STUDY OF PLASTICALLY DEFORMED ZnS:Mn CRYSTALS BY EPR

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The electronic paramagnetic resonance spectra in single crystals ZnS:Mn are researched. The regularities of the processes of modification of a structure and the local symmetry of impurity centers in the whole volume of the plastically deformed samples are clarified. It is shown with the use of the directed dosed deformations that there is a possibility to obtain ZnS crystals with any preset ratio of the volumes of differently oriented areas of sphalerite upon the concentration of stacking faults (SF) from the initial value up to zero.

It is known that zinc sulfide can be crystallized, depending on the external conditions, in several polymorphic modifications and shows a strong inclination to the twinning and formation of various polytypes [1]. As far as each structural modification is characterized by the own set of physical properties, it is clear that, to improve the quality and characteristics of existing instruments and to create new devices based on ZnS crystals, a direct solution of the problem of control over their structure is necessary. Quite promissing in this respect is the method of deformational recrystalization [2, 3]. It consists in modifying the structure of polytypes and microtwins of zinc sulfide upon the motion of partial dislocations which is stimulated by a plastic deformation of crystals. However, for a practical application of the method, it is necessary to extend its possibilities and the range of substances with similarly controlled structures ensuring a deeper understanding of the character of the processes running under the deformational recrystalization. In the present work, the method of electronic paramagnetic resonance (EPR) was used to obtain the necessary additional experimental data. Thus, the regularities of the processes of modification of a structure and a local symmetry of impurity centers in the whole volume of the researched samples were clarified. By using the directed dosed deformations, we show the possibilities to vary a structure of real crystals of zinc sulfide over a wide range and to obtain ZnS crystals with any given ratio of the volumes of differently oriented areas of sphalerite upon the concentration of SF from the initial value up to zero.

The research was conducted on monocrystals of zinc sulfide brought up using the Bridgman method from a melt under a pressure of argon $\sim$ 15 MPa. Two-valence ions of manganese introduced in crystals were used as a paramagnetic probe due to the doping by salt α-MnS. The concentration of impurity ions Mn^{2+} did not exceed 10^{-2} wt.%. Samples were cut as rectangular parallelepipeds with the size of the edges of the order of $2\times2\times4$ or $3\times3\times6$ mm^3, so that the (111) basic plane was oriented at 45^o relative to the deforming stress. The direction of deformation coincided with the height of samples. It is known that the system of a sliding for crystals with the structure of sphalerite is $\{111\}\ \langle110\rangle$. A feature of the researched samples is that the sliding in them can be carried out only in one basic plane (111). This plane is placed at an angle of 45° to a direction of compression.

During the experiments, there was a necessity to change the direction of shift forces to the inverse one. It can be realized by replacing the strain of compression by the strain of tension or the change of the direction of compression by 90° preserving the angle between the direction of the strain and the axis [111] to be equal to 45°. In the present work, the latter method was used.

The plastic deformation of crystals was accomplished with a constant speed of the order of 17 μm/min at a temperature of 200 °C.

The EPR-measurements were conducted using a radiospectrometer “RADIOPAN” SE/X-2543 at the temperature $T = 300$ K. To exclude the errors which can be caused by the reloading of samples after a deformation, the EPR spectrum of a standard sample was registered simultaneously with the researched EPR spectrum of Mn^{2+}. A ruby monocrystal was used as the measurement standard. It was introduced into the resonator through a lower hole and remained to be fixed throughout the experiment.

The choice of impurity ions Mn^{2+} as a paramagnetic probe was stipulated for several reasons. Firstly, the EPR spectra of Mn^{2+} in ZnS crystals are well investigated and are described in numerous works [4]. Secondly, the ions Mn^{2+}, by replacing Zn^{2+}, do not introduce practically noticeable distortions to the structure of the researched crystals and, as was shown in [5], take all possible types of sites in the crystalline lattice of ZnS with the identical probability.

In crystals of zinc sulfide, depending on the stacking sequence of closely packed strata, the existence of four types of substitutional sites is possible, upon the consideration of the distance along the C axis up to the third order. According to [6], the sites in sphalerite and wurtzite are designated as AN and PS, respectively, where the first letter determines a character of the environment (A — antiprismatic, P — prismatic), and the second one means the availability (S) or absence (N) of a single axial neighbourhood of the third order. The presence of SF in ZnS crystals, which are located on the boundaries of twinned areas of sphalerite, results in the emerging of two types of sites — AS and PN. A local symmetry of sites of the type AN is T_d, and that of sites of the type PS, AS, and PN is C_{3v}. In ZnS crystals which are grown from a melt and have the structure of microtwins of sphalerite, none sites of the type PS characteristic of wurtzite are detected. Moreover, this fact testifies to that the stacking faults in such crystals are mainly single-layer.

Thus, the EPR spectrum of Mn^{2+} observed in the researched microtwinned ZnS crystals represents a superposition of four “elementary” spectra. Two of them, the so-called “axial” EPR spectra, reflect the presence of SF in crystals and are stipulated by ions Mn^{2+} at sites of the AS and PN types. Responsible for “cubic” EPR spectra are sites of the AN type. These sites, being in differently oriented areas sphalerite — type I (the sequence of strata... ABC...) and type II (... ACB...), differ from one another by a turn by 180° (60°) around the axis $[111]_c$. This results in a shift of the angular dependences of the appropriate EPR spectra by 110°

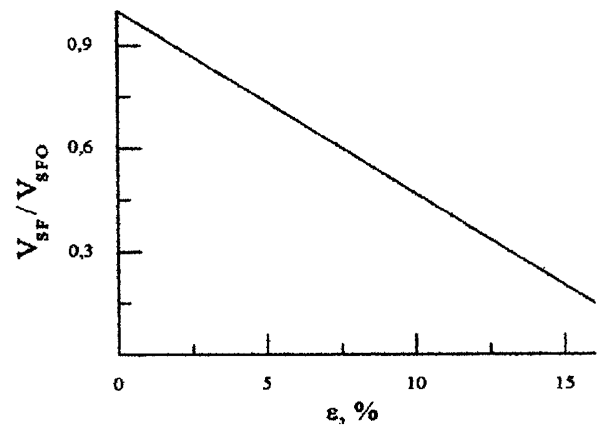

Fig. 1. Change of the volume occupied by SF upon a plastic deformation of ZnS crystals

(70°) upon the rotation of a magnetic field in the plane (110) and, therefore, in the possibility to observe the EPR spectra of Mn^{2+} in each component of a twin. Taking into account the fact of equiprobable local distribution of ions Mn^{2+} for all possible types of sites of the crystalline lattice of zinc sulfide, it becomes clear that their EPR spectra are the exact indicator which can help not only to clarify the nature and kinetics of the reorientation of the crystalline lattice in the whole volume of a sample stimulated by a plastic deformation but also to determine the character of changes in the local symmetry of impurity centers.

A plastic deformation of zinc sulfide crystals results in changes of the EPR spectra of impurity ions Mn^{2+}. The characters of observable changes for “cubic” and “axial” spectra are different. The intensity of lines of the “axial” EPR spectra decreases with increase in a strain, while the total intensity of two “cubic” spectra increases. This testifies to the presence of a reorientation of a crystalline lattice stimulated by by a strain in crystals, at which the areas with the hexagonal packing of zinc sulfide (i.e., SF) are rebuilt into the structure of sphalerite. Fig. 1 shows a change of both the relative number of centers Mn^{2+} with the local symmetry of the environment C_{3V} and, therefore, the relative volume occupied by SF is determined by the double integration of lines of the central transitions ($M = 1/2$). The last are registered separately upon the orientation of the crystal in a magnetic field $\vec{H}\perp[111]$. We can see that a decrease in the number of SF proceeds linearly in accordance with increase in the strain and is finished at $\varepsilon \approx 18$ %.

At the same time, the volumes $V_{\rm I}$ and $V_{\rm II}$ of differently oriented areas of cubic structures of types I

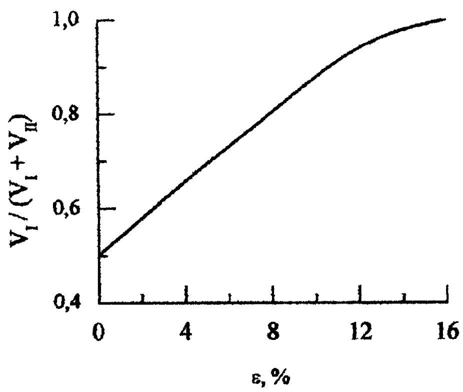

Fig. 2. Change of volumes of areas of sphalerite of types I and II at a plastic deformation of ZnS crystals

and II. So, while these volumes are practically identical ($V_{\rm I} = V_{\rm II}$) in the originally undeformed samples of microtwins and polytypes of ZnS, the volume by one area is increased during a plastic deformation, and that of the other is decreased. In Fig. 2, the dependence of the relative volume occupied in areas of type I, $V_{\rm I}/(V_{\rm I}+V_{\rm II})$, on the degree of a plastic deformation is indicated. As seen, the number of SF decreases linearly (Fig. 1), but the ratio $V_{\rm I}/(V_{\rm I}+V_{\rm II})$ versus a relative strain has a nonlinear character and is also finished at $\varepsilon \approx 18$ %. Such a nonlinear growth can be connected with the fact that the contribution to the increase of the volume of areas of type I is given not only by the reoriented regions of areas of type II, on which partial dislocations have already passed, but also by the volumes occupied by SF earlier on.

The fact that the processes of deformational recrystalization in ZnS:Mn crystals are finished at relative deformations $\varepsilon \approx 18$ % (according to the model submissions [2, 3], exactly this value of a relative deformation is necessary for both the passage of partial dislocations and the reorientation of a half of closely packed strata of zinc sulfide) testifies to that the impurity ions of manganese do not affect the kinetics of the structural phase transition.

It is known that the structure of the studied microtwinned ZnS crystals represents the alternation of the layers of areas of sphalerite with different sequences of closely packed strata ...ABCABC...or... ACBACB..., designated by us earlier on as areas of type I and II. Since only one of these two areas "survives" after the deformational recrystalization, the natural question arises: which of the two areas survives?

In work [7] based on the model ideas, the conclusion is made that the stability of this or that component of a microtwin is related to the crystallographic orientation

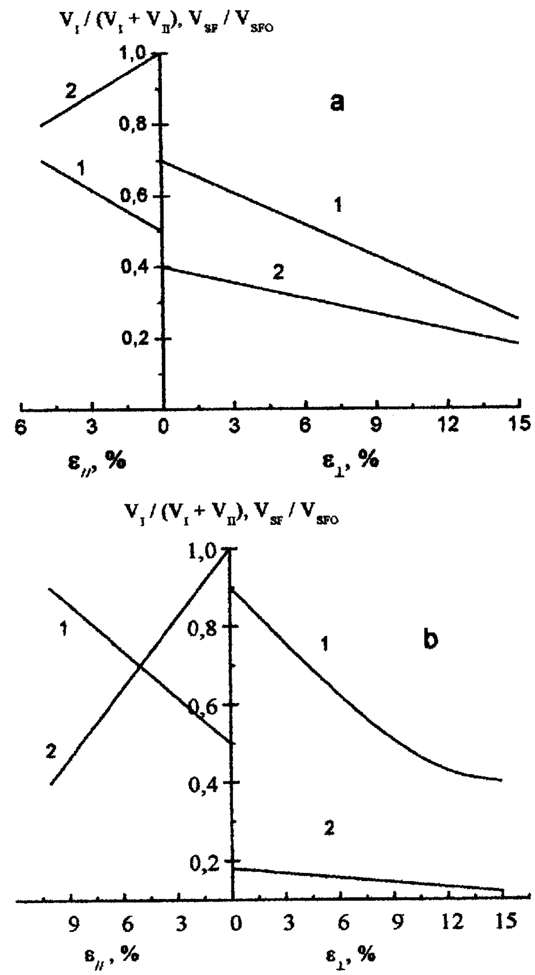

Fig. 3. Relative volumes occupied in areas of sphalerite of type I — $V_{\rm I}/(V_{\rm I}+V_{\rm II})$ (*1*) and SF $V_{\rm SF}/V_{\rm SFO}$ (*2*) versus the degree of a plastic deformation $\varepsilon_{\rm II}$ and $\varepsilon_{\perp}$ (*a* — $\varepsilon_{\rm II\,max} = 4\%$, *b* — $\varepsilon_{\rm II\,max} = 10\%$)

relative to a couple of shear forces. Namely, a change of the direction of shear forces into the opposite one should result in a change of the sequence of closely packed strata in the final 3*C*-structure. The experimental confirmation was obtained in [7] by using the method of a widely divergent bundle of X-rays. However, it should be noted that, in those experiments, two batches of samples were investigated. In one of the batches, the direction of a loading was close to the direction [001] for areas of type I. Whereas it was close to [001] for the areas of type II in the other batch. In the present work, a change of the loading direction was made for the partially deformed sample. So, after the realization of some strain $\varepsilon_{\rm II\,max}$, the sample was cut from the average part of the deformed crystal, the height of which coincided with the strain direction $\varepsilon_{\perp}$.

The results of studiesof the kinetics of the process of structural reorientation upon a change of the strain direction for partially deformated samples are shown in Fig. 3. In the left parts of the figure, we see the dependences of the volume occupied by SF V_{SF} and the relative volume $V_{\rm I}/(V_{\rm I} + V_{\rm II})$ on the degree of a strain for two samples deformed up to different values of $\varepsilon_{\rm II}$($\varepsilon_{\rm II\,max} = 4\%$ — Fig. 3,*a*; $\varepsilon_{\rm II\,max} = 10\,\%$ — Fig. 3,*b*). In the right parts of Fig. 3, we show, as a continuation, the analogous results obtained after the change of a direction of shear forces to the opposite one. The observable jump is connected with the following fact. As indicated in [3], the reorientation of a structure occurs on the initial stage of a strain (up to $\sim 10\%$) mainly in the central part of the sample which is used in the experiments after changing the direction $\varepsilon_{\rm II}$ by $\varepsilon_{\perp}$.

The obtained results testify to the following. First, the change of a direction of shear forces to the opposite one results in the inverse change of the volumes of differently oriented cubic areas. Secondly, the average thickness of twinned layers is increased in this case, whereas the number of SF continues to decrease. Thus, we can see that, by the appropriate selection of values of the deformations $\varepsilon_{\rm II}$ and $\varepsilon_{\perp}$ in samples of zinc sulfide, it is possible to create a necessary ratio of volumes $V_{\rm I}$ and $V_{\rm II}$ (from 0 up to 1) for any concentration of SF (from the initial one up to 0).

We note that the rate of a change of the number of SF decreases after the replacement of $\varepsilon_{\rm II}$on $\varepsilon_{\perp}$. The higher the initial strain degree $\varepsilon_{\rm II}$, the greater the decrease. This immediately testifies to the fact that, at $\varepsilon_{\perp}$, partial dislocations are moving on the planes already passed by them during a strain $\varepsilon_{\rm II}$, but in the opposite direction.

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ДОСЛІДЖЕННЯ ПЛАСТИЧНО
ДЕФОРМОВАНИХ КРИСТАЛІВ ZnS:Mn МЕТОДОМ ЕПР

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Р е з ю м е

Досліджено спектри електронного парамагнітного резонансу (ЕПР) в монокристалах ZnS:Mn. З'ясовано закономірності протікання процесів зміни структури і локальної симетрії домішкових центрів у всьому об'ємі досліджуваних пластично деформованих зразків. Показано, що за допомогою напрямлених дозованих деформацій можна отримати кристали ZnS з різним співвідношенням об'ємів різноорієнтованих областей сфалериту при концентраціях дефектів пакування від початкового значення до нуля.