which is (roughly) determined by the thickness of the absorber.

2. The negative "charge asymmetry" is significant for low energy π-mesons.

3. The ratio π^+/π^- changes only slightly in going from a heavy element (Pb) to a light element (C).

4. The magnitude of the ratio π^+/π^- increases in going from a mountain altitude to the stratosphere. All these regularities are easy to explain, if we take account of the fact that an overwhelming part of the slow π-mesons is generated by neutrons. The participation of protons in the formation of π-mesons increases with increasing energy of the π-mesons.

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SOVIET PHYSICS JETP VOLUME 5, NUMBER 3 NOVEMBER, 1957

Construction of the Thermodynamic Potential of Rochelle Salt from the Results of the Optical Investigation of Domains

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From the experimental temperature dependence of the monoclinic parameter η and the specific heat c_p, the thermodynamic potential of Rochelle salt can be constructed with accuracy to terms of the order of η^4. The advantages of the optical method of determination of the monoclinic parameter are analyzed in comparison with the electrical and mechanical methods. Results of calculation of the thermodynamic potential surface from the temperature dependence of the angle of spontaneous rotation of the optical indicatrix are given. The possibilities of a rigorous construction (without interpolation) of this surface from data of the optical investigation of domains are pointed out.

AS GINSBURG HAS SHOWN[1], the theory of piezoelectric phenomena can be developed on the basis of the general theory of phase transitions of the second kind[2]. In the general theory it is demonstrated that in the vicinity of the Curie point $T = \Theta$, the expansion of the thermodynamic potential in a power series of the parameter η which characterizes the degree of asymmetry of the system has the form

$$\Phi = \Phi_0 + A\eta^2 + C\eta^4 + \cdots \qquad (1)$$

Ordinarily it is assumed that in expansion (1) we can confine ourselves to only the terms written down, for which $A = a(T - \Theta)$, and C = const. (hereinafter the pressure is assumed constant). The following expressions are then obtained for the temperature dependence of the asymmetry parameter and of the heat capacity.

$$\begin{aligned} &\text{For } T > \Theta: \ \eta = 0, \ c_p = c_{p_0}; \\ &\text{For } T < \Theta: \ \eta^2 = -A/2C, \ c_p = c_{p_0} + Ta^2/2C. \end{aligned} \tag{2}$$

Here $c_{p_0} = -T\partial^2\Phi_0/\partial T^2$. The jump in the specific heat at the Curie point is evidently $\Delta c_p = \Theta a^2/2C$.

In the theory of ferroelectricity, the polarization P is chosen as the asymmetry parameter and the effect of an external electric field E is taken into account by adding the term $-PE$ to the thermodynamic potential [Eq. (1)]. In the case of Rochelle salt there is only one ferroelectric axis, parallel to the x axis. Therefore the additional term has the form $-PE_x$.

Considering a characteristic property of Rochelle salt, namely, its having two Curie points, Ginsburg[1] showed that the function $A(T)$ in this case must be described by a cup-shaped curve whose points of intersection with the abscissa coincide with the Curie points. Only in the neighborhood of these points can we assume $A = a(T - \Theta)$ and have confidence in the correctness of expressions of the type of Eqs. (2).

The question arises whether it is permissible to piece together the form of the function $A(T)$ and in general the complete contour of the thermodynamic potential over the entire ferroelectric interval from the experimental data. First of all, let us forego the simplifying assumptions made in the derivation of Eqs. (2) and assume simply $\Phi = \Phi(T, \eta^2)$. The dependence of the asymmetry parameter on temperature is found from the conditions $\partial\Phi/\partial\eta = 0$, and $\partial^2\Phi/\partial\eta^2 > 0$, whence there follow two solutions: $\eta = 0$ for $(\partial\Phi/\partial\eta^2)_{\eta=0} > 0$ (outside the piezoelectric interval) and $\eta = \eta_0$, where $\eta_0(T)$ satisfies the equation $(\partial\Phi/\partial\eta^2)_{\eta=0} = 0, (\partial^2\Phi/\partial(\eta^2)^2)_{\eta=0} > 0$ (in the piezoelectric interval). Differentiating Φ twice with respect to temperature along the the equilibrium curve $\eta = \eta(T)$, we obtain the expression for the specific heat

$$c_p = -T\left[\frac{\partial^2}{\partial T^2} - \left(\frac{d\eta^2}{dT}\right)^2 \frac{\partial^2}{\partial(\eta^2)^2}\right]\Phi. \tag{3}$$

If η and c_p were known as functions of temperature it would be possible to set up the position of the equilibrium curve of the phases in (Φ, η, T) space. Unfortunately, reliable data even on the magnitude of the jumps of the specific heat at both Curie points[3] are not available. Meanwhile, these data already would allow one to determine the character of the temperature dependence of the coefficient C in the expansion Eq. (1). Actually, from Eq. (3) it follows that at the Curie point ($T = \Theta$, $\eta = 0$)

$$\Delta c_p = \Theta\left(\frac{d\eta^2}{dT}\right)^2 \frac{\partial^2\Phi}{\partial(\eta^2)^2} = 2\Theta\left(\frac{d\eta^2}{dT}\right)^2 C(\Theta). \tag{4}$$

In the case C = const., the value of the jump at one Curie point can be predicted from the known jump of the specific heat at the other Curie point.

We set aside for the time being the question of the rigorous construction of the surface $\Phi = \Phi(T, \eta)$ and note that this surface can be found from the two known functions $\eta = \eta(T)$ and $c_p \doteq c_p(T)$, naturally, only by way of interpolation.

Thus if we confine ourselves to terms of the order η^4 in the expansion Eq. (1) (which, as Ginsburg noted[1] is apparently fully admissible) for Rochelle salt these two functions permit us to find the coefficients $A(T)$ and $C(T)$. For C = const. in the Curie interval

$$A(T) = -2C\eta^2(T) = -\frac{\Delta c_p}{\Theta}\left(\frac{d\eta^2}{dT}\right)^{-2}_{T=\Theta} \eta^2(T). \tag{5}$$

There remains to find the temperature dependence of the asymmetry parameter. The monoclinic angle, the spontaneous polarization, or the spontaneous deformation can serve as this parameter—the monoclinic parameter—for the given case of Rochelle salt. It turns out, however, that X-ray determination of the monoclinic angle[4] gives only semi-quantitative results and studies of the macroscopic polarization[5, 6] or of the macroscopic deformation[7] on specimens which consist of domains of opposite signs do not permit one to strictly distinguish the changes in characteristics of the individual domains, which interest us, and the effects brought about by the motion of domain (twin) boundaries.

Use of the optical method[8, 3] which permits one to obtain an individual characteristic of the domains, appears more reliable. Here it is convenient to take as the asymmetry parameter the angle of rotation of the optical indicatrix about the x axis, proportional to the spontaneous deformation of the domain. This angle is simply determined from the angle 2α between the positions of extinction in neighboring domains[3].

The results of a preliminary study of the temperature dependence of the asymmetry parameter chosen in this manner (the monoclinic parameter) are brought to light in the dissertation of one of the authors[3]: the results of a more careful investigation were reported at the recent conference (June of this year) on ferroelectricity.

The measurement of the angle between the positions of extinction in the components of a twin (of adjacent antiparallel domains) was carried out by means of a bi-quartz plate. In connection with the observed dispersion of the extinction positions, the measurements were carried out with a 540 mμ filter (transmission bandwidth 10 mμ).

The results of the measurements carried out on one of the specimens are presented in Fig. 1. Each point corresponds to the arithmetic mean of not less than five readings. The monoclinic parameter of Rochelle salt crystals in the interval between the Curie points varies continuously and reaches a maximum value at a temperature which lies midway between the Curie points (about 3°C). In accordance with Eqs. (2) the curve displays in the vicinity of the Curie points characteristic parabolic portions, which are linear if one plots the curve $\eta^2 = \eta^2(T)$. The latter curve also characterizes the temperature dependence of the coefficient A.

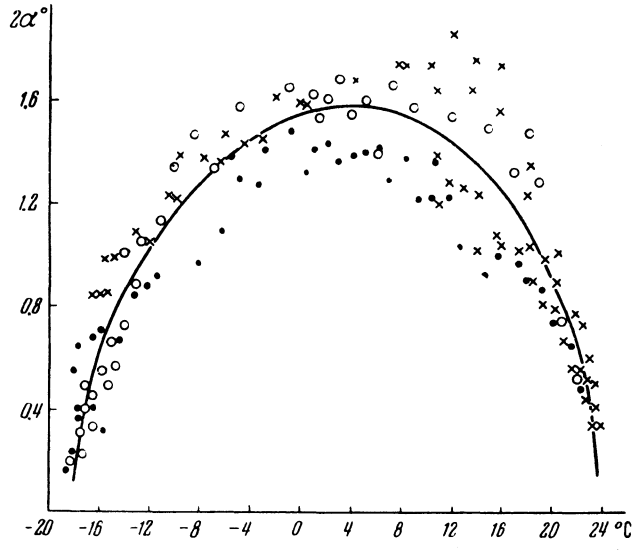

FIG. 1. Temperature dependence of the angle between the positions of extinction in adjacent domains in a Rochelle salt crystal.

We calculated the coefficient C from the jump in specific heat (5 cals/mol)[9, 5] at the upper Curie point to be approximately 5.10^7 cal/mol (the monoclinic parameter expressed in radians, $\eta = \alpha^\circ \pi/180$). Since the maximum value of the monoclinic parameter is $\eta_{\max} = 1.4 \times 10^{-2}$, the maximum change of the value of the thermodynamic potential brought about by a deviation of the system from the symmetrical state amounts to $\Delta\Phi = -C\eta^4_{\max} = -2$ cal/mol.

The surface of the thermodynamic potential calculated according to Eq. (1) is characterized in Fig. 2 by a contour plan corresponding to constant values of the thermodynamic potential (relative to Φ_0). Curves outside the ferroelectric interval are obtained by extrapolation. The general form of the three dimensional model of the surface $\Phi = \Phi(T, \eta)$ constructed from this data is shown in Fig. 3. In the ferroelectric region the "gorge" goes over to a "valley" with two depressions of depth 2 cal/mol.

Conversion from one monoclinic parameter to another (for example, to the polarization P_x or to the deformation ϵ_{yz}) corresponds simply to a change in one of the scales of the model. The slope of the curves obtained in cross-sections for $T = \text{const.}$ gives the value of the generalized force pertaining to this parameter (for example, the electric field intensity E_x or the tangential stress τ_{yz}), while the curvature of these curves gives the corresponding moduli (for example, the dielectric constant of the crystal or the shear modulus).

The effect of a mechanical-stress field or of an external electric field is taken into account by adding to the thermodynamic potential terms of the type $-P_x E_x$ and $-\epsilon_{yz}\tau_{yz}$ which is equivalent to a rotation of the base of the model about the temperature axis. This causes the equilibrium positions on the potential wells to shift until the slope exceeds a certain critical value and one of the equilibrium positions becomes unstable. At this instant one of the domain systems in the specimen must completely disappear.

The above points to the possibility of a rigorous construction of the thermodynamic potential surface (without interpolation) directly from the optical characteristics of the domains measured on loaded crystals. By such means, evidently, it is possible to obtain experimental points on any portion of the surface with the exception of the region of unstable equilibrium adjoining the temperature axis, in which in general the system of domains under study fades out.

In conclusion the authors express deep thanks to V. I. Ginsburg for his interest in the work and for his valuable comments during its discussion.

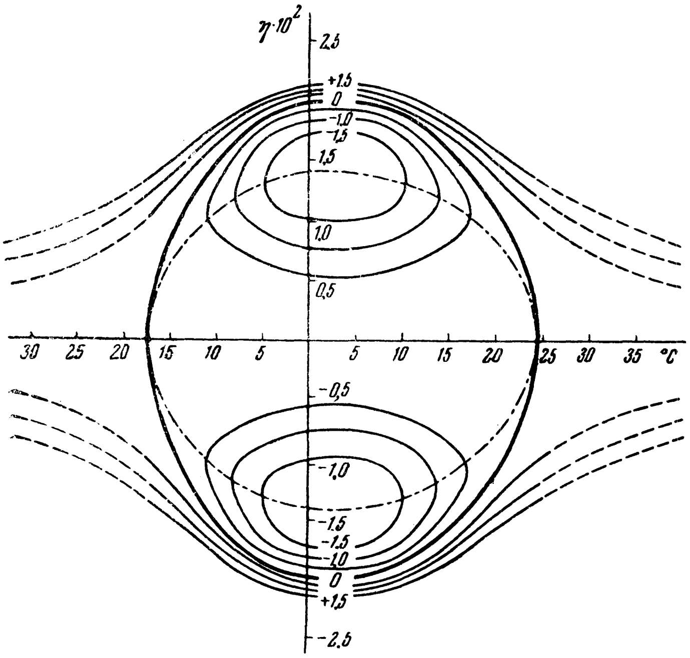

FIG. 2. Chart of the thermodynamic potential surface. The numbers on the contours are in cal/mol. The zero contours are set off by broad lines. The portions of the contours outside the ferroelectric region are obtained by extrapolation and are marked by dashes. The dot-dash curve gives the experimental temperature dependence of the monoclinic parameter.

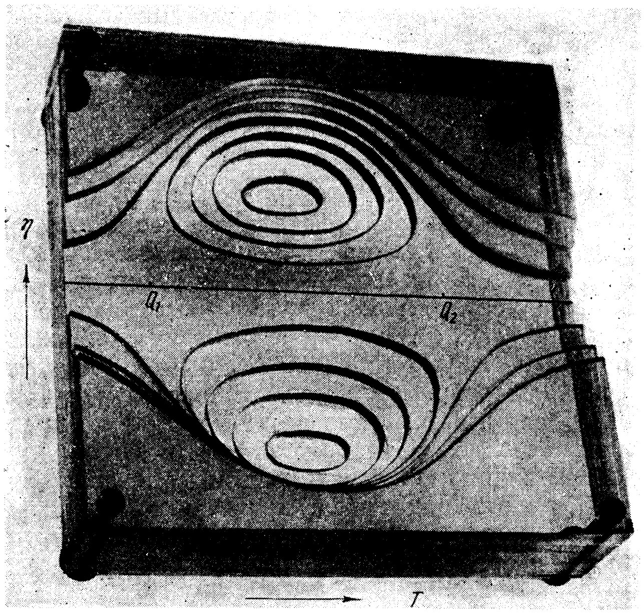

FIG. 3. Three dimensional model of the thermodynamic potential. The scale is 0.5 cal/mol per step. The zero contour consists of the straight line parallel to the temperature axis, and of an oval curve which envelops the potential wells intersecting at the Curie points (denoted by Q_1 and Q_2 in the figure).

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The Effect of Fast Neutron Irradiation on the Recombination of Electrons and Holes in Germanium Crystals

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It is found that irradiation of germanium crystals with fast neutrons leads to an increase of the rate of volume recombination. The probability of recombination trapping of charge carriers by defects which appear as a result of irradiation is estimated. The strong effect of neutron irradiation on the lifetime of carriers can be used to record and measure integral fluxes of fast neutrons.

1. STRUCTURAL DEFECTS OCCUR in crystals under the influence of fast neutrons. The disturbance of the periodic structure changes the mechanical, electrical, and optical properties of the crystals. The changes of the electrical conductivity of germanium and of silicon subjected to the action of fast neutrons have been studied by many investigators, in particular Lark-Horowitz[1] and Fan [2], and have been utilized in a dosimeter proposed by Cassen[3].

Structural defects in crystals of semiconductors serve as recombination trapping centers for electrons and holes. The effective capture cross-section for holes by defects formed in the bombardment of germanium by electrons with energy above 0.5 Mev was estimated in our work[4] and came to $0.7 \cdot 10^{-16}$ cm^2, *i.e.*, close to the capture cross-section of thermoacceptors, according to the data of Kalishnikov and Ostroborodova[5].

The purpose of the present work is to estimate the effect of germanium-crystal neutron-produced lattice defects on the recombination of electrons and holes.

The number of germanium nuclei displaced owing to scattering of fast neutrons by the lattice sites as a result can be calculated on the basis of data on the transverse cross-sections for the interaction of fast neutrons with Ge nuclei[6]. According to Ref. 6, the transverse cross-sections for the scattering of germanium nuclei by fast neutrons with energy E_n in the range 0.4 – 3.5 Mev are respectively

E_n, Mev	0.4	1.0	1.5	2	3.5	14
T, barns	5.5	5.0	3.5	3.3	3.5	2*

As a consequence of the fact that the energy transferred to a germanium nucleus by fast neutron can amount to a significant figure ($0.054\,E_n$), secondary and higher atomic displacements can occur. Ref. 7, gives a method of calculating the total number $\bar{N}_d$ of Ge atoms displaced as a result of primary energy transfer. Allowing for the possibility that an

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*The atlas of transverse cross-sections contains no data on σ_t for $E_n = 14$ Mev. The value 2×10^{-27} cm^2 is obtained by extrapolation. The accuracy of the estimate is not lower than ± 50%.