ESR study of ScF$_3$ crystals and the crystals of ScF$_3$ based solid solutions

V.N.Voronov, E.A.Petrakovskaya, A.A.Alexandrovich

L.Kirensky Institute of Physics, Russian Academy of Sciences, Siberian Branch, 660036 Krasnoyarsk, Russia

The ScF$_3$ crystals belong to the perovskite family but, in contrast to other fluorides of that class, exhibit cubic symmetry. The ESR study of those crystals has shown that the spectra of impurity-free crystals as well as those containing Ga, Mg, Sb, Al, Fe include lines that can be ascribed to the local defects of the crystal structure. Those defects have been evidenced most reliably in ScF$_3$ single crystals with Ga and Fe impurities as well in the impurity-free ones. In all the cases, the spectra show the presence of defects related to six fluorine atoms. This fact is most pronounced in the crystals with Fe impurity. A local distortion of cubic symmetry has been revealed unambiguously at the defect center sites. The letter seem to be fluorine octahedrons.

Кристаллы ScF$_3$ относятся к семейству перовскитоподобных, но, в отличие от других фторидов этого класса, обладают кубической симметрией. Исследование кристаллов методом ЭПР показало, что в спектрах беспримесного кристалла, а также кристаллов с примесями Ga, Mg, Sb, Al, Fe есть линии, которые можно приписать к локальным дефектам кристаллической структуры. Наиболее надежно эти дефекты идентифицированы в монокристаллических образцах ScF$_3$ с примесями Ga и Fe и в отсутствие примесей. Во всех случаях наблюдаемые спектры показали наличие дефектов, связанных с шестью ионам фтора. Наиболее четко это проявилось в кристаллах с примесью Fe. Получено однозначное свидетельство наличия локального искажения кубической симметрии в местах расположения дефектных центров. Есть версия, что это октаэдры фтора.

1. Introduction

Fluorides of trivalent metals belong to the family of perovskite compounds with the general formula ABX_3, where the position of one cation is vacant. Within the framework of ab initio simulations, the lattice dynamics in the cubic phase of the AlF_3, GaF_3 or FeF_3 crystals isomorphic to ScF_3 was calculated [1], Fig. 1, and it was shown that there are no imaginary frequencies in the vibrational spectra of these crystals. But in the Raman spectrum of ScF_3 crystal, there is a weakly dispersive line (between the points R and M in the Brillouin zone) at an anomalously low frequency. In this vibration branch, there is a triply degenerated mode $R5$ at point R and undegenerated

modes in the direction $R \to M$ (including the point M) corresponding to the vibrations where the fluorine ions are displaced. The structural phase transitions in most perovskite halides are stimulated by the condensation of modes in this vibration branch. In a pure ScF_3 crystal, no structural transformations are detected within the range from room temperature to 4 K [1]. Also, the phase diagram sensitivity to the structural defects and impurities was assumed. In this study, we investigated the compound ScF_3 with various impurities, which may induce the internal pressure in the crystals. The change in the local symmetry due to the introduction of the impurities in the crystal has been verified by the ESR.

2. Experimental

Due to high melting points of both pure ScF_3 (1550°C), and ScF_3 with different impurities, the crystals were grown from the melt-solution. The molten sodium fluoride was used as the solvent. The mixture of powdered reagents containing 40 mol. % of scandium fluoride was heated to melting in a platinum boat. The crystallization was carried in argon atmosphere (the axial temperature gradient of 10–20 deg/cm, the speed 3.5 mm/h). The pure blocks were sealed in platinum ampoules with 0.2 mm thick walls. During 14 days, the ampoule were lowered into a vertical tube furnace with the axial temperature gradient of 20 deg/cm at a speed of 0.8 mm/h from 1400 K to 400 K. The crystals containing the AlF_3, SbF_3, GaF_3, MgF_2, FeF_3 (3–5 %) impurities were prepared in a similar manner. After cooling, the obtained samples had cylindrical shape without visible defects or inclusions in the bottom transparent part of 10 mm diameter and up to 7 mm height.

The X-ray phase analysis at room temperature has shown that all the obtained crystals, including those with the impurities, had the structure of the cubic ScF_3, with the unit cell parameters $a_0 = 4.01$ Å within the experimental error. All the crystals show optical isotropy in polarized light (that is typical for cubic symmetry) within the range from room temperature to 120 K. To clarify the states of the ions introduced into the crystal, the local changes in the crystal structure due to such introductions were investigated by ESR using a spectrometer Elexys E580 (Bruker) in the temperature range (293–77) K and the derivatives from the absorption lines were recorded.

A characteristic feature of the ESR spectra of the polycrystalline samples ScF_3 with different impurities is the presence of a narrow line with $g = 1.998$. In the samples with Mg, this line is weak and becomes visible only at 77 K. Another characteristic feature of the spectra is the presence of broad lines with the g-factor 2.25–2.73 for colored powders of polycrystalline samples. The temperature behavior of these lines (a decrease in intensity at 77 K and a shift to lower fields that is not typical of paramagnetic centers in crystals) allows one to relate them to the superparamagnetic particles [2] which are not included in the crystal structure of ScF_3. The appearance of
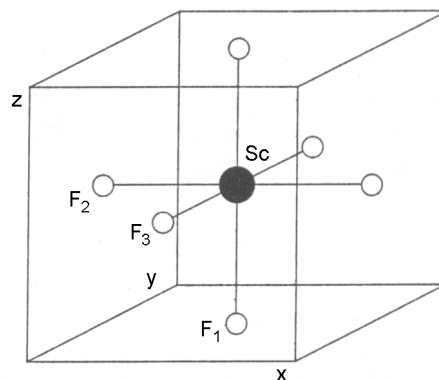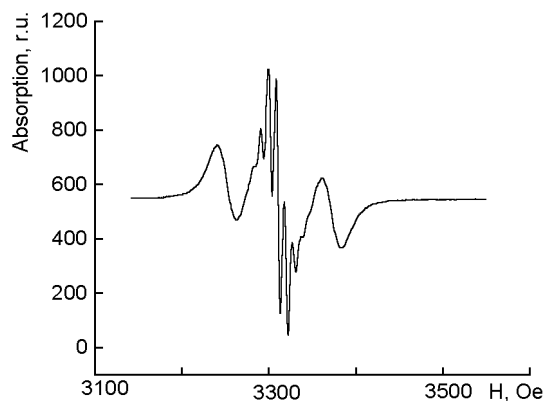

Fig. 1. The cubic unit cell of ScF_3.

Fig. 2. ESR spectrum of the Ga doped ScF_3 crystal at 77 K.

these lines is connected most likely with the impurities of oxidized iron. In samples with an admixture of Ga, Al and Sb (white), these impurities are absent.

No broad lines are observed in the single-crystal samples of pure ScF_3 and crystals doped with Ga. Only the line with $g = 1.998$ is remained. Fig. 2 shows an example of the ESR spectrum for a crystal with Ga at 77 K. The central line characterizes hyperfine structure (SFS) consisting of 7 components with a splitting 8 Oe due to the delocalization of the electrons among 6 fluorine ions with the nuclear spin $I = 1/2$. A similar spectrum is also observed for the impurity-free ScF_3 single crystal.

Fig. 3 shows the angular dependence of the spectrum for a ScF_3 single crystal with Ga in the plane [100] at 293 K. It is seen that the ESR spectrum answers to two paramagnetic centers in a distorted cubic position and consists of two spin triplets. The triplets divergence is maximum of 90 Oe, when the magnetic field coincides with the axis of the position distortion (Fig. 3a), and 45 Oe in the direction perpendicu-
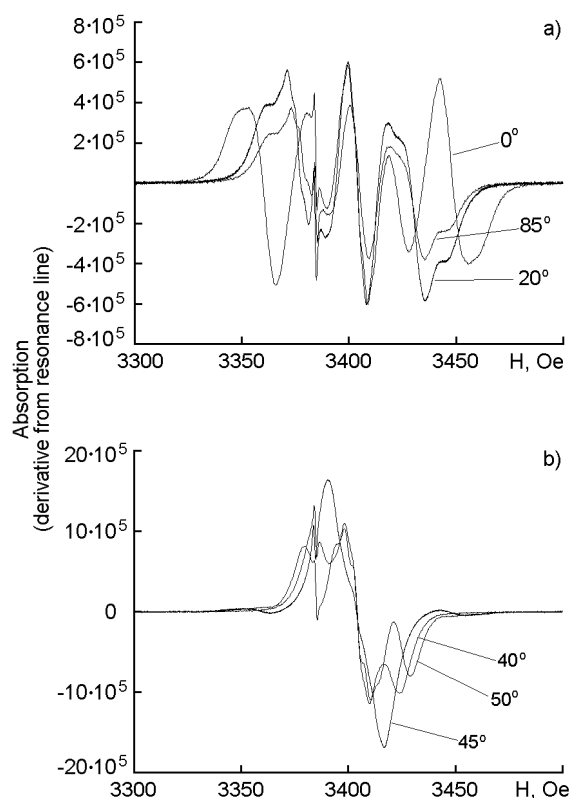
Fig. 3. ESR spectrum of the Ga doped single ScF$_3$ crystal as a function of the crystal orientation.

Fig. 4. Spectrum of the iron doped ScF$_3$ single-crystal.

lar to the distortion axis. In an intermediate position, the entire spectrum is collapsed to a single broad line (Fig. 3b).

For an impurity-free crystal, a similar behavior is observed with the distance between the HFS components of 4 Oe. The angular dependence of the spectrum shows that the distortion axes for each of these triplets are mutually perpendicular: the maximum splitting of one is accompanied by an approximately 2 times smaller splitting of the second. At the 90° rotation, they become swapped.

For the iron-doped ScF$_3$ single crystal, the ESR spectrum is more complex (Fig. 4). In this case, well pronounced are three spectral lines of the, each consisting of 7 slightly overlapping HFS components. The central line has $g = 1.998$. There is a change in the angular positions of these lines and this fact indicates a local distortion of the cubic symmetry in the center site. When the magnetic field is directed along the distortion axis (Fig. 4), the spectrum splitting will be the largest, but in the direction perpendicular to the axis, the spectrum width decreases (Fig. 4b). The dis-
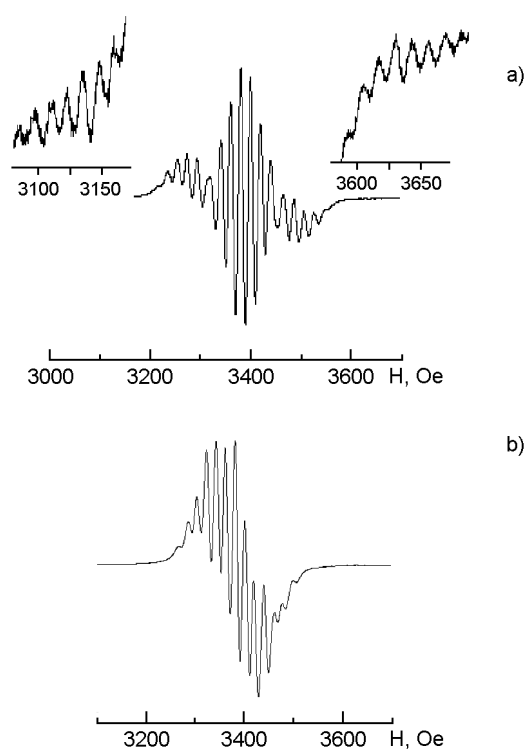
tance between the adjacent HFS components is 19 Oe. Such a structure of the spectrum is related to the delocalization of electrons between the six fluorine ions. This is evidenced by the 7-component structure for each of the transitions. That structure is most pronounced at the center line and partially overlapped for the side components. On either side of the spectrum, there are two 7-component transitions of weak intensity. Their location is independent of the crystal orientation and the hyperfine constant is 13 Oe. At the maximum splitting of the triplet (Fig. 4a), the distance between components is 106 Oe.

3. Discussion

In the pure ScF$_3$ crystal as well as in the samples doped with Al, Mg, Sb, Ga, lines with $g = 1.998$ are observed. Those can be ascribed to the presence of defects [3]. As noted in [4], the presence of cationic vacancies in these cubic crystals results in an increased sensitivity to various impurities and structural defects. The displacement of Sc^{3+} ions to the vacant positions is possible. In this case, since we observe the ESR spectrum presented by the triplet fine structure, it is natural to assume that the absence of charge compensation for the fluo-

ride ions will cause a shift of three electrons ($S = 3/2$) towards the vacant position. The remaining three electrons move to another vacant position of the defect. The distortion axes of these centers are mutually perpendicular, as follows from the observed angular dependence of the spectra. The local distortion of the cubic structure, according to our results, is assumed to be due to the compression or stretching of the fluorine octahedrons. The observed interaction of the electrons of these vacant positions with six fluorine nuclei is indicative of their arrangement within the fluorine octahedron.

In the crystals with iron impurity, the local symmetry of the defect centers is lower than the cubic one. This fact is manifested as the angular dependence of the spectrum. Seven characteristic HFS lines indicate the bonds with the six ions F^- and are observed in all the spectral lines. The observed spectrum is rather similar to the ESR spectra of the color centers in BaF_2 [5], but in that case, the structure differs from our crystals in the electron spin value of the defect center. The side components having significantly lower intensity (Fig. 4a) arise by analogy with [5] because one electrons also encounters the coupling with the Sc nucleus which has a nuclear spin $I = 7/2$. We may construct the ESR spectrum assuming that a (Sc^{3+}) = 3.5a (F^-), where a is the isotropic hyperfine constant due to the contact interaction with nucleus. This ratio is based upon the observation that the distance between the extreme sidebands in Fig. 4a is 495.6 Oe (which equals to $7a$ (Sc^{3+})).

The revealing of the unpaired electron delocalization in the form of spin density distribution over the molecule using the ESR method is possible only in the cases where the displacement speed exceeds considerably the frequency of our measurement method. The resolved SHFS indicates that the delocalization rate is much greater than the distance between the HTS components [6, 7]. The values of these distances are the biggest in the case of iron impurity (20 Oe), while being 9 Oe for gallium and 4 Oe in the pure crystal.

The increased electron delocalization as compared to the pure crystal is observed in the spectra of crystals with iron (FeF_3 additive about 5 % in the synthesis), however, we do not observe the spectral characteristic of Fe^{3+}. One possible explanation for this phenomenon may be the assumption that iron is included in the +2 valence state in the scandium vacancy, which does not allow us to observe the spectrum in our temperature range.

In the crystals doped with Al, Mg, Sb, no resolved HFS spectra are observed as well as the fine structure of the defects. The presence of components with $g = 1.998$ indicates the presence of defects in these polycrystals, too. It is not yet possible to make a conclusion about the implantation of impurities in the structure of these samples. For more information, the experiments on single crystals are planned in future.

4. Conclusion

In the pure ScF_3 crystal and in the samples with diamagnetic impurities Al, Mg, Sb, Ga, a spectrum typical of crystalline defects is observed. The defects can be attributed to the presence of vacancies in the structure in the Sc^{3+} positions occupied by free electrons. For polycrystalline samples with magnesium and antimony and for pure crystals, there are broad lines that characterize the presence of casual impurities. In the pure ScF_3 single crystal as well as in the iron and gallium doped crystals, seven characteristic HFS lines are observed indicating the binding of electrons in the defect centers with six fluorine ions. For the sample with gallium, for the pure crystal and for the iron doped crystal, the HFS constants are different, which may indicate the implantation of these impurities in the crystal lattice. Basing on the published data and the electromagnetic field frequency value in our measurements (9 GHz), the delocalization of the electron density occurs at a frequency in the 10^{14} to 10^{11} s^{-1} range [6, 7]. The highest electron mobility, according to these data, is in the crystals with iron. The angular dependence of the ESR spectra in the single crystals ascribed to the defects suggests the local distortions of the crystal symmetry in these positions. Such defects are not registered with X-rays because of the low density. The local distortion of cubic symmetry, according to our results, can be attributed to distorting of octahedra formed by fluorine ions. The defect centers in the crystals with iron are the crystal color centers. The structure of the defects and the nature of the distortion depend on the type of the impurity ions. A model of the defect centers is planned to be proposed in the future.

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Дослідження кристалів ScF_3 та твердих розчинів на основі ScF_3 методом ЕПР

В.Н.Воронов, Е.А.Петраковська, А.А.Александрович

Кристали ScF_3 належать до групи перовскітоподібних, але, на відміну від інших фторидів цього класу, мають кубічну симетрію. Дослідження кристалів методом ЕПР показало, що у спектрах бездомішкового кристала, а також кристалів з домішками Ga, Mg, Sb, Al, Fe є лінії, які можна приписати локальним дефектам кристалічної структури. Найбільш надійно ці дефекти ідентифіковано у монокристалічних зразках ScF_3 з домішками Ga та Fe та у бездомішковому кристалі. У всіх випадках спектри, що спостерігалися показали присутність дефектів, пов'язаних з шістьма іонами фтору. Найбільш чітко це виявлено у кристалах з домішкою Fe. Одержано однозначне свідоцтво наявності локального порушення кубічної симетрії у місцях знаходження дефектних центрів. Є версія, що це октаедри фтору.