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G. A. Smolenskii. Phase Transitions in Certain Magnetically Ordered and Ferroelectric Crystals.

Investigation of phase transitions is one of the central problems of contemporary physics. Substantial progress has been made in this field during recent years. The thermodynamic theory of second-order phase transitions has been improved and developed, a scaling theory has been created, specific models have been calculated, including the Ising model, the productive notion of the "soft" mode is being developed successfully, critical indices have been determined for various substances, etc.

It is therefore interesting to accumulate experimental data from study of phase transitions in various crystals. This paper briefly illuminates the results of studies of phase transitions in certain magnetically ordered substances and ferroelectrics.

It is known that a compensation point is observed, in accordance with Neel's theory, in rare-earth ferrimagnetics with garnet-type structure. This point is not a critical point in the absence of a magnetic field. But when an external magnetic field is applied, induced phase transitions appear near the compensation point. A theoretical analysis of this problem was carried out first for an isotropic ferrimagnetic, and then with consideration of magnetic anisotropy.

Two induced phase transitions were observed in terbium iron garnet in^[1]. As the temperature was raised, a transition occurred from one collinear ferrimagnetic phase to a noncollinear (antiferromagnetic) phase and then to another collinear ferrimagnetic phase. These transitions are accompanied by sign reversal of magnetic birefringence, and light scattering by fluctuations of the magnetic moment is observed.

Another example of the phase transitions studied is the spin reorientation in rare-earth orthoferrites with rhombic structure of the perovskite type. At temperatures above 10°K, only the magnetic moments of the iron ions form a magnetically ordered structure. These substances belong to the class of weak ferrimagnetics. At high temperatures, the magnetic-moment vector is directed along the c axis, and the antiferromagnetism vector along the a axis. As the temperature is lowered, a continuous transition occurs in many of these crystals, with the magnetic-moment vector stabilizing along the a axis and the antiferromagnetism vector along the c axis. K. P. Belov et al. showed that second-order phase transitions correspond to the beginning and end of the reorientation range. Investigation of the spin mode corresponding to joint oscillations of the magnetic-sublattice vectors in the a-c plane showed that the frequency of these oscillations drops to zero at the beginning and end of the reorientation range. The appearance of a "soft" spin mode results from the change in magnetic symmetry and not from a change in crystallographic symmetry, as is the case in ferroelectrics.

Studies of the elastic and magnetoelastic properties of various orthoferrites were investigated in^[2] in the frequency range 50 - 1500 MHz. It was shown that the velocity and damping of elastic waves decrease noticeably in the reorientation range along certain crystal-

lographic directions, owing to the coupling of the elastic waves with the soft spin mode.

Experiments were also carried out with magnetostrictive excitation of a high-frequency magnetic field at the fundamental and second-harmonic frequencies by elastic waves. Effective excitation was observed only in the spin-reorientation range.

It was necessary to consider not only the magnetoelastic energy, but also the piezomagnetic energy in order to explain the experimental data on the basis of a thermodynamic analysis.

In contrast to classical ferroelectrics, no distinct phase transition is observed in ferroelectrics of complex composition with perovskite-type structure, such as $\text{RbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. This gave rise to the term "ferroelectric with smeared phase transition." A relaxation type of dielectric polarization is observed in the region of the phase transition in ferroelectrics of this group^[3]. These and other experimental facts can be explained if it is assumed that the smearing of the phase transition is governed by composition fluctuations. In this view, different regions of the crystal (of linear dimension $\sim 100 \text{ \AA}$) have different Curie points. It is assumed that the relaxation is due to: 1) motion of the boundaries between polar and nonpolar phases or 2) the production and vanishing of polar regions. The latter mechanism was calculated in^[4], in which the Debye theory was generalized to the case in which the number of relaxors varies with temperature (with a maximum at the average Curie point T_{av}). It is then possible to explain a number of experimental facts, including the experimentally observed temperature dependence of ϵ : $1/\epsilon = A + B(T - T_{av})^2$.

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V. L. Ginzburg. Surface Excitons of the Electron-Hole Type. It is obvious even from highly general considerations that various surface states (levels) whose populations correspond to the appearance of excitations or quasiparticles (surface phonons, excitons, magnons, electrons at surface levels, etc.) can exist on the surfaces of solids and liquids. It is also natural to assume the possibility of observing surface (i.e., two-dimensional or quasi-two-dimensional) analogs of ferromagnetism, ferroelectricity, superconductivity, superfluidity, etc.

Unfortunately, the investigation of this circle of problems is usually very complex because of the difficulty of obtaining sufficiently perfect surfaces or homogeneous surface layers, because of masking of surface phenomena by bulk effects, and for certain other reasons. As a result, clarification of numerous questions has dragged out over decades; an example is found

in the study of electron surface levels, a problem posed back in 1932^[1] but still unsolved in many respects^[2]. However, the situation has recently been changed by the development of effective methods for production of very high vacuums, monitoring and investigation of surfaces properties^[3], and observing various surface excitations (see, for example, ^[4]). It appears that surface superfluidity of helium was recently observed^[5]. It can be predicted that progress will also be made in regard to such collective effects as surface superconductivity^[6], ferromagnetism^[7,8], the liquid-crystal state^[9], and ferroelectricity^[1]. Another collective phenomenon is exciton condensation, which was discussed for the bulk case in the paper presented here by L. V. Keldysh (see^[13]). It is also natural to discuss this problem as it affects two-dimensional (surface) excitons, as noted by the author at one of the sessions of the Division of General Physics and Astronomy of the USSR Academy of Sciences^[14]. It is the basic purpose of the present paper to discuss the problem of surface excitons and their condensation. We shall not concern ourselves with the macroscopic theory of surface excitons^[15] or the quasimicroscopic theory of the exciton ensemble^[16], but only with surface excitons of the Wannier-Mott type, i.e., hydrogen-like "atoms" consisting of an electron and a hole, which have been studied quite thoroughly for three-dimensional semiconductors^[17].

It is assumed that on the surface of a dielectric 1 that borders on dielectric 2 (one of these media may be a vacuum) there exist two surface bands of electron states analogous to the conduction and valence bands in the three-dimensional problem. To find the levels of surface excitons of the Wannier-Mott type, which may exist in such a system, it is necessary to consider the electrostatic interaction not only directly between the electron and the hole, but also with consideration of the polarizations of media 1 and 2. In a certain approximation^[18] in which the macroscopic theory can be used (the basic requirement is sufficiently large dimensions of the exciton), the interaction energy can be assumed equal to $V = -2e^2/(\epsilon_1 + \epsilon_2)r$, where ϵ_1 and ϵ_2 are the respective dielectric constants of media 1 and 2. Then in the simplest case of isotropic parabolic bands for the electrons and holes, the binding energy of the surface exciton equals

$$E_n = -\frac{2me^4}{\hbar^2(\epsilon_1 + \epsilon_2)^2(n+1/2)^2} \quad (n=0, 1, 2, \dots),$$

where m is the reduced mass of the electron-hole system; the characteristic radius of the exciton in the ground state is $r_0 = \hbar^2(\epsilon_1 + \epsilon_2)/4me^2$ and is found to be large with $(\epsilon_1 + \epsilon_2) \gg 1$ and $m \ll m_0 = 9 \cdot 10^{-28}$ (by comparison with $a_0 = \hbar^2/me^2 = 0.529 \cdot 10^{-8}$ cm). For the three-dimensional case, $E_n = -m'e^4/2\hbar^2\epsilon^2n^2$ ($n = 1, 2, \dots$), so that the difference between the bulk and surface levels is very large even when $\epsilon_1 \approx \epsilon_2 \approx \epsilon$ and the masses m and m' are equal. In a more general case (with consideration of anisotropy and outside of the confines of the macroscopic approximation), the levels of the surface exciton will also, generally speaking, differ strongly from the levels of bulk excitons. The determination of these levels, i.e., observation of surface excitons of the type under discussion, is, of course, a problem of absolutely prime importance. It is highly improbable, though not impossible, that we could observe and study the behavior of a collective of surface excitons without investigating the individual excitons of this type.

It is known that any attraction between particles, no matter how weak, leads to the appearance of a bound level in the two-dimensional problem. Thus, surface excitons that are attracted to one another will always form biexcitons. On a further increase in the exciton concentration n , with the condition $nr_0^2 \gg 1$, the exciton and biexciton gas is collectivized, and we may expect the formation of "metallic" drops and other effects characteristic of the three-dimensional case^[13]. At $r_0 \gtrsim 10^{-6}$ cm, condensation intervenes at $n \lesssim 10^{12}$ cm⁻². Considerations analogous to the above also pertain to the one-dimensional case, which might perhaps be of interest in application to dislocations, "whiskers," the edges of faces, and polymers. Here condensation sets in even at $nr_0 \gtrsim 1$ or $n \lesssim 10^6$ cm⁻¹ (at $r_0 \gtrsim 10^{-6}$ cm).

It is possible to observe individual excitons and the above collective effects, it will also be worthwhile, of course, to study the influence of magnetic fields and deformations, to take anisotropy into consideration, etc. Unfortunately, it is not yet clear to what degree study of Wannier-Mott surface excitons is at all realistic at the experimental level. At the same time, it is clearly not enough to confine ourselves to mere theoretical estimates or even quantitative calculations in this area.

¹For certain types of systems (and superconductors in particular), two-dimensional long-range order, not to mention one-dimensional, cannot exist as a thermodynamic concept. Quite aside from the fact that in many cases (for example, for systems of the Ising type) two-dimensional long-range order is possible even in the thermodynamic equilibrium state, it must be remembered that superfluidity, superconductivity, ferromagnetism, and other "ordering effects" may obtain in the two-dimensional and even in the one-dimensional case, at least in a practical sense, i.e., as the corresponding ordering with arbitrarily large (as $T \rightarrow 0$) lifetimes [¹⁰] or as states with negligibly small (though formally nonzero) resistivity or friction, as states with infinite magnetic susceptibility, etc. (see [^{11,12}]).

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S. I. Radautsan. *Investigation of Compound Semiconductor Materials in the Moldavian SSR*. Experimental study of semiconductors was begun in Moldavia in 1953 at Kishinev State University under the supervision of Prof. M. V. Kot. It is now being developed successfully in the institutes of the Moldavian Academy of Sciences and in a number of the republic's higher educational institutions.

The laboratories of the Institute of Applied Physics of the Moldavian Academy and the departments of the Kishinev Polytechnic Institute are engaged in work on the preparation of compound semiconductors, coordinated study of their properties, and the development of semiconductor devices from them. The objects of study have been defect-type diamond-like semiconductors such as $A_2B_3^6$ and solid solutions in them^[1,2], excess semiconductors of the $A_2B_2^5$ type^[3], gallium and indium phosphides^[4,5], zinc telluride^[6] and solid solutions in them, phases in the cadmium-indium-selenium-tellurium^[7], zinc (cadmium)-indium-sulfur^[8], and indium-antimony-tellurium^[9] systems, and other materials.

Thermal, x-ray-phase, and microstructural analytical methods have been used to study interactions in the ternary indium-antimony-tellurium, indium-arsenic-tellurium, cadmium-indium-selenium, cadmium-zinc-tellurium, and indium-phosphorus-selenium systems, and in certain binary sections of the types $A^3B^5 - A_2B_3^6$, $A^2B^6 - A_2B_3^6$, and $A^2B^6 - A_2B_2^5$. Phase diagrams were constructed as a result of the studies, and new semiconductive phases were discovered, e.g., In_3SbTe_2 , In_2SbTe_3 ^[10], InP_2Se_4 ^[11], and $CdIn_6Se_{10}$ ^[12]. One of the methods of mathematical planning—the simplex array method^[13]—was used for the first time in constructing the phase diagrams of the ternary systems.

Data on phase equilibria in the systems studied were used as a basis for development of a technology for production of the semiconductive materials in the crystalline and vitreous states. Methods were also developed for preparation of anisotropic media based on the indium antimonide-nickel antimonide system and dislocation-free gallium phosphide whiskers^[14]. Work has also been done on the production of thin films and microconductors based on compound semiconductors.

Samples of these systems are used to study the mechanical-property anisotropy and dislocation structure that appear around indentations and scratches. In particular, a qualitative explanation has been offered for the hardness anisotropy observed in the zinc telluride-cadmium telluride system, and it has been shown that slip systems constitute the basic factor leading to the hardness anisotropy of these crystals^[15].

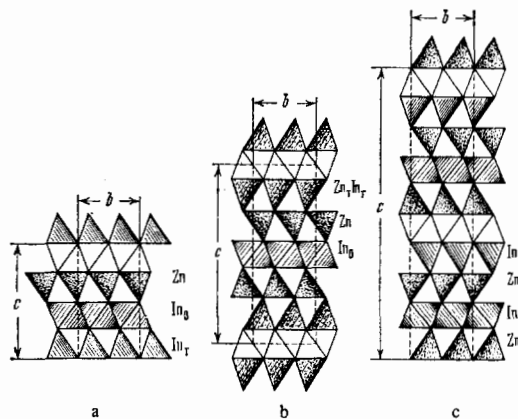


FIG. 1. Projections of structures onto the plane $(2\bar{1}\bar{1}0)$ of the single-packet polytype $ZnIn_2S_4$ ($x = 0.25$) (a), the two-packet polytype $Zn_3In_2S_5$ ($x = 0.40$) (b), and the single-packet polytype $Zn_3In_2S_6$ ($x = 0.50$) (c).

The structures of $Zn_3In_2S_6$ ^[16] and $Zn_2In_2S_5$ ^[17] were deciphered for the first time by x-ray methods. Polytypism of the ternary phases in the $ZnS - In_2S_3$ system was observed and investigated^[18]. Figure 1 presents models of the polytype structures of three compounds in this system, which crystallize with hexagonal symmetry and differ, according to composition, in respect to the lattice parameter along the c axis and the layered disposition of the cations in the tetrahedral and octahedral spaces. The ternary phases of this system can be assigned the general formula $Zn_mIn_2S_{3+m}$, where $m = 1, 2, 3, \dots$. The composition of the phase is determined by the number m . The number of sulfur atoms in the unit cell of the polytypic modification family of a given phase is determined as $N = Z(3 + m)$ (Z is the number of packets in the elementary cell). The formation of various polytypic modifications has made it possible to explain the physical-property scatter reported in the literature for the ternary phase $ZnIn_2S_4$.

The energy-band structure and spectral features of the local states of certain A^3B^5 , A^2B^5 , and A^2B^6 , $A^2B_2^3C_4^6$ crystals, their solid solutions, and vitreous $A_2B_3^6$ semiconductors have been investigated. Band structures were constructed for the first time in the region of the interband-gap minima of certain crystals of the types $A^2B_2^3C_4^6$, $A_2B_3^6$, and A^2B^5 . Values of the energy intervals at the vital points of the Brillouin zone and the splitting due to the crystal field, the spin-orbital interaction, and other effects have been determined. An effect of surface state on the nature of interband transitions in cadmium telluride and mercury telluride crystals and their solid solutions has been observed.

The kinetic coefficients of cadmium arsenide and phosphide single crystals in strong magnetic fields have been studied as functions of field intensity, and the energy-spectrum parameters of the carriers have been determined^[3].

The luminescence properties of compound semiconductors have been investigated. It has been shown that the luminescence centers in crystals of the cadmium-indium-sulfur and zinc-indium-sulfur systems are nonstoichiometric structural defects of the cation-vacancy type with tetrahedral or octahedral coordination of the anions. A relation between the forms of polytypism and features of the luminescence bands has been observed in the zinc-indium-sulfur system^[18]. Thus, Fig. 2 shows luminescence spectra of a single crystal of