The luminescence and electrical characteristics of ZnS crystals undergoing plastic deformation

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The spectrum of the pulsed luminescence occurring during plastic deformation of microtwinned ZnS crystals was investigated. It was shown that charged partial dislocations which move during deformation bring a charge out to the surface of the sample, and this charge induces surface electroluminescence. The dependence of the dislocation charge on the deformation rate and the sample temperature was investigated. The detection of a stationary component in the luminescence occurring during deformation of ZnS crystals is reported.

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1. INTRODUCTION

The occurrence of luminescence during plastic deformation of ZnS crystals has been reported earlier.[1,2] In contrast to the well understood stationary deformation luminescence of colored alkali halide crystals,[3,4] the deformation of ZnS single crystals results in the emission of short pulses of light, i.e. the luminescence has a nonstationary character. In addition, plastic deformation of ZnS crystals causes an electric charge to appear on the surface of the sample.[5,6] Simultaneous investigations of these two processes in the present work have shown that the pulsed luminescence of ZnS crystals observed during plastic deformation is electroluminescence of the sample caused by moving charged partial dislocations. The motion of these same dislocations leads to the appearance of an electric charge on the surface of the sample.

The paper reports the discovery of a stationary component of the deformation luminescence in A^2B^6 crystals. Spectral investigations are presented, and a mechanism is proposed for this process.

2. SAMPLES. EXPERIMENTAL TECHNIQUE

Single crystals of ZnS were grown from the melt by the Bridgman method in an atmosphere of argon at a pressure of 150 atm. Both ZnS crystals specially left undoped and having a dark resistivity of $\rho \approx 10^{13}\ \Omega \cdot \text{cm}$, and crystals doped with manganese and nickel (~0.1 wt. % impurity in the melt) having resistivities ρ of 10^{11} and $10^{12}\ \Omega \cdot \text{cm}$, respectively were investigated. Studies were made of samples doped with Al_2S_3 to stabilize the $6H$ and $4H$ polytype structures. The dark resistivity of the polytypes was $\rho \approx 10^8\ \Omega \cdot \text{cm}$.[1)] According to x-ray investigations the structure of the initial crystals may be represented in the form of thin layers of sphalerite rotated through 60° with respect to one another around a selected [111] axis.[7] The (111) plane perpendicular to this selected axis is a twinning plane. X-ray rocking patterns indicate that the thicknesses of the regions of cubic structure are statistically distributed. Comparison of the birefringence and x-ray data shows that the average thickness of the sphalerite layers in the samples investigated is ~30 Å. The initial sample is thus a sphalerite microtwin. The presence of a twinning plane makes the motion of dislocations difficult in all the (111) planes except the one selected by the twinning which we shall denote by (0001) in hexagonal indices.

The samples were cut with dimensions of 2×2×4 mm and 3×3×6 mm so that the slip plane active during deformation was at an angle of 45° to the deforming stress. Various methods of loading the crystals were used:

1) loading with rectangular mechanical-stress pulses (pulse amplitude 0–5 kgf, duration 0.5–20 sec)

2) deformation at a constant rate of $\dot{\varepsilon} = (1-5)\times 10^{-4}\ \text{sec}^{-1}$.

To study the spectral characteristics of the luminescence photoelectric recording was done using low-noise, high-sensitivity photoelectron multipliers of types FÉU-79 and FÉU-106, and Monospec-600, SPM-2, and Hitachi monochromators. The time characteristic of the luminescence and birefringence were recorded with a time electron multiplier type FÉU-77, and S1-37 and S1-11 oscilloscopes.

To determine the charge on the dislocations and to investigate the influence of the electric field on the movement of charged dislocations, indium contacts were attached to the $(10\bar{1}1)$ faces of the crystal with an ultrasonic welder (Fig. 1). The signal from the contacts was fed to the input resistance R_{in} of an oscilloscope or an

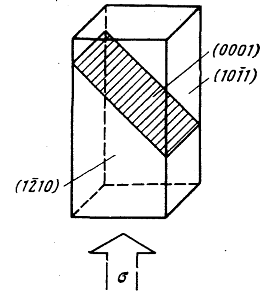

FIG. 1. Diagram illustrating the orientation of a ZnS sample during uniaxial deformation. The indices of the faces are given in the hexagonal system.

electrometric amplifier. In all the investigations the sample resistance R_{sam} was $\gg R_{in}$.

3. EXPERIMENTAL RESULTS

Plastic deformation of microtwinned ZnS crystals results in short pulses of light with a duration of $\tau \sim 40$ nsec. The amplitude and duration of the luminescence flashes does not depend on the deformation rate or the temperature. On the other hand, the number of luminescence flashes in unit time N is determined by the plastic deformation rate $\dot{\varepsilon}$ (Fig. 2), N always being proportional to $\dot{\varepsilon}$ ($\dot{\varepsilon} = \varepsilon_0 N$); consequently, the residual deformation is $\varepsilon = \varepsilon_0 N t_0$, where ε_0 is the deformation for one flash, and t_0 is the time for which the sample is stressed. The proportionality between the number of luminescence flashes $n = Nt$ and ε is preserved up to a crystal deformation of 17 %.

The residual deformation ε_0 for one luminescence flash may vary in the range 0.16–0.3 μm for different ZnS ingots.

Investigation of the birefringence of a sample when it is loaded with rectangular pulses of mechanical stress showed that in the elastic deformation region ($\sigma < \sigma_{el}$, where σ_{el} is the elastic limit) the change in birefringence is only observed at the instant the crystal is stressed. For $\sigma > \sigma_{el}$ the birefringence varies monotonically during plastic deformation of the sample (Fig. 3). The cyclic nature of the process is noteworthy. At the beginning a relatively rapid change in the birefringence is observed which then reaches saturation. The cycle ends with a stepwise change in the birefringence and is repeated again. (We do not examine the change in birefringence at the instant the mechanical stress pulse is applied, which is due to elastic deformation of the crystal.)

In synchronism with the jump in the birefringence a luminescence flash is observed. The duration of the stepwise change in birefringence proved to be ~80 nsec, i.e. of the order of the duration of the luminescence flash. The coincidence of the durations and the synchronism of the appearance of luminescence flashes and the jumps in birefringence indicate that they are due to the same process. The variation in birefringence during the time preceding the jump in it, and consequently, preceding the luminescence flash as well, is evidence of the dynamic process (dislocation movement) which builds up the luminescence flash.

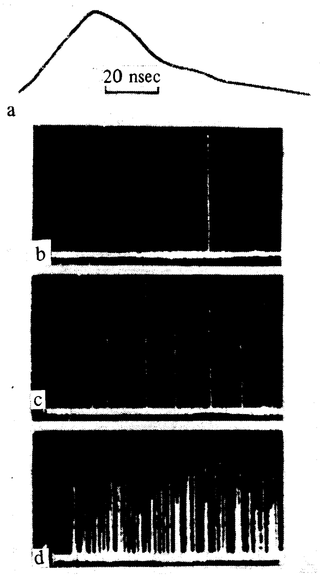

FIG. 2. The shape of an individual luminescence pulse (a) and the dependence of the number of flashes in unit time N on the rate of plastic deformation. The latter is equal to 2 (b), 10 (c), and 80 (d) μm/min respectively. Total scale = 5 sec.

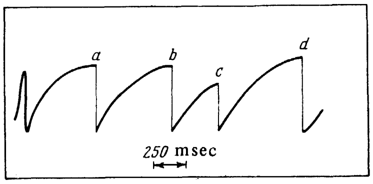

FIG. 3. The variation in birefringence during plastic deformation of a sample. *a*, *b*, *c*, and *d* are jumps in the birefringence accompanying pulsed luminescence. *c* is a jump in the birefringence initiated by a nitrogen laser pulse ($\lambda = 337$ nm) at a voltage below breakdown ($U < U_{br}$).

The linear relationship between the number of flashes and the residual deformation of the crystal, and the results of the investigations of the birefringence of crystals undergoing deformation make it possible to conclude that the flashes of luminescence occurring during deformation are the consequence of the plastic deformation, i.e. they have a dislocation nature. Evidence in favor of this is also provided by the absence of luminescence in the region of elastic deformation of a sample and on loading a crystal cut so as to make the movement of dislocations difficult (basal plane parallel to the direction of deformation).

As was shown in[1], other, nondislocation mechanisms for the occurrence of luminescence flashes (triboluminescence and the piezo-effect) do not explain a number of the experimental results.

4. THE CHARACTERISTICS OF THE DISLOCATIONS GIVING RISE TO PLASTIC DEFORMATION OF ZnS CRYSTALS

The dislocation structure of A^2B^6 crystals, particularly of ZnS, is very diverse.[8] Plastic deformation may be the result of the movement both of complete (30°, 60°, edge, and screw) dislocations, and of partial ones. X-ray and optical investigations of crystals undergoing deformation permits one to pick out that type of dislocation whose motion gives rise to the plastic deformation of the sample. As investigations of x-ray rocking patterns and Debye patterns showed, a plastically deformed ZnS sample contains all the features characteristic of the cubic modification of ZnS, i.e. it is a single crystal of sphalerite.

Observation of deformed samples in crossed polarizing prisms indicates that the transition of the initial microtwinned modification to the 3*C* structure starts at the very first stages of plastic deformation and is complete for $\varepsilon \sim 20\%$. As shown in[7,9], the microtwinned—sphalerite transition is brought about in ZnS crystals through the movement of partial dislocations, and the deformation needed for the full transition is determined by the number of partial dislocations needed for a complete reorientation of the crystal.

Thus, plastic deformation of microtwinned crystals is the result of the movement of partial dislocations.

An analysis of the possible structures of the partial dislocations moving in the basal plane carried out in[10,11] showed that the core of a dislocation may contain up to three excess broken bonds on Zn^+ or S^- atoms. The crystals we investigated had a dark resistivity of ~ 10^{13} Ω · cm and a Debye screening radius of ~ 1 mm, and consequently it may be assumed that the free carriers will not screen the "geometrical" charge of a dislocation. Consequently, the partial dislocations which bring about the plastic deformation of microtwinned crystals may be charged and have a charge greater than $\pm 1e$ per interatomic distance.

5. EXPERIMENTAL STUDY OF THE CHARGE ON PARTIAL DISLOCATIONS IN ZnS CRYSTALS

The appearance of a charge on the surface of samples that are being deformed was first observed by Stepanov in alkali-halide crystals (the Stepanov effect).[12,13] The occurrence of an electric potential on the faces of ZnS and ZnSe crystals undergoing deformation was first reported in[6]. It was also shown in the latter that plastic deformation in these samples is brought about through the movement of charged dislocations. In A^2B^6 crystals dislocations of different mechanical sign have opposite electric charges.[5,8,11] During deformation dislocations with dissimilar charges (α and β) move in opposite directions and produce the charge on the $(10\bar{1}1)$ crystal faces observed experimentally. If the $(10\bar{1}1)$ surface to which the contacts are attached is connected with a recording instrument for which $R_{\text{in}} \ll R_{\text{sam}}$, then the crystal will be a current source during plastic deformation. Since this current is due to moving dislocations, it is natural to term it the dislocation current i_d.

As was noted in[5,14], the charge brought to the surface of the sample by the moving dislocations is equal to

$$Q=\int_0^{t_0} i_d\,dt. \qquad (1)$$

If the residual deformation which builds up this charge is determined, it is easy to find the average charge of a mobile dislocation.[5,14]

The change in the height of the sample Δh may be determined from the motion of dislocations in the following way:

$$\Delta h=\sum_i (\mathbf{b}_i\mathbf{n})\frac{\Delta S_i}{S_0}, \qquad (2)$$

where S_0 is the area of the slip plane, ΔS_i is the area swept out by a dislocation, $\mathbf{n}$ is the direction of deformation, $(\mathbf{b}_i \cdot \mathbf{n})$ is a factor taking account of the geometry of deformation, and $\mathbf{b}_i$ is the Burgers vector of the i-th dislocation. When such deformation occurs, the charge arising on the surface of the sample is

$$Q=\sum_i q_i\frac{\Delta S_i}{L_0}, \qquad (3)$$

where q_i is the linear charge density of the i-th dislocation, and L_0 is the distance between the $(10\bar{1}1)$ crystal faces in the (0001) plane.

To estimate the average charge of the dislocations we shall assume that during deformation of ZnS crystals movement of partial dislocations of one type takes place and then we obtain from (1)–(3)

$$q=\left(\frac{L_0}{S_0}\right)\frac{(\mathbf{bn})}{\Delta h}\int_0^{t_0} i_d\,dt. \qquad (4)$$

At 350 K the average charge of the partial dislocations in crystals specially left undoped determined from this relationship turned out to be equal to $0.9 \pm 0.1e$ per interatomic distance along the line of the dislocation.

In[14] too large a value was obtained for the linear density of dislocation charge in ZnS crystals ($1.3 \pm 0.15e$/lattice point) since the authors considered that deformation was brought about by the movement of complete dislocations and not partial ones as is actually the case.[7,9] Recalculation of the data in[14] gives a value of $q \approx 0.9 \pm 0.15e$/lattice point, which is in good agreement with our results.

The linear density of charge on a dislocation of $q \approx 0.9e$/lattice point found in the present work agrees with the estimate of the linear density of dislocation charge of $q \approx 1e$/lattice point obtained in[6] by another method based on studying the "odd" electroplastic effect (the electrostatic interaction of charged dislocations with an external field).

Determination of the charge on the dislocations at various stages in plastic deformation showed that the value of q in ZnS single crystals is practically independent of the degree of deformation of the sample for $\varepsilon > 3\%$ (Fig. 4). The investigation of the dislocation charge was therefore carried out at deformations greater than 3%. It turned out that the charge on the dislocations depends on the rate of deformation and on the temperature at which the sample is deformed. Increasing the temperature in ZnS crystals specially left undoped leads to a reversible increase in the charge on the dislocations (Fig. 5). Figure 6 shows the dependence of q on the deformation rate at various temperatures. Increase in the deformation rate at constant temperature results in a decrease in the magnitude of the dislocation charge. The introduction of manganese or nickel impurity into a

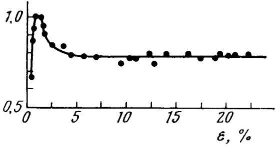

FIG. 4. Dependence of the dislocation charge on the degree of sample deformation ($[q]=1$ electron per lattice point along the dislocation line); $T=360$ K.

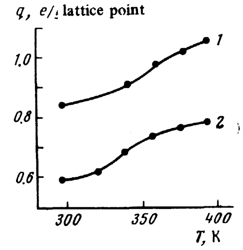

FIG. 5. Dependence of the dislocation charge on the deformation temperature of the sample: 1—ZnS crystal specially left undoped, 2—ZnS doped with nickel (0.05 wt.% in the melt).

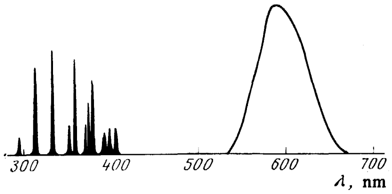

FIG. 7. Pulsed luminescence spectrum of a microtwinned ZnS : Mn crystal.

ZnS crystal produces some decrease in the dislocation charge but the character of the temperature dependence $q=q(T)$ remains unchanged (Fig. 5). A significant change in the charge on the dislocations is observed on doping ZnS with Al_2S_3 (polytypes 6*H* and 4*H*). For 6*H* polytype crystals $q \approx 0.3e$/lattice point. In addition, a decrease in the dislocation charge occurs in these samples with increase in the temperature at which the crystal is deformed.

Investigation of the electrical characteristics of plastically deformed crystals permits the following conclusions to be drawn.

1. Plastic deformation of microtwinned ZnS crystals is brought about by charged partial dislocations whose charge at $T=350$ K is equal to $q \approx 0.9 \pm 0.1e$/per interatomic spacing along the dislocation line.

2. The charge on the partial dislocations is weakly dependent on the impurity content of microtwinned (ZnS : Mn and ZnS : Ni) crystals. An increase in temperature results in an increase in the value of q, while an increase in the deformation rate causes a decrease in the dislocation charge in a microtwinned crystal. The variation in the dislocation charge on varying the temperature and rate of deformation of the crystal is probably associated with the movement of different types of partial dislocations (having different values of q) on varying the experimental conditions.

3. In polytype crystals the value of q is $\sim 0.3e$/lattice point at $T=300$ K; with increase in temperature a decrease occurs in the dislocation charge, apparently associated with screening of the "geometric" charge by free carriers.

6. SPECTRAL CHARACTERISTICS AND THE MECHANISM OF PULSE LUMINESCENCE

The spectrum of the luminescence occurring during plastic deformation of microtwinned ZnS crystals consists of a series of narrow bands in the 290–430 nm region (2976, 3158, 3365, 3535, and 3576 Å, see Fig. 7). In the luminescence of samples doped with manganese activator luminescence from Mn^{2+} ions ($\lambda_{max}=585$ nm) is observed along with the bands indicated. Narrow spectral lines of the pulsed luminescence lie in the edge luminescence region of ZnS, while some of the bands are in the intrinsic absorption region of the crystal. Luminescence spectrally coincident with the pulsed deformation luminescence was observed on exciting surface electroluminescence in ZnS crystals. The short-wave bands (290–430 nm) were ascribed to the luminescence of atomic oxygen absorbed by the surface. The coincidence of the spectra of these two processes is evidence in favor of the view that the mechanisms of these phenomena are related. In fact, the dislocations bring to the $(10\bar{1}1)$ surfaces of the crystal charges of opposite sign[5,6,14] which accumulate on the faces due to the low concentration of free carriers in the sample ($\rho \approx 10^{13}\ \Omega \cdot$ cm). In this process a difference in potential arises between the $(10\bar{1}1)$ faces of the sample which, when the breakdown voltage U_{br} is reached, results in an electroluminescence pulse. Naturally, there is some apprehension as to whether breakdown through the air and luminescence of the atmospheric oxygen occur when U_{br} is reached. Investigation of the spectrum of the luminescence pulses in the uv region showed that luminescence of wavelength $\lambda < 290$ nm is absent, whereas the intensity of the luminescence during a discharge in air increases with decrease in wavelength down to the limit of sensitivity of the FÉU-106 ($\lambda=200$ nm).

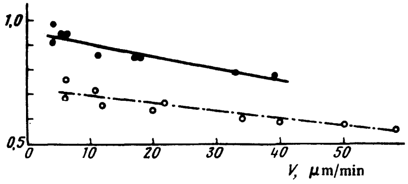

FIG. 6. Dependence of the dislocation charge on the deformation rate of the ZnS sample at $T=380$ K (●) and $T=320$ K (○).

If the mechanism proposed for the pulsed luminescence of microtwinned ZnS crystals is correct, the pulsed luminescence should be expected to disappear in conditions under which a charge cannot accumulate on the surfaces of the samples. In fact, the deformation of ZnS crystals immersed in a liquid which conducts electrically, but which does not absorb light (an aqueous solution of KCl) does not result in pulsed luminescence.

The mechanism proposed for the occurrence of pulsed luminescence as surface electroluminescence explains all the experimental facts described above. Let us dwell on the interpretation of the variation in birefringence (Fig. 3). Dislocations moving during plastic deformation bring charges of opposite sign to opposite $(10\bar{1}1)$ faces of the sample. These charges produce an electric field U in the sample, which in turn causes a change in the birefringence (the electrooptic effect). The change in birefringence copies the behavior of the electric field which has arisen. This electric field makes the motion of subsequent dislocations difficult as a result of the electrostatic interaction of the charged dislocations with it (electroplastic effect "odd" with respect to the field).[6] The hardening of the crystal results in a reduction of the plastic deformation rate and a slowing down of the rate of change of the birefringence signal. When the electric field reaches the critical value U_{br}, electroluminescence occurs in the ZnS crystal—a light pulse is emitted, U undergoes a step change down to zero, and this results in a sharp jump in the birefringence signal as well. Since the electric field which produces the hardening of the sample disappears, the plastic deformation rate increases. The accumulation of charges on the surface of the sample starts again, and the cycle, which finishes with a luminescence pulse, is repeated.

We attempted to simulate the process described: the birefringence was studied while an electric voltage was applied to a ZnS crystal from an external source. The simulation completely confirmed the concepts developed. Consequently, the luminescence pulses stimulated by deformation are surface electroluminescence of the ZnS crystal which occurs as a result of charges being brought out to the crystal faces by dislocations.

Taking the proposed mechanism for the occurrence of luminescence pulses as a basis, one can easily explain the softening of the crystal on illuminating it with light of wavelength $\lambda_{max} = 340$ nm discovered in[2]. Study of the absorption spectrum of thin ZnS crystals (0.3 mm) showed that the absorption coefficient for light of wavelength 340 nm is $\sim 3\times10^3$; consequently, the penetration depth is ~3 μm. Along with the principal volume conductivity maximum ($\lambda = 390$ μm) a maximum is observed at $\lambda = 340$ μm in the photoconductivity spectrum $J_{ph}(\lambda)$ of ZnS samples; in accordance with what has been said above, one may attribute this maximum to the surface photoconductivity of ZnS.

If a voltage U near U_{br} has arisen between the faces of a crystal as a result of the movement of dislocations, then the generation of free carriers on illuminating the sample with light ($\lambda_{max} = 340$ nm) induces electroluminescence at $U < U_{br}$. Since this electric field slows down the movement of subsequent dislocations, the reduction in U results in softening of the sample. In a certain sense this phenomenon is analogous to a short-circuit effect.[14]

Confirmation of what has been said above is provided by experiments on the stimulation of luminescence flashes in a crystal being deformed by single pulses from a nitrogen laser ($\lambda = 337$ nm). The electroluminescence pulse and the jump in the birefringence accompanying it were initiated by a laser pulse producing carriers in the surface layer (Fig. 3).

As already noted, for a luminescence pulse to occur it is necessary to generate a potential U between the faces of the sample equal to the breakdown value U_{br}. This is possible provided the dislocation current i_d producing this potential exceeds the leakage current through the crystal, i.e.,

$$i_d > U_{br}/R_{sam} \quad . \tag{5}$$

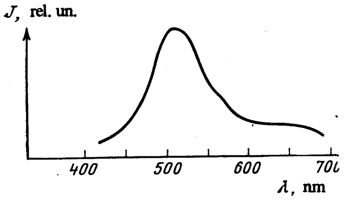

FIG. 8. Continuous deformation luminescence spectrum of a 6*H*-polytype ZnS : Cu crystal.

From the relationships (1)–(3) we obtain

$$i_d = \dot{h}\frac{q}{(\mathrm{bn})}\left(\frac{S_0}{L_0}\right). \tag{6}$$

Consequently, a necessary condition for the occurrence of luminescence pulses is that the inequality

$$\dot{h} > \frac{U_{br}}{R_{sam}}\frac{(\mathrm{bn})}{q}\left(\frac{L_0}{S_0}\right). \tag{7}$$

is fulfilled. For the crystals we investigated which were specially left undoped, this condition is fulfilled at deformation rates of $\dot{h} > 3$ μm/min. Consequently, at rates below 3 μm/min luminescence pulses should not be observed. Experiment completely confirms this deduction. Thus the mechanism proposed for pulse luminescence in ZnS crystals stimulated by deformation explains all the available experimental facts and we consider it completely proven. It amounts to the following. Charged partial dislocations which move during plastic deformation bring out to the crystal surface a charge which, on accumulating, creates the conditions for a surface electroluminescence pulse to occur. It is therefore natural to give the flashing luminescence occurring during deformation the name "deformation electroluminescence" (DE).

As was earlier the case in CdS, ZnSe, and colored alkali halide crystals, it was possible to detect stationary luminescence produced by deformation in addition to the pulsed luminescence in ZnS crystals. Against the background of intensive bursts of deformation electroluminescence the relatively weak continuous luminescence cannot be recorded. It is exhibited only in conditions where DE is absent: on immersing crystals specially left undoped in an electrically conducting, but optically transparent medium; on examining heavily doped samples, e.g., 6*H* and 4*H* polytypes, for which condition (7) is not fulfilled.

The spectral characteristics of the deformation-stimulated luminescence of 6*H* polytype crystals doped with manganese or copper coincide with the intracenter luminescence of Mn^{+2} ions[15] and the green luminescence of copper complexes[16] respectively (Fig. 8).

Bands of luminescence which coincide with the continuous deformation luminescence are observed on exciting ZnS : Mn and ZnS : Cu crystals with light corresponding to band-to-band absorption. This indicates that all the optically active impurities present in these samples are excited during deformation. The stationary luminescence probably arises as a result of excitation of luminescence centers by charged dislocations moving during plastic deformation. At the present time the detailed mechanism of this process is being investigated.

[1)] The ZnS crystals were kindly provided by M. P. Kulakov, to whom the authors express their sincere gratitude.

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Helicoidal and sinusoidal spin ordering in quasi-one-dimensional magnets

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Using as an example a chain of spins interacting via the conduction electrons, the possibilities of helicoidal and sinusoidal ordering are considered. Expressions are obtained for the correlation functions and for the structure factor. Substances in which observation of this order is possible are indicated.

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1. INTRODUCTION

By now there are a large number of known substances that are quasi-one-dimensional in their magnetic properties (see the reviews[1,2]). The properties of most of them are satisfactorily described by a model with exchange interaction between the nearest spins that are arranged in a chain. The interaction between spins of different chains is assumed to be small. Depending on the type and magnitude of the single-ion anisotropy, the system is described by the Heisenberg model, by the XY model, or by the Ising model. If the interaction along a chain of spins that are not nearest neighbors becomes substantial, then more complicated states with helicoidal and sinusoidal magnetic structures are possible. We consider the properties of such systems using as a model spins interacting via conduction electron. The simplest example of the realization of such a model is a chain of atoms of transition elements. The s-shell electrons become collectivized, and they can be regarded as free, while the f or d electrons are localized on the sites. The localized spins interact with one another via direct exchange, and also indirectly via the conduction electrons. The last interaction is long-range and therefore, even it is small, can substantially alter the properties of a quasi-one-dimensional system.

Assume first that there are no fluctuations. We regard the functional of the free energy of the system as a function of the wave vector of the spin structure. The functional of the energy of the direct interaction of the spin is of the form

$$F_S[q]=2J(q)\mathrm{S}_q\mathrm{S}_{-q},$$

where

$$\mathrm{S}_q=N^{-1/2}\sum_i \mathrm{S}_i\exp(iqx_i),\qquad J(q)=\sum_i J_{ik}\exp[iq(x_i-x_k)].$$

If only the nearest spins interact, then the characteristic scale of the variation of the quantity $J(q)$ is of the order of the period Q_0 of the reciprocal lattice. The electrons are acted upon by a spin field with wave vector q and with an amplitude proportional to $\langle S\rangle$. If q is

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