

Paramagnetic centers of Gd^{3+} in chromium doped Y_2SiO_5

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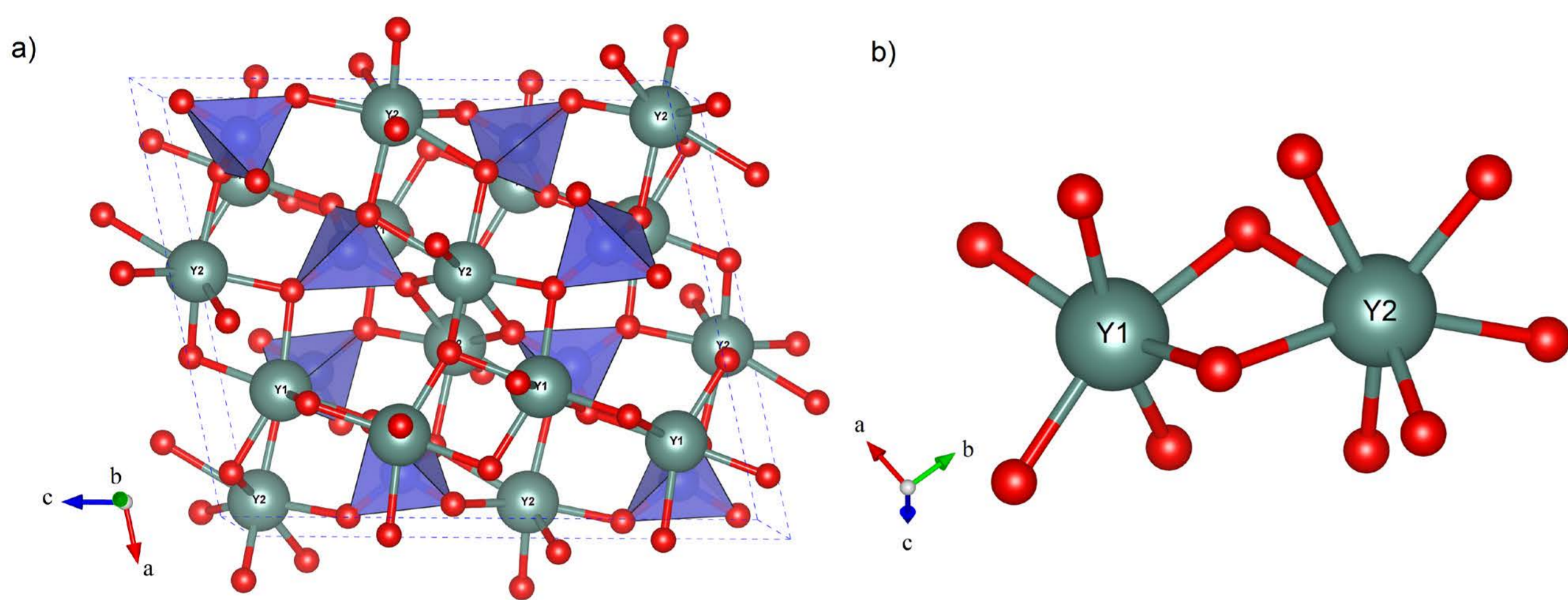
$Cr:Y_2SiO_5$ (YSO) is considered as an active medium for solid-state lasers operating in the near-infrared spectral region [1,2] and as saturable absorbers for Q-switch lasers [3].

In [4], we have studied a Y_2SiO_5 crystal doped with the odd isotope ^{53}Cr ($I = 3/2$). We have detected and described the EPR spectra of two Cr^{3+} centers located in two non-equivalent sites of Y^{3+} ions and having intensities that differ by two orders of magnitude. Besides that, we have also distinguished a lot of weak (in comparison with intense Cr^{3+} spectra) narrow signals in the EPR spectra of $Cr:YSO$ and $^{53}Cr:YSO$ crystals at room temperature, which cannot be assigned to Cr^{3+} centers. It was suggested that these signals correspond to the uncontrolled Gd^{3+} impurity ions.

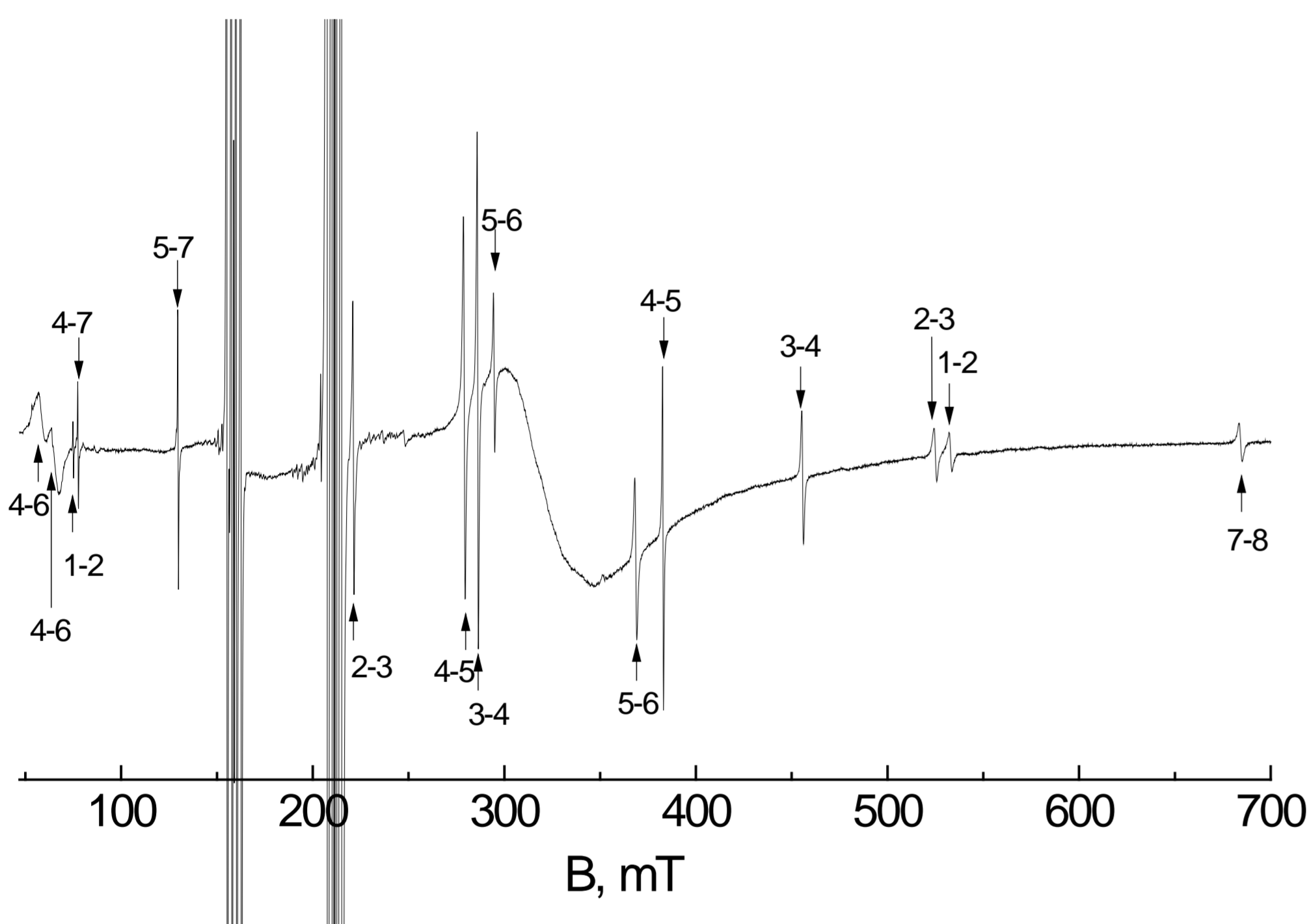
Samples: $^{53}Cr:Y_2SiO_5$ single crystal for studies was grown by Czochralski method using the $^{53}Cr_2O_3$ chemical having $^{53}Cr(97,5\%)$ and $^{52}Cr(2,5\%)$ isotopes content. For the determination of the actual concentration of chromium and uncontrolled impurities, the part of the grown crystal was analyzed by spark mass-spectrometry at JMS-01-BM2 (JEOL, Japan) [4]. The paramagnetic uncontrolled impurities of iron (40 ppm), nickel (2 ppm), and copper (3 ppm) were found in the crystal. The concentration of the other uncontrolled paramagnetic impurities were below the method sensitivity.

Equipment: X-band EPR spectrometer Bruker EMX Plus in fields up to 1450 mT (UrFU, Ekaterinburg);

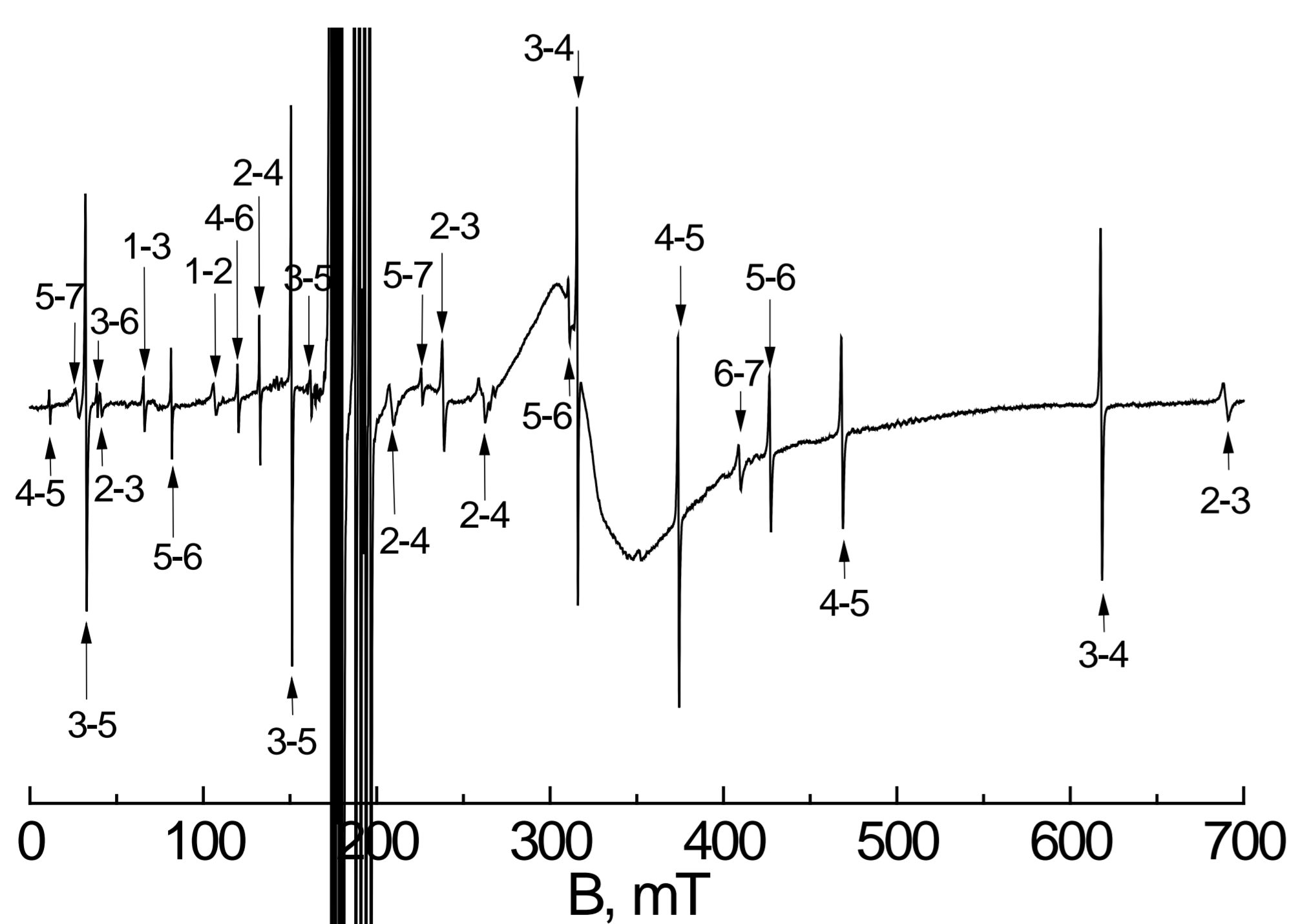
Structure: The YSO crystal has a monoclinic structure with the space group $C2/c$. The lattice parameters in the unit cell $I12/a1$ are $a = 1.041$ nm, $b = 0.672$ nm, $c = 1.249$ nm, $\beta = 102.65$ [5,6]. Y and Si sites have the local point symmetry 1 ($C1$). Si is surrounded by a distorted oxygen tetrahedron, Y ions occupy two non-equivalent sites with the coordination numbers 6 and 7. Each site is replicated by the unit cell symmetry elements (inversion center and $C_2||b$ axis) up to 4. Since the paramagnetic centers related by the inversion operation are indistinguishable in magnetic resonance, only two magnetically nonequivalent spectra can be observed when a paramagnetic ion is located in any site. These EPR spectra transform into each other when rotating the crystal by 180 degrees around the crystallographic b -axis. If the external magnetic field direction is in the ac -plane or at $B||b$ (B is the magnetic field induction), these two spectra become equivalent.



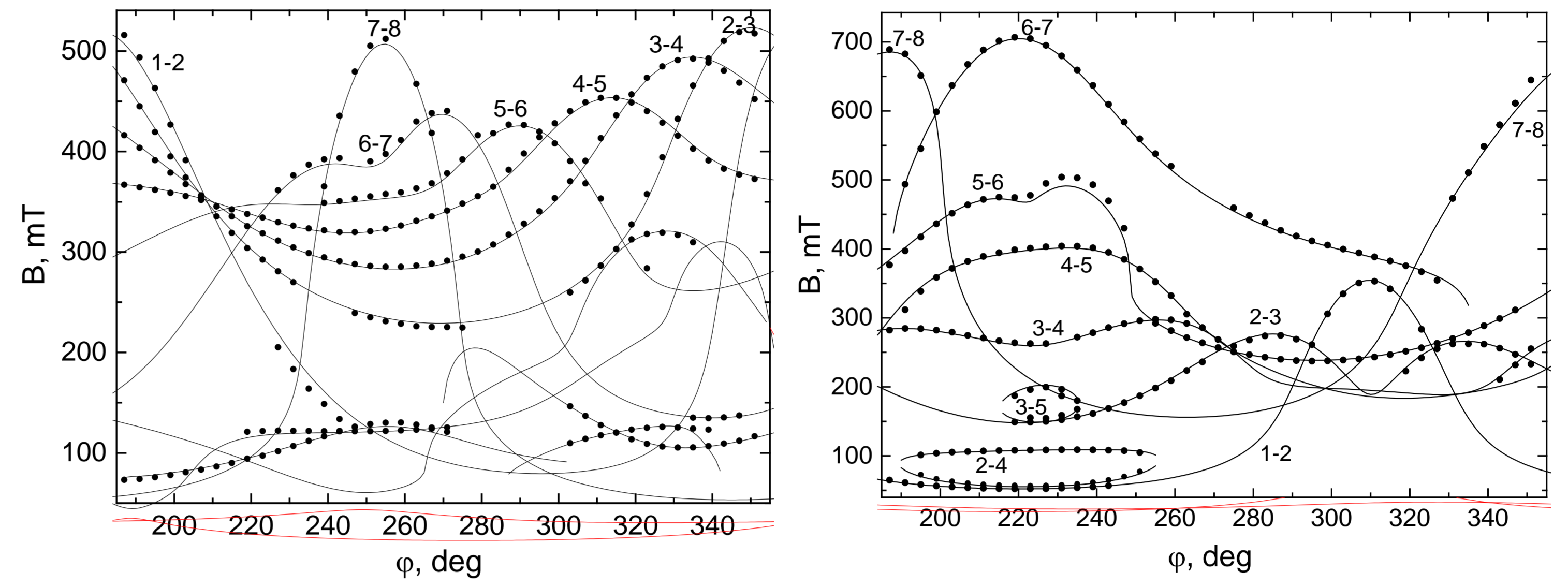
(left) unit cell of YSO (I12/a1) and (right) two structurally non-equivalent yttrium sites surrounded by 6 (Y1) and 7 (Y2) oxygen ions.



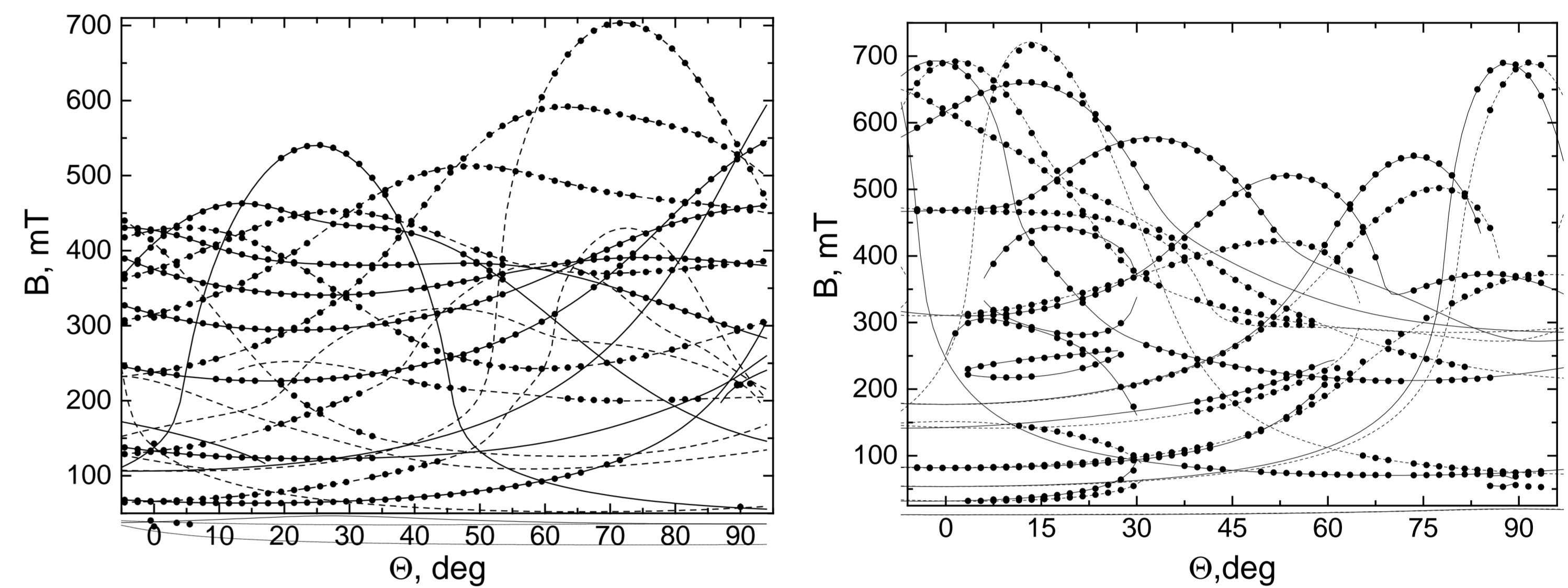
EPR spectrum (the first derivative of the absorption spectrum) of chromium doped YSO crystal at $\theta = 90$ deg, $\phi = 180$ deg at room temperature. The operating frequency of the spectrometer is 9869 MHz. Two intense off-scale signals correspond to the transitions of the $^{53}Cr^{3+}$ center. The signals of the Gd1 centers are indicated by the upper arrows denoting the numbers of energy levels, Gd2 are marked with the lower ones. The wide signal in the field 320 mT is caused by the sample holder



EPR spectrum of $Cr:YSO$ at $B||b$, room temperature, 9869 MHz



Angular dependencies of the positions of the Gd1 (left) and Gd2 (right) centers transitions in Y_2SiO_5 when the magnetic field rotates in the ac -plane (xy) at room temperature at a frequency of 9448 MHz; curves are calculations with parameters from table



Orientational behavior of the positions of the transitions for two magnetically nonequivalent Gd1 (left) and Gd2 (right) centers when the magnetic field rotates in the $z(-x)$ plane (perpendicular to ac -plane). The operating frequency is 9869 MHz. Solid and dashed lines are calculated with the parameters given in table.

Spin Hamiltonian with $S = 7/2$ describing all observed angular dependences:

$$H_{sp} = \beta (\mathbf{BgS}) + \frac{1}{3} \sum_m (b_2^m O_2^m + c_2^m \Omega_2^m) + \frac{1}{60} \sum_m (b_4^m O_4^m + c_4^m \Omega_4^m) + \frac{1}{1260} \sum_m (b_6^m O_6^m + c_6^m \Omega_6^m)$$

g is g -tensor, β is the Bohr magneton, O_n^m and Ω_n^m are the Stevens spin operators, b_n^m and c_n^m are the fine structure parameters [7].

Fine structure parameters for two Gd^{3+} triclinic centers in YSO at room temperature in the xyz ($z||b$, x and y are in the ac -plane, the angle between the x and a^* axes is about 6.5 degrees, a^* is the projection of the a -axis onto the plane orthogonal to the c -axis) coordinate system in MHz. Double signs of the parameters correspond to two magnetically nonequivalent centers, b_n^m and c_n^m are SH parameters, F is root-mean-square deviation of the calculated signals positions from the experimental ones. N is the number of the experimental resonant field used in the optimization procedure. The fitting was carried out under the assumption of an isotropic g -factor, which components are equal to 1.99

Second-rank fine structure parameters (in MHz) and the Euler angles (in degrees) of two Gd^{3+} centers in YSO in the local coordinate system. The sets of the Euler angles correspond to two magnetically nonequivalent centers. (right table)

Parameters	Gd1	Gd2
b_2^0	1839	3029
b_2^2	1320	1939
$\alpha 1, \text{deg}$	345.95	266.23
$\beta 1, \text{deg}$	65.98	18.87
$\gamma 1, \text{deg}$	51.59	46.14
$\alpha 2, \text{deg}$	165.95	86.23
$\beta 2, \text{deg}$	65.98	18.87
$\gamma 2, \text{deg}$	51.59	46.14

Parameters	Gd1, MHz	Gd2, MHz
b_2^0	-588	2550
b_2^1	± 3628	∓ 1619
b_2^2	2122	-639
c_2^1	∓ 3328	∓ 5514
c_2^2	-540	-1765
b_4^0	24	-3
b_4^1	∓ 55	± 33
b_4^2	43	-54
b_4^3	± 21	± 80
b_4^4	-5	-14
c_4^1	∓ 40	∓ 45
c_4^2	22	27
c_4^3	± 560	∓ 14
c_4^4	62	12
$F(N)$	19(500)	21(276)

The measurements and analysis of the orientation behavior of weak EPR signals observed in $Y_2SiO_5:Cr$ crystal besides the previously studied in [4] signals of Cr centers have been performed. These weak signals were shown to be due to the transitions of two different Gd^{3+} ($S = 7/2$) centers, which are present in the crystal as an uncontrolled impurity and located in the triclinic yttrium site Y1 and Y2. The parameters of the spin Hamiltonian of these centers were determined.

References

- J. Koetke, S. Kück, K. Petermann, G. Huber, G. Cerullo, M. Danailov, V. Magni, L.F. Qian and O. Svelto, Opt. Commun. 101, 195 (1993)
- B. H. T. Chai, Y. Shimony, C. Deka, X. X. Zhang, E. Munin, M. Bass, Laser Performance of $Cr^{4+}:Y_2SiO_5$ at Liquid Nitrogen Temperature, Vol. 13 of OSA Proc. On Advanced Solid-State Lasers, paper CL7, 1992.
- C.-K. Chang, J. Chang, Y.-K. Kuo, Optical performance of $Cr:YSO$ Q-switched $Cr:LiCAF$ and $Cr:LiSAF$ lasers, in: High-Power Lasers and Applications II, Vol. 4914 of Proc. SPIE, 2002
- V.A. Vazhenin, A.P. Potapov, K.A. Subbotin, D. Lis, M.Yu. Artyomov, V. Sanina, E.V. Chernova, A.V. Fokin, Opt. Mat. 117, 111107 (2021)
- B. Maksimov, L. Demyanets, V. Iliukhin, L. Kharitonov, N. Belov, Crystal structures and comparative crystal chemistry of synthetic Sc and Y germanates (silicates), Sov. Phys. Cryst 21 (1976) 539–542.
- N. Leonyuk, E. Belokoneva, G. Bocelli, L. Righi, E. Shvanskii, R. Henrykxson, N. Kulman, D. Kozhbakhteva, Crystal Growth and Structural Refinements of the Y_2SiO_5 , $Y_2Si_2O_7$ and $LaBSiO_5$ Single Crystals, Appl. Magn. Reson. 34 (1999) 1175–1185
- S. A. Altshuler, B. M. Kozlyev, Electron paramagnetic resonance in compounds of transition elements, John Wiley&Sons Inc, NY, 1974