3$=1:1.2:1.3, as shown in Fig.5. Figure 6 is the comparison of experimental spectrum (a) with the simulated one (b).

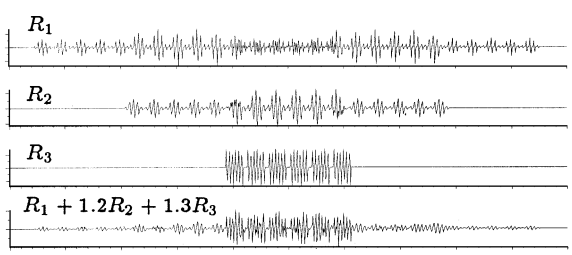


Fig.5. The simulated spectra with a strength ratio of R_1:R_2:R_3=1:1.2:1.3.

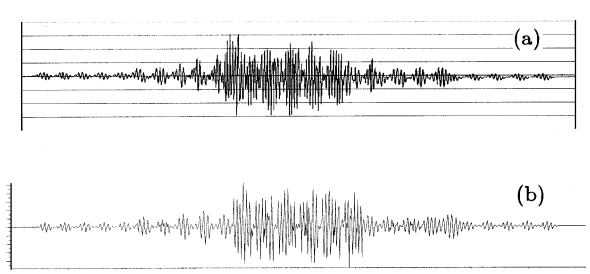


Fig.6. The experimental spectrum (a) in contrast with the simulated spectrum (b).

Hyperfine splitting constants of the multinuclear free radicals from simulation analysis are listed in Table 1.

The R_1 radical is composed of: one F^- with hyperfine splitting a_1=0.08192T, two F^- with hyperfine splitting a_2=0.03968T, one ^{25}Mg with hyperfine splitting a_3=0.0080T, and four F^- with hyperfine splitting a_4=0.0016T.

The R_2 radical is composed of: two F^- with hyperfine splitting a_1=0.04224T, one ^{25}Mg with hyperfine splitting a_2=0.00832T, and four F^- with hyperfine splitting a_4=0.0016T.

The R_3 radical is composed of two ^{25}Mg. For nuclear spin of ^{25}Mg I=5/2, the R_3 consists of six sets of equal strength peaks with hyperfine splitting a_1=0.00896T, in which each set has six equal strength peaks with hyperfine splitting a_2=0.00128T.

Table 1. Hyperfine splitting constants of the multinuclear free radicals from simulation analysis in MgF_2 crystal.

Multinuclear free radicals	$^{25}Mg^{2+}$	Number of $^{25}Mg^{2+}$ ions	F^-	Number of F^- ions
R_1	a_3=0.0080T	1	a_1=0.8192T	1
			a_2= 0.03968T	2
			a_4=0.00160T,	4
R_2	a_2=0.00832T	1	a_1=0.04224T	2
			a_4=0.00160T	4
R_3	a_1= 0.00896T	1		
	a_2= 0.00128T	1		

3. Conclusion

Because the nuclear spin of atom F is I=1/2 and ^{25}Mg is I=5/2, there exist very complicated and stable paramagnetic solid free radicals in MgF_2 and MgF_2:Co crystals.

The same anisotropic ESR spectra has been observed both in MgF_2 and in MgF_2:Co crystals. Thus we can conclude that the dopant Co^{2+} produces defects that induce the same multinuclear radicals, as the dislocations do in the pure MgF_2 crystal.

We have carried out the tentative simulation analysis of the ESR spectrum at θ=90° (i.e. $H\perp c$-axis), using a method for analysing a liquid model. The signals were derived from three different types of multinuclear free radicals: R_1, R_2 and R_3 with strength ratio R_1:R_2:R_3=1:1.2:1.3.

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