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EPR OF THE COPPER CENTERS IN DOUBLE LEAD MOLYBDATE CRYSTAL

For the first time EPR spectra are studied in double lead molybdate crystal Pb_2MoO_5 , doped with Cu ions. It is shown that in Pb_2MoO_5 structure copper ions are in $^2D_{5/2}$ ($S=1/2$, $I=3/2$) state. Orientational diagrams of Cu^{2+} EPR spectra are measured at magnetic field rotating with respect to the crystal axes. Angular dependences of the spectra are described on the basis of a spin-Hamiltonian including electronic Zeeman and electron-nuclear hyperfine interactions. On the basis of the data obtained, the components and axes directions of g-factor and hyperfine interactions tensor A are calculated. Anisotropy and multiplicity of the EPR spectra testify that in Pb_2MoO_5 lattice Cu ions occupy monoclinic positions of C_5 symmetry. Positional symmetry and comparison of the ionic radiuses and charges of impurity and cations in Pb_2MoO_5 formulae unit, allow to assume that copper ions substitute lead host ions in one of two structurally nonequivalent sites $Pb1$ or $Pb2$. Additional splitting of the hyperfine lines owing to the interaction of copper electron spin with nuclei of surrounding ^{207}Pb isotope is observed. Anisotropy of superhyperfine interaction with ligands nuclei shows that in Pb_2MoO_5 structure substitution of copper ions with lead in the first position $Cu \rightarrow Pb1$ is more probable.

Keywords: acousto-optic materials, Pb_2MoO_5 crystal, EPR spectroscopy.

Уперше вивчені ЕПР спектри кристалів подвійного молібдату свинцю Pb_2MoO_5 , активованих іонами Cu . Показано, що в структуру Pb_2MoO_5 парамагнітні іони міді входять у стані $^2D_{5/2}$ ($S=1/2$, $I=3/2$). Проведено вимірювання орієнтаційних залежностей ЕПР спектрів Cu^{2+} при обертанні магнітного поля відносно осей кристала. Кутіві залежності спектрів описано на основі спінового гамільтоніана, що включає електронну зєманівську й електрон-ядерну надтонку взаємодії. На основі отриманих результатів проведено розрахунок компонент і напрямку головних осей g-фактора та тензора A надтонкої взаємодії. Анізотропія і кратність ЕПР спектрів свідчать, що в решітці Pb_2MoO_5 іони Cu розташовуються в позиціях моноклінної групи C_5 . Симетрія спектрів, а також співставлення іонних радіусів і зарядів домішкових центрів і катіонів, що входять до формульної одиниці Pb_2MoO_5 , дозволяють припустити заміщення іонами міді іонів свинцю в одному з двох структурно-нееквівалентних вузлів $Pb1$ або $Pb2$. Виявлено додаткове розщеплення надтонких ліній унаслідок взаємодії електронного спіну міді з навколишніми ядрами ізотопу ^{207}Pb . Анізотропія супернадтонкої взаємодії показує, що більш вірогідним є заміщення домішковими іонами міді іонів свинцю в першій позиції $Cu \rightarrow Pb1$.

Ключові слова: акустооптичні матеріали, кристали Pb_2MoO_5 , ЕПР спектроскопія.

Впервые изучены ЭПР спектры кристаллов двойного молибдата свинца Pb_2MoO_5 , активированных ионами Cu . Показано, что в структуру Pb_2MoO_5 парамагнитные ионы меди входят в состоянии $^2D_{5/2}$ ($S=1/2$, $I=3/2$). Проведены измерения ориентационных зависимостей ЭПР спектров Cu^{2+} при вращении магнитного поля относительно осей кристалла. Угловые зависимости спектров описаны на основании спинового гамильтонiana, включающего электронное зеемановское и электрон-ядерное сверхтонкое взаимодействия. На основе полученных результатов проведен расчет компонент и направления главных осей g-фактора и тензора A сверхтонкого взаимодействия. Анизотропия и кратность ЭПР спектров свидетельствуют, что в решетке Pb_2MoO_5 ионы Cu располагаются в позициях моноклинной группы C_5 . Симметрия спектров, а также сопоставление ионных радиусов и зарядов примесных центров и катионов в формульной единице Pb_2MoO_5 , позволяют предположить замещение ионами меди ионов свинца в одном из двух структурно-неэквивалентных узлов $Pb1$ или $Pb2$. Обнаружено дополнительное расщепление сверхтонких линий вследствие взаимодействия электронного спина меди с близлежащими ядрами изотопа ^{207}Pb . Анизотропия суперсверхтонкого взаимодействия с ядрами лигандов показывает, что в структуре Pb_2MoO_5 более вероятным является замещение примесными ионами меди ионов свинца в первой позиции $Cu \rightarrow Pb1$.

Ключевые слова: акустооптические материалы, кристаллы Pb_2MoO_5 , ЭПР спектроскопия.

1. Introduction

Single crystals of $PbO-MoO_3$ family are considered as promising to be used in acousto-optic devices. In addition to classic acousto-optic $PbMoO_4$ with scheelite structure, double lead molybdate crystal Pb_2MoO_5 attracts attention owing to strong anisotropy of acousto-optic parameters [1-4]. According to [5], Pb_2MoO_5 structure of lanarkite type belongs to space symmetry group C_{2h}^3 , and the unit cell contains four formulae units $Z=4$ and has parameters: $a = 14.225 \text{ \AA}$, $b = 5.789 \text{ \AA}$, $c = 7.336 \text{ \AA}$, $\beta=114^\circ$. Pb_2MoO_5 crystal lattice is characterized by cleavage plane $(\bar{2}01)$ in accordance with axes setting $[010]||\mathbf{b}||C_2$.

Yellow colour and photochromic effect hamper practical use of lead molybdate crystals in acousto-optic devices. It is expected that doping with small amount of certain impurities could decrease concentration of the defects responsible for worsening of optical quality. Choice of the dopants is based on knowledge of a microscopic structure of impurity centers in the structure. In the paper we present the first study of EPR spectra anisotropy in double lead molybdate crystal Pb_2MoO_5 doped with copper ions.

2. Experimental results

Pb_2MoO_5 single crystals were grown from the melts by Czochralski method with addition of CuO (0.03 % wt.) to stoichiometric reagents [6]. Samples for EPR experiment were cut off as parallelepipeds with main facets parallel to (010) and $(\bar{2}01)$ planes. EPR spectra were measured by using the conventional radiospectrometer Radiopan 25/47 operating in X frequency band (9 GHz).

EPR spectrum of $Pb_2MoO_5:Cu$ crystal is presented in the insert to Fig. 1. The quartet of well resolved lines, resulting from hyperfine (HF) interaction of electron spin $S=1/2$ with nuclear spin $I=3/2$, evidences to $^2D_{5/2}$ state of bivalent Cu^{2+} ions. For the components of HF quartet the doublets from copper isotopes ^{63}Cu ($I=3/2$) and ^{65}Cu ($I=3/2$) [7] are well distinguished. Moreover, there is an additional splitting with the components intensity decreasing from the centre to both sides of the lines groups. Such contour of lines is typical for superhyperfine (SHF) interaction of the active center electron spin with the nuclear spin moments of surrounding atoms [7, 8].

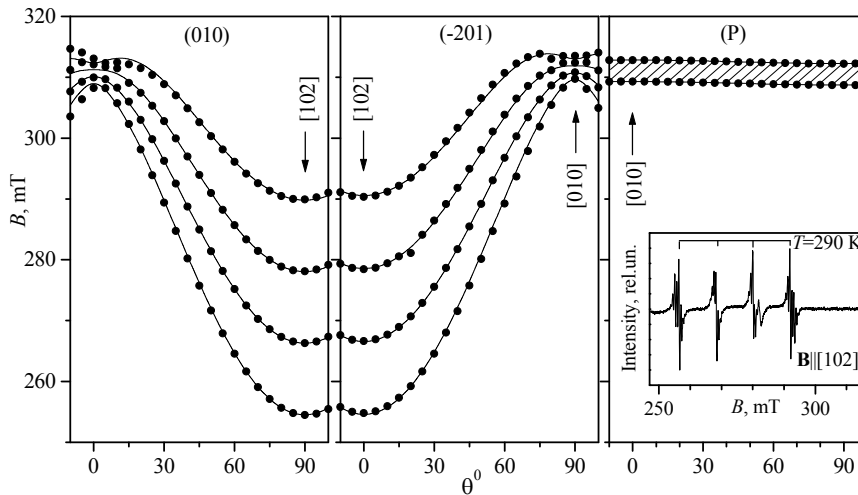


Fig. 1. Angular dependences of EPR line positions in $Pb_2MoO_5:Cu$ at magnetic field B rotating in (010) , $(\bar{2}01)$ and (P) planes. The experimental data are given by circles for ^{63}Cu isotope. Solid lines are calcu-

lated on the basis of SH (1) and parameters given in Tab.1. In the insert: EPR spectrum of $Pb_2MoO_5:Cu$ crystal at $B||[102]$.

In order to determine the positional symmetry of Cu centers, we measured angular dependences of EPR line positions at magnetic field \mathbf{B} rotating in (010), $(\bar{2}01)$ and (P) planes, the latter of which is perpendicular to (010) and $(\bar{2}01)$. So, in the laboratory coordinates system used, axis 3 $||[010]$, axis 2 $||[102]$ and axis 1 is perpendicular to 2 and 3. Angular dependences of EPR hyperfine line positions are plotted in Fig.1 for ^{63}Cu isotope. It can be seen that only one spectrum is observed in experiment, i.e. magnetic multiplicity of the spectrum is $k_m=1$ [9]. It means that Cu centers occupy structurally equivalent positions of a single type. EPR line positions and hyperfine line splitting demonstrate axial symmetry with the main axis parallel to $[102]$ direction. In (P) plane, which is perpendicular to axial direction $[102]$, splitting between outside components of the spectrum is about ~ 3.5 mT. Since the individual line width is about 0.3 mT, determination of line positions of the overlapped components and identification of certain electron transitions are difficult. Therefore for (P) plane in Fig.1 the positions are plotted only for outside lines.

The angular dependences of Cu^{2+} EPR line positions are described by the spin-Hamiltonian (SH)

$$\mathcal{H} = \beta \mathbf{B} \mathbf{g} \hat{\mathbf{S}} + \hat{\mathbf{S}} \mathbf{A} \hat{\mathbf{I}}, \quad (1)$$

which includes electron Zeeman and HF interactions [8, 10]. Description of Cu^{2+} EPR spectra on the basis of SH (1) makes it possible to determine the main values and directions of axes of \mathbf{g} -factor and HF interaction tensor \mathbf{A} . The values, presented in tab.1, show that \mathbf{g} -factor and \mathbf{A} tensor are nearly axial: $g_{||} = 2.349$, $g_{\perp} (\approx g_x \approx g_y) = 2.057$, $A_{||} = 130.3 \cdot 10^{-4} \text{ cm}^{-1}$, $A_{\perp} (\approx A_x \approx A_y) = 17 \cdot 10^{-4} \text{ cm}^{-1}$. It should be noted that the components in Tab.1 are obtained in assumption that the main axes of \mathbf{g} -factor and \mathbf{A} tensor coincide. The angular dependences of EPR line positions calculated on the basis of SH (1) and parameters in Tab.1 are plotted by lines in Fig.1. Comparison of the experimental and calculated data demonstrates that anisotropy of HF structure of Cu EPR spectra is described within the first order of the perturbation theory with good accuracy.

Table 1
Parameters of SH (1) and SHF tensor as well as directions of magnetic axes calculated from EPR spectra in $Pb_2MoO_5:Cu^{2+}$ (T=290 K, values of \mathbf{g} -factor and HF tensor are given for ^{63}Cu isotope)

\mathbf{g} -factor	HF tensor \mathbf{A} (10^{-4} cm^{-1})	SHF tensor \mathbf{A}^L (10^{-4} cm^{-1})
$g_x = 2.058$ (1); $g_y = 2.055$ (1); $g_z = 2.349$ (1); $\mathbf{Z} [102], \mathbf{Y} [010]$	$A_x = 11$ (2); $A_y = 22$ (5); $A_z = 130.3$ (0.5)	$(A^L)_x = 3.7$ (0.5); $(A^L)_y = 16.3$ (0.5); $(A^L)_z = 10.4$ (0.5); $\mathbf{Z}^L [010], \angle \mathbf{Y}^L, [102] = 4$ 0.5 $^\circ$

3. Discussion

In accordance with [5], in Pb_2MoO_5 unit cell Mo atoms and four oxygen atoms $O1-O4$ form MoO_4 tetrahedra. Lead atoms occupy two structurally nonequivalent sites $Pb1$ and $Pb2$. Oxygen atoms $O5$, which are located apart from MoO_4 complexes, form the rows oriented along \mathbf{b} axis and are coordinated with four Pb atoms in the corners of slightly distorted tetrahedra.

According to [9] magnetic multiplicity of EPR spectrum $k_m = 1$ indicates that in Pb_2MoO_5 structure with C_{2h}^3 space symmetry group, Cu centers occupy positions with point symmetry of C_{2h} , C_2 or C_s groups. The data in [5] show that in Pb_2MoO_5 unit cell all cations sites Mo , $Pb1$ and $Pb2$ correspond to monoclinic symmetry group C_s . Taking in

mind the coincidence of ionic charges and ratio of ionic radiuses, it is reasonable to assume that impurity centers Cu^{2+} ($r_{Cu^{2+}} = 0.72 \text{ \AA}$) substitute Pb^{2+} host ions ($r_{Pb^{2+}} = 1.20 \text{ \AA}$). Since one spectrum is observed in experiment ($k_m = 1$, Fig.1), it means that copper centers substitute lead ions only in one of two structurally nonequivalent positions. According to [5], the nearest surroundings of $Pb1$ and $Pb2$ sites are formed by four oxygen atoms $O3, O4, O5'$ and $O5''$. $O3-O5''$ atoms are located in the corners of distorted squares, plane of which is perpendicular to (010) and lies away from lead atom sites. Distances from $Pb1,2$ sites to the nearest neighbours are: $d(Pb1-O3, O4) = 2.30 \text{ \AA}$, $d(Pb1-O5', O5'') = 2.39 \text{ \AA}$, $d(Pb2-O3, O4) = 2.46 \text{ \AA}$, $d(Pb2-O5', O5'') = 2.37 \text{ \AA}$. The lines connecting $Pb1$ and $Pb2$ sites with the "centre of masses" of oxygen squares $O3-O5''$ lie in (010) plane and deviate from [102] direction on 3.5° and 3.8° , correspondingly. These lines practically coincide with a perpendicular to the plane of $O3-O5''$ squares, so that disorientation is only 0.1° and 0.4° for $Pb1$ and $Pb2$ sites correspondingly. Thus, the main axis $Z \parallel [102]$ of g -factor is rather close to the line connecting $Pb1$ and $Pb2$ sites with the "centre of masses" of oxygen group $O3-O5''$ in the nearest surroundings of lead atoms. Such result supports the assumption of $Cu \rightarrow Pb$ substitution. At the same time, the nearest neighborhood for both $Pb1$ and $Pb2$ sites is formed by the same groups of four $O3, O4, O5'$ and $O5''$ oxygen atoms. Besides that, the direction of main magnetic axis Z should be expected to be close to [102] for both assumed versions of the doping ions localization $Cu \rightarrow Pb1$ or $Cu \rightarrow Pb2$. Hence, examination of g -factor and A tensor main axes directions does not allow to decide in what site ($Pb1$ or $Pb2$) the copper centers are localized.

To answer this question, let us consider additional splitting of EPR lines (the insert to Fig.1) resulting from SHF interaction of Cu electron spin with the spins of ligand nuclei. Corresponding SHF structure of EPR spectrum can be described SH (1) by addition of a sum $\mathcal{H}_{SHF} = \sum_i \hat{S} A^{Li} \hat{I}^{Li}$, which takes into account interaction of paramagnetic center

electron spin \hat{S} with nuclear spins \hat{I}^{Li} of surrounding atoms. As it was shown in [8], EPR line contour can be attributed to SHF interaction of Cu electron spin with nuclei of isotope ^{207}Pb ($I = 1/2$, $c = 22.6 \%$) [7]. Angular dependences of SHF line splitting, measured as distance between ^{65}Cu line and the nearest low field SHF component, are plotted for (010) and $(\bar{2}01)$ planes in Fig. 2.

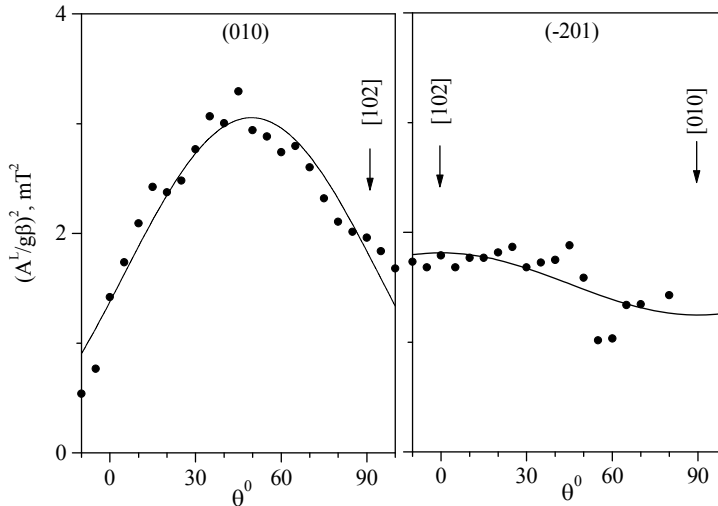


Fig. 2. Angular dependences of SHF splitting for low field component of HF line $|m_l| = 3/2$ in EPR spectrum of $Pb_2MoO_3:Cu$. Circles – experimental data, lines are calculated by using of SHF tensor A^L pa-

rameters given in Tab.1.

On the basis of the angular dependences in Fig. 2, the components and axes directions of SHF tensor \mathbf{A}^L are determined and presented in Tab. 1. It can be seen that \mathbf{A}^L tensor axes \mathbf{X}^L , \mathbf{Y}^L , \mathbf{Z}^L do not coincide with direction of the \mathbf{g} -factor axes \mathbf{X} , \mathbf{Y} , \mathbf{Z} (Tab.1). Axis \mathbf{Y}^L , along which SHF splitting is maximal, lies in (010) plane and deviates by 40.5° from [102] direction. According to the structural data [5], the line connecting $Pb1$ site with the nearest $Pb1'$ atom ($d = 3.80 \text{ \AA}$) also lies in (010) and makes an angle 37.0° with [102] direction. The lines connecting $Pb2$ with the nearest $Pb2'$ ($d = 3.68 \text{ \AA}$) and $Pb2''$ ($d = 3.76 \text{ \AA}$) lie in (010) plane and deviate from [102] by 114.8° and 46.3° correspondingly. Thus comparison of orientation of \mathbf{A}^L tensor axes (tab.1) with $Pb1,2$ surroundings gives the evidence in favour of paramagnetic centers substitution with lead atoms in the first position $Cu \rightarrow Pb1$.

3. Conclusions

A state of copper impurity centers in Pb_2MoO_5 crystal is identified as $Cu^{2+} (^2D_{5/2})$ on the basis of studying EPR spectra. Measurements of EPR spectra angular dependences make it possible to determine positional symmetry C_S of Cu^{2+} centers, and to calculate the main values and magnetic axis directions of \mathbf{g} - factor and tensors of HF and SHF interactions. The obtained data allow to assume that in Pb_2MoO_5 lattice impurity copper ions substitute with lead host ions in the first structurally nonequivalent position $Cu \rightarrow Pb1$. In order to verify this assumption it is planned to study SHF line contour for various orientations of magnetic field \mathbf{B} with respect to the crystal axes in more details.

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