grows according to the law $I \sim \varepsilon^{-0.22}$, that is, the intensity of the scattered light increases when the temperature of the solution is decreased. This "strange" phenomenon, of course, was not explained in the cited work.[8] Yet is is easily and naturally explained if the effect of narrowing of a broader region of the RLW in the same solution is considered; we reported this narrowing earlier (Refs. 3 and 10). Studies of the temperature dynamics of the RLW in the present work and also in previous works (Refs. 2–5, and 10), and the results of studies of the temperature dynamics of the width of depolarized lines in Raman scattering of light (LRSL) (Refs, 4 and 16) clearly show that the widths of RLW and LRSL decrease upon approach to the critical stratification point. The results give grounds for assuming that upon approach to the critical point of the solution the character of the orientational motion of the molecules of the medium is changed.

The authors wish to thank A. S. Zolot'ko for help in conducting the experiments.

[1)] For sufficiently large frequencies, much higher than the reciprocal of the shortest relaxation time, the intensity of the RLW can depend on the frequency in accord with another law, in particular, exponentially. The authors did not investigate this frequency region in this work.

[2)] Equation (3) is cited by Wilson[14] without proof. We did not find in the literature a proof of the validity of replacing r by r_c in the well known formula for D_r.

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Adiabatic mechanism of broadening of zero-phonon lines in impurity-crystal spectra

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It is demonstrated experimentally that the adiabatic mechanism of electron-phonon interaction is responsible for the temperature broadening of optical zero-phonon lines (ZPL) in the spectra of the impurity centers of crystals. A quantitative correlation is established between the rate of the temperature broadening of the ZPL and the nonspecularity of their accompanying phonon wings in the fluorescence and absorption spectra. It is shown that the quadratic electron-phonon interaction that leads to the broadening of the investigated ZPL is strong, i.e., it cannot be accounted for by perturbation theory. The temperature dependence of the Debye-Waller factor is investigated and it is established that the Herzberg-Teller interaction is reponsible for the formation of the phonon wing in the allowed electronic transition. The theory is compared with experiment without the use of free parameters.

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1. INTRODUCTION

It is known[1–3] that the homogeneous width of the optical zero-phonon lines (ZPL) in the spectra of impurity crystals exceeds by one or two orders, even at liquid-helium temperature, the natural width γ connected with the level lifetime τ by the usual relation $\gamma = \hbar/\tau$. Various mechanisms were proposed for the temperature broadening of the ZPL.[4–6] The most accepted was the adiabatic mechanism proposed by Silsbee.[6] He has shown theoretically that if electronic excitation of the impurity center is accompanied by a change in the force constants that couple it with the environment, then the second moment of the optical ZPL depends on temperature. This mechanism is described by an electron-phonon interaction that is quadratic in the phonon operators. It was shown theoretically[7,8] that the quadratic interaction is capable of broadening not only optical ZPL but also Mössbauer lines.[1)]

Perturbation theory yielded formulas for the ZPL temperature broadening,[8,9] and the ZPL turned out to have a Lorentz shape. Although these formulas were subsequently repeatedly used to interpret the experimentally observed broadening,[10] the question of the responsibility of the Silsbee adiabatic mechanism for the broadening of optical ZPL is still open. The point is that the criterion used in all papers to assess the correspondence between the theory and the experiment was the coincidence of the theoretical $\gamma(T)$ curve with the experimental one. Yet the theoretical formula for $\gamma(T)$ contains two unknown quantities—the interaction constant and the spectrum of the phonons responsible for the broadening. Therefore the agreement attained by suitable choice of the corresponding parameter can naturally not serve as the basis for concluding that the theory agrees with experiment. We shall demonstrate this later on (see also Ref. 10).

The purpose of the present study was to demonstrate experimentally that the change of the crystal force matrix is responsible for the temperature broadening of the optical ZPL. The proof is based on the use of quantitative relations[11] between two different effects—the nonspecularity of the phonon wings (PW) in the fluorescence and absorption spectra, and the temperature broadening of the ZPL. The change of the force matrix of the crystal upon excitation of the impurity leads to a specific violation of the mirror symmetry of the PW,[11] and if the temperature broadening of the ZPL is due, as proposed by Silsbee,[6] to the same cause, then the two effects should correlate with each other. It is precisely such a correlation which is established in the present paper. This makes it possible to eliminate the free parameters of the theory and carry out an unambiguous comparison of the experimentally observed and theoretically calculated broadenings. It was established in passim that the Herzberg-Teller interaction is responsible for the formation of the phonon satellites of the ZPL. What is unexpected here that the Franck-Condon interaction does not take part in the formation of the PW of the dipole-allowed electronic transition. This fact is proved by comparison with a theory that contains no free parameters.

2. EXPERIMENTAL PROCEDURE

The method of quasi-line spectra is used.[12] A flat quartz cell with a solution of 3, 4, 6, 7-dibenzopyrine in n-octane was placed in a metallic helium cryostat with quartz windows. To prevent distortion of the excitation spectrum, as well as to eliminate the influence of the reabsorption on the fluorescence spectrum, we used weak solutions (10^{-5}–10^{-6} mole/liter) and thin cells (50–100 μm). The freezing was by slow cooling of the solution in the cryostat for 20–30 min. The cryostat was provided with an automatic temperature control system. The temperature was measured with a calibrated carbon resistor and maintained constant within 0.1.°

The fluorescence was excited with a mercury lamp and a filter that separated the 313 nm lime, and was registered with a DFS-12 diffraction spectrometer. The light source used to obtain the excitation spectra was a DKSL-1000 lamp. In this case the DFS-12 spectrometer was used as an exciting monochromator, and the fluorescence was registered with an MDR-72 monochromator. The light-sensitive receiver was an FÉU-79 photomultiplier operating in the photon-counting mode. The spectral width of the DFS-12 slit was 0.2 Å when used to register the fluorescence and 0.5 Å in the case of the excitation spectra. The experimental results were reduced with an EC-1022 computer.

3. EXPERIMENTAL RESULTS AND DISCUSSION

We chose for the experimental investigation an impurity 3, 4, 6, 7-dibenzopyrene crystal in n-octane. The choice of this crystal was governed by a very important, for our purposes, feature of its spectra, which are shown in Fig. 1. The fluorescence and excitation spectra in the region of the 0–0 transition of the impurity at 4.2 K consist of an intense ZPL (3962 Å) and two symmetrically located weak phonon satellites.

Attention is called to the unusually narrow PW, whose width ~7 cm^{-1} is comparable with the ZPL width, whereas the PW previously observed in n-paraffins[13] were several dozen reciprocal centimeters wide. Inasmuch as in our case the PW is much narrower than the spectrum of the acoustic phonons, it can be regarded as a manifestation of a quasilocal vibration. Such a PW offers a number of advantages when it comes to quantitative reduction of the spectrum, since the one- and two-phonon transitions are separated in frequency; this ob-

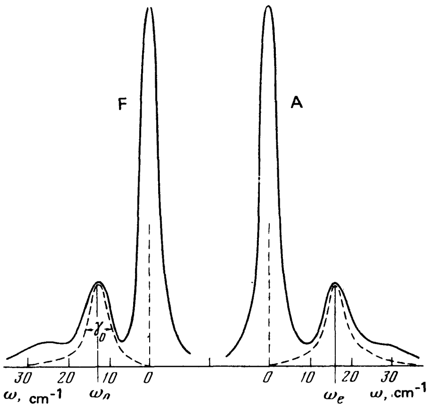

FIG. 1. Spectra of fluorescence (F) and of fluorescence excitation (A) in the region of the 0—0 transition of the solution of 3,4,6,7-dibenzopyrene in n-octane at 4.2 K (solid line—observed spectrum, dashed—spectrum after exclusion of the inhomogeneous broadening; $\omega_0 = 13.1\ \text{cm}^{-1}$, $\omega_e = 15.6\ \text{cm}^{-1}$, $\gamma_0 = 4.6\ \text{cm}^{-1}$).

viates the need for separating from the PW the one-phonon transitions needed for the calculation of the temperature effects (see Sec. 3c below). In addition, the temperature-broadening formulas take in this case the simplest form (see footnote 2).

Figure 1 shows also distinctly the weak peaks corresponding to the second photon of the quasi-local vibration. The absorption and emission spectra exhibit an approximate mirror symmetry, which manifests itself in particular in the fact that the Debye-Waller factor α, defined by the ratio of the integrated ZPL intensity to the combined intensity of the ZPL and the PW in both spectra, turned out to be the same at 0.71–0.73. At the same time, the PW has a somewhat different shape, as manifest by the fact that the frequency of the local phonon in the excited state is approximately 20% higher than in the ground state.

We have investigated the temperature dependence of the spectra in the temperature interval 4.2–40 K. Two different temperature effects were investigated—the change in the distribution of the intensity in the spectra, and the ZPL broadening. The first is mainly caused by that term in the electron-phonon-interaction operator which is linear in the nuclear coordinates,[14,15] or by the Herzberg-Teller interaction.[10] The strength of this interaction is characterized by the Debye-Waller factor. The value of α obtained by us is typical of spectra with undeveloped PW and is evidence that this interaction is weak. At the same time, the electron-phonon interaction quadratic in the coordinates of the nuclei, and the associated temperature broadening of the ZPL, will be shown to be far from weak.

a. *Temperature broadening of the ZPL.* The line widths in the spectra obtained in frozen *n*-paraffine matrices contains an appreciable contribution of inhomogeneous broadening, and is determined by the latter practically completely at 4.2 K.[16,17] This raised the question of separating the homogeneous width from the experimentally measured one. It was established by the gap-burning method[1-3] that the homogeneous line width at 4.2 K amounts to ~0.01 cm^{-1}, whereas the ZPL investigated by us has at this temperature a width 3.8 cm^{-1}. It can therefore be assumed with good accuracy that the homogeneous width at 4.2 K is zero, and the considered ZPL contour can be regarded at this temperature as a function of the inhomogeneous distributionof the impurity centers. Then the ZPL at higher temperatures should constitute a convolution of the homogeneous component and of the ZPL contour at 4.2 K.

Using the known result of the theory,[8-11] according to which the temperature broadening leads to a Lorentz shape of the ZPL, we have convoluted the inhomogeneous distribution function with a set of trial Lorentz contours of various widths and compared the calculated contour with the measured one. The trial contour for which the agreement was best taken to be the true one. The homogeneous obtained in this manner was compared with the theoretical one. The same method was used to obtain the homogeneous width of the PW (see Fig. 1). We note that the method used sometimes to find the homogeneous width by arithmetic subtraction of the inhomogeneous component from the observed width leads to substantial errors. For example, the average rate of temperature broadening calculated by this method would be 0.06 cm^{-1}/deg, as against the actually much larger 0.1 cm^{-1}/deg. However, whereas in the former case the electron-phonon interaction can still be regarded as weak, in the latter it is strong, i.e., it cannot be treated by perturbation theory.[10]

To interpret the experimentally observed broadening we resorted to a recently developed theory[10,11] used in the case of an arbitrary strength of the electron-phonon interaction and based only on the adiabatic and harmonic approximation. According to this theory, the formula for the temperature broadening of the ZPL can be represented in the form

$$\gamma(T)=\int_0^\infty \frac{d\omega}{2\pi}\ln[1+4W^2n(\omega)(n(\omega)+1)\Gamma^0(\omega)\Gamma^e(\omega)]. \tag{1}$$

In this formula W is a parameter that characterizes the strength of the electron-phonon interaction, $n(\omega)=(e^{\hbar\omega/kT}-1)^{-1}$, and the functions $\Gamma^0(\omega)$ and $\Gamma^e(\omega)$ determine the intensity distributions in the PW of the fluorescence and absorption spectra, respectively, and can be obtained in principle from the PW. Since these functions are not independent, but are interrelated [see Eq. (4)]. it suffices to know only one of them, e.g., $\Gamma^0(\omega)$. We have simply approximated it by a Lorentz contour with a width equal to the homogeneous width of the PW.

Special calculations, which are briefly discussed in Sec. 3c below, show that the true shape of $\Gamma^0(\omega)$ differs only insignificantly from a Lorentz contour, and these differences are inessential in the calculations that follow. Since the function $\Gamma^0(\omega)$ is normalized by the condition

$$\int_0^\infty \frac{d\omega}{\pi}\omega\Gamma^0(\omega)=1, \tag{2}$$

it can be uniquely determined by measuring in the spectrum only the position of the maximum (ω_0) and the homogeneous width of the PW (γ_0) at 4.2 K (Fig. 1). The latter was obtained by the procedure described above and amounted to $\gamma_0=4.6$ cm^{-1}.

Thus, to calculate the temperature broadening of the ZPL it suffices to find the parameter W. In the case of a strictly localized vibration it is determined by the simple relation

$$W={}^1/_2(\omega_e^2-\omega_0^2), \tag{3}$$

where ω_0 and ω_e are the frequencies of the local vibration in the ground and excited states, respectively.[2)] It is seen therefore that the larger the frequency difference and the associated deviation of the fluorescence and absorption spectra from mirror symmetry, the stronger the ZPL temperature broadening. This effect was observed qualitatively by Meletov and Sheka.[18]

In the case of a continuous frequency spectrum, the parameter W can be obtained with the aid of the formula that connects the intensity distributions in the fluorescence and absorption spectra[11]:

$$\Gamma^e(\omega)=\frac{\Gamma^0(\omega)}{[1-W\Omega(\omega)]^2+[W\Gamma^0(\omega)]^2}, \tag{4}$$

where

$$\Omega(\omega)=\int_0^\infty\frac{d\nu}{\pi}\,\frac{2\nu\Gamma^0(\nu)}{\omega^2-\nu^2}.$$

the parameter W was chosen such that when the function $\Gamma^0(\omega)$ with the maximum at the point ω_0 and with half-width γ_0 is substituted in (4) the result is the maximum of the function $\Gamma^e(\omega)$ at the frequency ω_e (see Fig. 1). The dimensionless parameter $b=W/\omega_0^2$ is then equal to[3)] 0.19.

Thus, all the quantities in (1) were determined directly from experiment. In addition to Eq. (1) we calculated the temperature broadening of the ZPL also by using the weak-coupling formulas[8] derived especially for the case of interaction with one local phonon, assuming a weak quadratic electron-phonon interaction:

$$\gamma(T)=\frac{2W^2}{\omega_0^2\gamma_0}n(\omega_0)\,(n(\omega_0)+1). \tag{5}$$

Equation (5) is used very frequently to describe the experimental function $\gamma(T)$. We therefore compare (1) and (5) in light of our experimental data. The result of calculation by Eqs. (1) and (5), as well as the measured broadening, is shown in Fig. 2. As seen from the figure, Eq. (5) cannot describe the experimental data. At the same time Eq. (1), which exhibits saturation as a function of W, agrees well with experiment. The results prove that the adiabatic mechanism[6] is responsible for the temperature broadening of the ZPL.

We turn now to Eq. (5) and show with the aid of simple estimates that it cannot be applied in our case also on theoretical grounds. As was established in Ref. 10, at $W\Gamma^0(\omega)\ll 1$ Eq. (1) goes over into (5) if the distribution $\Gamma^0(\omega)$ has a Lorentz shape. It can then be easily shown that the criterion of applicability of Eq. (5) reduces to the requirement $2W/\gamma_0\omega_0\ll 1$. In our case, however, this quantity is equal to 1.1, thus attesting to a strong electron-phonon interaction. If we do not adhere rigorously to the experimentally determined parameters but find them by fitting as is customarily done, then Eq. (5) can also be used to describe well the observed broadening. We have performed the corresponding calculation, specifying an experimentally obtained value of one of the parameters (ω_0 or W) and varying the other. In both cases, at the optimal parameters, the average deviation of the calculated values of $\gamma(T)$ from the specified ones did not exceed 0.2 cm^{-1}, which is within the limits of the measurement error. This calculation shows clearly that a comparison of theory with experiment on the basis of selection of the parameter is incorrect.

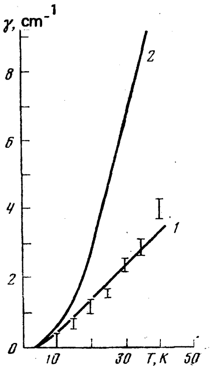

FIG. 2. Temperature broadening of ZPL (3962 Å): 1—calculated from Eq. (1), 2—from Eq. (5); vertical bars—experimental values.

b. *Temperature dependence of the intensity distribution in the spectra.* Two different interactions take part in the formation of the PW of the optical spectra of the impurity centers. The Franck-Condon (FC) electron-phonon interaction[14,15] based on an approximation in which the electron dipole moment of the transition is assumed to be independent of the coordinates of the nuclei, leads to equality of the factor α in the absorption and emission spectra. If we take into account in addition the dependence of the dipole matrix element on the coordinates of the nuclei (the Herzberg-Teller interaction), then this leads to violation of the symmetry of the emission and absorption spectra over the area under the PW.[19] Finally, one cannot exclude in principle a situation wherein the PW is determined entirely by the Herzberg-Teller (HT) interaction, in analogy with the case of forbidden electronic transitions. In this case the emission and absorption spectra turn out again to be symmetrical. For dipole-allowed electronic transitions, however, such a possibility seems quite exotic and is disregarded in practice.

In our case, the equality of the factors α in the absorption and fluorescence spectra, as well as the allowed character of the electronic transition, suggest the FC mechanism for the appearance of the PW. In this case we can calculate the temperatuare dependence of the Debye-Waller factor from the known function[13] $\Gamma^0(\omega)$ with the aid of the formula

$$\alpha(T)=\exp\left\{-A\int_0^\infty d\omega\,\Gamma^0(\omega)\,[2n(\omega)+1]\right\}, \tag{6}$$

where A is a constant obtained by calibrating $\alpha(T)$ at 4.2 from the experimentally measured value. We have carried out the calculation by formula (6) and found an utter disagreement between theory and experiment (Fig. 3, curve 1). The theory called for a rapid fall-off of the ZPL intensity with temperature, whereas in fact the ZPL intensity hardly decreased, and the ZPL was clearly observable even at 50 K. It remained to assume that the PW is due entirely to the HT interaction.

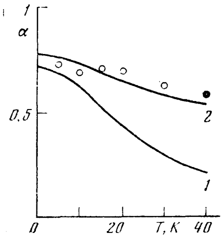

FIG. 3. Temperature dependence of the Debye-Waller factor: 1—calculated from Eq. (6), 2—from Eqs. (7) and (8); points—experimental values.

To check on this assumption, a calculation was performed using the Osad'ko formulas.[19] According to the theory, in the case of an HT interaction with one vibration the temperature dependence of the integrated intensity of the ZPL, $I_0(T)$, and of the intensity $I(T)$ of the entire ZPL + PW band, are determined by the expressions

$$(I_0(T))^{1/2}=\int_{-\infty}^{\infty}\frac{d\rho}{\pi^{1/2}}e^{-\rho^2}M(R), \tag{7}$$

$$I(T)=\int_{-\infty}^{\infty}\frac{d\rho}{\pi^{1/2}}e^{-\rho^2}M^2(R); \tag{8}$$

$$\rho=\frac{R}{2^{1/2}}\left(\operatorname{th}\frac{\hbar\omega_0}{2kT}\right)^{1/2},$$

where $M(R)$ is the electronic matrix moment of the transition. Expanding $M(R)$ in terms of the coordinates of the nuclei and retaining the first three terms of the expansion, we have calculated the temperature dependence of the Debye-Waller factor $\alpha(T)$. This dependence is determined completely by the coefficients M_0, M_1, and M_2 of the corresponding powers of R. The coefficients can be easily obtained from the spectrum[10] using the values of the integrated intensity of the ZPL, the peak of the local vibration, and its second quantum. According to our experimental data, $M_1/M_0=0.64$ and $M_2/M_0=0.17$. These values were substituted in Eqs. (7) and (8). As seen from Fig. 3 (curve 2), the calculation and the experimental data agree well, thus attesting to the HT mechanism of the appearance of the PW in the allowed electronic transition.

Thus, there is no nonlinear FC interaction within the limits of the experimental accuracy.4) Simple estimates show that it is at least several times weaker than the quadratic FC interaction. This surprising result contradicts the widely held opinion that the strength of the linear electron-phonon interaction predominates.

c. *Connection of* $\Gamma^0(\omega)$ *and* $\Gamma^{\bullet}(\omega)$ *with the one-phonon transition probability*. Since, as seen from Fig. 1, the region of the one-phonon and two-phonon transitions is spectrally resolved and the contribution of the multiphonon transitions is negligibly small, the one-phonon function $v^0(\omega)$, which has the meaning of the probability of the one-phonon transitions, agrees, apart from a constant, with the homogeneous part of the PW. On the other hand, the function $v^0(\omega)$ is connected with the function $\Gamma^0(\omega)$ by the relation[11]

$$v^0(\omega)=a^2(\omega-\Delta)^2\Gamma^0(\omega)e^{-2\psi(-\omega)}; \tag{9}$$

$$\Delta=\int_0^{\infty}\frac{d\nu}{-\pi}\Delta(\nu);\qquad \psi(-\omega)=\int_0^{\infty}\frac{d\nu}{\pi}\frac{\Delta(\nu)}{\omega+\nu};$$

$$\Delta(\nu)=\operatorname{arctg}\frac{W\Gamma^0(\omega)}{1-W\Omega(\omega)},$$

where a is a constant equal to the shift of the equilibrium position of the oscillator in the electronic transition.

The results of the present study show that it is possible to use in lieu of (9) a very simple connection between $\Gamma^0(\omega)$ and $v^0(\omega)$; in our case, at any rate, these quantities can be regarded as simply proportional. This is illustrated in Fig. 4, which shows the results of the calculation of the function $v^0(\omega)$ for a given function $\Gamma^0(\omega)$, using the exact expression (9). As seen from the figure, the widths and the positions of the maxima of both functions are practically the same, and their difference reduces to a small change in the shape of the contour (and also to a difference in the integrated intensity). The contour shape, however, does not play an important role in the calculation of the temperature broadening of the ZPL. Thus, for example, if $\Gamma^0(\omega)$ is specified to be a Gaussian distribution, the calculated width of the ZPL at 30 K changes by only 12%. It is therefore possible to replace $\Gamma^0(\omega)$, with sufficient accuracy, by the function $v^0(\omega)$ obtained from the spectrum, normalize the latter with the aid of expression (2), and then use it to calculate the temperature broadening of the ZPL. The proportionality of the functions $v^0(\omega)$ and $\Gamma^0(\omega)$ is a very important factor in the practical utilization of the strong-coupling formulas.

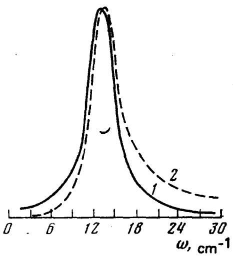

FIG. 4. Calculation of the function $v^0(\omega)$ calculated with the aid of Eq. (9) (curve 2) given the function $\Gamma^0(\omega)$ (curve 1).

We have thus suceeded in this paper in describing quantitatively two essentially different temperature effects, without using even a single parameter that cannot be obtained directly from the spectrum. This is evidence of the applicability of the adiabatic theory of the impurity center for the description of the experimental results. We have proved that the quadratic electron-phonon interaction is responsible for the temperature broadening of the ZPL. It was established that the phonon satellites of the ZPL are due to Herzberg-Teller interaction. It was shown that in our case the linear Franck-Condon interaction is negligibly small compared with the quadratic one.

In conclusion the authors consider it their pleasant duty to thank I. S. Osad'ko for help with the work and for helpful discussions.

1) In the latter case the quadratic electron-phonon interaction is due to the change of the mass of the nucleus following emission of the γ quantum.[7]

2) In the case of an arbitrary phonon spectrum, W represents generally speaking a matrix that degenerates into a number only for the simplified model of the interaction.[10,11] In our investigation, since the PW is narrow, we can approximate W by a number.

3) It is of interest to note that the values obtained for the parameter from Eqs. (3) and (4) differed by only 10%. This is the consequence of the narrowness of the PW and confirms the interpretation according to which the PW is formed by one quasilocal vibration.

4) A definite contribution to the temperature dependence of the Debye-Waller factor can be made also by the quadratic FC interaction. This contribution, however, is negligibly small.

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Energy and angular distributions of particles reflected in glancing incidence of a beam of ions on the surface of a material

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An analytic solution is obtained of the problem of a reflection of a wide beam of charged particles incident at a glancing angle on the surface of a material. The angular and energy distributions are found for a wide range (from atomic to relativistic) of ion velocities. The theoretical results are in good agreement with experiments.

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1. INTRODUCTION

Reflection of particles from the surfaces of materials plays an important role in the problems of radiation stability of surfaces and radiation shielding. Moreover, reflection of particles from surfaces is the basis of various methods for investigating surface layers. In particular, sputtering of a surface by a glancing ion beam is used to determine the chemical composition of surface layers.

In the last two decades the problem of reflection of particles from the surfaces has been investigated intensively both experimentally[1-12] and theoretically.[13-20] The results of experimental investigations on the backscattering of ions by solid targets were summarized by Mashkova and Mochanov,[4] who formulated the following characteristic features established experimentally.

1. At low glancing angles ζ_0 the energy spectrum of reflected particles is very narrow.

2. When the scattering angle $\vartheta = \zeta_0$ is doubled (Fig. 1), the half-width of the energy spectrum changes by an order of magnitude.

3. The form of the energy spectrum is invariant under the transposition $\zeta_0 \rightleftarrows \zeta$.

4. The relative intensity of the reflected particles decreases on reduction in the nuclear charge Z_2 of the target atoms.

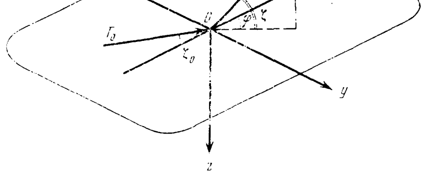

FIG. 1. Target surface coincides with the xy plane and the z axis is directed into the target. The primary beam of ions of kinetic energy T_0 is incident at an angle ζ_0 to the surface. The angular and energy distributions of the reflected particles are characterized by the angles ζ, φ and by the energy T.