

located near that end of the sample which was in contact with the cooling salt. The distance between them was 3 cm.

The results of the measurement of a^2 are shown in Fig. 1c.

The specific heat of the investigated sample was calculated from the curves of Fig. 1. As can be seen from Fig. 2, at temperatures above 0.15°K, the specific heat in the intermediate state changes in proportion to the temperature, $C_n = \alpha(\eta)T$, regardless of what fraction η of the sample is in the normal phase. This variation of $C_n(T)$ is to be expected in the absence of quantization of the energy levels, since both the specific heat of the lattice and the specific heat connected with the change in the magnetic energy are negligibly small at the investigated temperatures and magnetic fields. In the region of lower temperatures, deviations from the law $C_n = \alpha(\eta)T$ are observed, and are more strongly pronounced the smaller the fraction of the sample in the normal phase. According to [3], a similar character of the variation of the specific heat offers evidence of the appearance of quantization of the energy levels of the electronic excitations. The difference by almost a factor of 2 between $T_0 = \epsilon_0/k$ and the temperature with which the deviations from the $C_n = \alpha(\eta)T$ appear can be readily related to the form of the electronic excitation spectrum [3].

Thus, the measurements made in the region 0.1 - 0.15°K showed that the specific heat of a superconductor decreases in the intermediate state. Although this decrease is only 2 - 3 times larger than the possible experimental error, it can be related to the quantization of the energy levels of the electronic excitations considered by Andreev [3].

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THREE-PHOTON MOLECULAR SCATTERING OF LIGHT

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The subject of this note is an estimate of the cross sections of three-photon Rayleigh and Raman scattering of light in gases and liquids. A study of such scattering yields information on the nonlinear properties of individual molecules (we recall that the known experiments on the observation of coherent three-photon processes in solids provide data on the nonlinear properties of a dielectric medium as a whole). We present below the probabilities of three-photon processes calculated by perturbation theory; an interesting result of our ana-

lysis is that the three-photon scattering cross section can be related to the two-photon absorption cross section, which has been repeatedly measured in various media. The latter makes it also possible to estimate the prospects of observing a new effect - stimulated three-photon Raman scattering.

Let the dipole moment of the molecule be represented in the form $\hat{d} = \alpha \underline{E} + \chi \underline{E} \cdot \underline{E} \dots$; usually the investigated spontaneous two-photon (Rayleigh and Raman) scattering is connected with the first term in this expansion. We now proceed to analyze the spontaneous scattering processes connected with the term that is quadratic in the field. If we ignore the internal motions of the molecule, then we arrive at a double-frequency Rayleigh-scattering scheme (Fig. 1). Just as in two-photon scattering, the internal motions lead to modulation of the quadratic polarizability χ (Fig. 2), and the frequency ω_{21} can be, for example, the oscillation frequency of the nuclei. The radiation scattered by the system of molecules is here also connected with the fluctuations of the anisotropy and density, and is proportional in the case of a gas to the number of particles N . The intensity I of the double-frequency Rayleigh scattering can be roughly estimated by starting from the values of χ for crystals, which are known from experiments on frequency doubling. We have

$$I = (2^{10} \pi^6 N \chi^2 / 3 c \lambda^4) I_0^2$$

where I_0 is the intensity of the incident radiation. Let $N = 10^{19}$, $\lambda_1 = 2\lambda_2 = 0.5\mu$, $\chi = 10^{-31}$ (cgs), $I_0 = 10^9$ W/cm²; then $I = 10^{-5}$ W.

The probabilities of the processes under consideration can be estimated with the aid of a formula analogous to the Kramers-Heisenberg dispersion formula. Assume that the molecule is acted upon by a field $\underline{E}(t) = (1/2)(\underline{E}_1 \exp(-i\omega_1 t) + \underline{E}_1 \exp(-i\omega_1^* t) + \text{c.c.})$. We assume for the time being, for the sake of generality that $\omega_1^* \neq \omega_1$; the frequency of the scattered radiation is $\omega_2 = \omega_1 + \omega_1^* - \omega_{21}$. We obtain then by third-order perturbation theory the following expression for the probability of spontaneous three-photon transition from state 1 into state 2:

$$W_{sp}^{(3)} = (4/3\hbar)(\omega_2 n_2 / c)^3 |\hat{d}|^2 \quad (1a)$$

$$\hat{d}_i = \sum c_{ijk} E_{ij} E'_{ik} \quad (1b)$$

$$c_{ijk} = (1/4\hbar^2) \sum_{m,n} \hat{P} [d_{im}^{(i)} d_{mn}^{(j)} d_{n2}^{(k)} / (\omega_{m1} - \omega_i)(\omega_{n1} + \omega_k)] \quad (1c)$$

Here n_2 is the refractive index of the medium at the frequency ω_2 , $d_{mn}^{(i)}$ are the components of the dipole-moment matrix element, and \hat{P} is the operator that permutes the indices i, j , and k ; after the permutation we must put $\omega_i = -\omega_2$, $\omega_j = \omega_1$, and $\omega_k = \omega_1^*$. In the degenerate case (when $\omega_1^* = \omega_1$) the right side of (1c) must be divided by 2. c_{ijk} is a third-rank

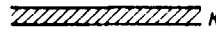


Fig. 1



Fig. 2

tensor analogous to the tensor introduced by Placek for two-photon processes. When considering the "Rayleigh" scattering we replace in (1c) the subscript denoting the state 2 by 1, and we put $\omega_{21} = 0$; c_{ijk} has then the meaning of the spectral component at the frequency $\omega_2 = \omega_1 + \omega_1'$ of the molecule's quadratic polarizability tensor $\chi_{ijk}(\omega_2)$. It can be shown that if Placek's polarization theory is applicable then $c \approx (\partial\chi/\partial q)_0 q_{12}$, where q is the normal coordinate of the oscillation with frequency ω_{21} .

As in the case of two-photon scattering, we must expect a sharp increase in the efficiency of the process at resonance, i.e., when $\omega_{k1} \approx \omega_1$, or $2\omega_1$, or $-\omega_2$, or $\omega_1 - \omega_2$ (here and throughout we assume that $\omega_1' = \omega_1$ and $2\omega_1 - \omega_2 = \omega_{21} > 0$). In practice the most interesting resonance is of the type $\omega_{k1} \approx 2\omega_1$; if we include in (1c) only the resonant terms, then the probability of three-phonon scattering is proportional to the probability of induced two-photon absorption: $|\underline{d}|^2 \approx |\underline{d}_{2k}|^2 W_{ind}^{(2)} / \Delta\omega$, where $\Delta\omega$ is the line width of the $1 \rightarrow k$ transition (we assume that the line is uniformly broadened). The three-photon scattering cross section $\sigma_{sp}^{(3)}$ is connected with the two-photon absorption cross section $\sigma_{ind}^{(2)}$ by the relation

$$\sigma_{sp}^{(3)} / \sigma_{ind}^{(2)} = r_0 \omega_2^4 n_2^3 f_{2k} / 3 c \omega_1 \omega_{k2} \Delta\omega \quad (2)$$

where $r_0 = e^2/mc^2$, f_{2k} is the oscillator strength of the transition $2 \rightarrow k$ (for "Rayleigh" scattering it is necessary to replace the index of the state 2 in (2) by 1). Let $\sigma_{ind}^{(2)} = 2 \times 10^{-3} \text{ cm}^4 \text{ erg}^{-1} \text{ sec}^{-1}$ [1], $\omega_e \approx \omega_{k2} \approx 2\omega_1 \approx 2.2 \times 10^{14} \text{ cm}^{-1}$, $n_2 = 1$, $f_{2k} = 10^{-3}$, $\Delta\omega = 10^3 \text{ cm}^{-1}$, $N_0 = 10^{19} \text{ cm}^{-3}$, and $I_0 = 10^9 \text{ W/cm}^2$; then $I = \sigma_{sp}^{(3)} N_0 I_0^2 \approx 1 \text{ mW/cm}^3$.

The probability of induced three-photon emission of the Stokes frequency under the influence of a field $(1/2)(\underline{E}_2 \exp(-i\omega_2 t) + \text{c.c.})$ is equal to $g(\nu) |\underline{d} \cdot \underline{E}_2 / 2\hbar|^2$ [$g(\nu)$ is the normalized line-shape function], and in the case of resonance it is also proportional to the two-photon absorption. Analogously, the two-photon scattering probability is proportional in the case of resonance to ordinary absorption. Therefore the threshold pump intensities necessary to obtain stimulated emission at frequencies $2\omega_1 - \omega_{21}$ and $\omega_1 - \omega_{21}$ will be of the same order of magnitude if the coefficients of the one- and two-photon absorption at frequency ω_1 become comparable (as observed, for example, in [1]; we assume that one level k determines the efficiency of all four processes in question).

The foregoing estimates show that three-photon scattering processes can be observed in gases and liquids [1]. For double-frequency Rayleigh scattering to occur, the molecules must not have inversion centers. Three-photon Raman scattering is possible in the case of molecules possessing inversion centers, and then the active oscillations will be the same as in the infrared absorption. Further selection rules can be obtained by expanding the representation obtained by means of the third-rank tensor in irreducible representations of the symmetry group of the given molecule. It is of interest, in our opinion, to investigate experimentally the directivity patterns of three-photon scattered radiation and its polarization characteristics, and to do the same for three-photon scattering processes in crystals.

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COHERENT EXCITATION OF OPTICAL SPECTRA OF ATOMS PASSING THROUGH A CRYSTAL

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The author has considered in another paper [1] the possible existence of an effect of coherent Coulomb excitation of nuclei passing through a crystal. The same paper contains estimates showing that, owing to thermal motion of the crystal atoms, observation of this effect on nuclei entails (at the present level of the technology of heavy-nucleus acceleration) certain difficulties. A suggestion was made that an effect similar to coherent excitation of nuclear levels can occur when atoms travel through a crystal, wherein the interaction between the traveling atoms and the crystal atoms leads to coherent excitation of the optical levels of the traveling atoms.

Below are presented estimates offering evidence that the observation of such an effect is perfectly feasible. We propose a concrete experiment in which coherent excitation of optical spectra of atoms should be observable. Qualitatively, such an effect is possible because a particle passing through the crystal moves in the periodic electric field of the crystal atoms. The transition of the moving atom to the excited state is due to a time-dependent perturbation, which in this case is the energy of interaction between the traveling atom and the crystal atoms. The dependence of the energy $V(t)$ between the traveling particle and the crystal atoms has the form of a periodic sequence of single bursts (Fig. 1a), each of which is due to the interaction of the traveling particle with one of the crystal atoms. The Fourier frequency spectrum of a single interaction $S_0(\omega)$ is shown in Fig. 1b for two different velocities of the traveling atom. The Fourier spectrum of the perturbation experienced by the atom following interaction with n atoms of the crystal is connected with the spectrum of the single interaction $S_0(\omega)$ by the relation

$$|S_n^0(\omega)|^2 = |S_0(\omega)|^2 [\sin^2(\omega T/2) n] / [\sin^2(\omega T/2)] \quad (1)$$

The dependence of the factor $[\sin^2(\omega T/2) n] / [\sin^2(\omega T/2)]$ on ω for $n = 2, 3, 4$ and for large n is shown in Fig. 1 (c, d, e, f). The resultant spectrum $|S_n^0(\omega)|^2$, for a large number of interactions n and for two velocities of the traveling atom, is shown in Fig. 1g.

From relation (1) and from Figs. 1 (b - g) we see that the spectral density $S_n^0(\omega)$ at the frequencies $\omega_m = 2\pi m/T$ ($m = 0, 1, 2, 3, \dots$) increases in proportion to the number n of the interactions, and the frequency band occupied near each ω decreases simultaneously like $1/n$ ($\Delta\omega_m \sim \pi/nT$). This change in the spectrum $S_n(\omega)$ with increasing number of interactions n is connected with the coherence of the spectral components $S_0(\omega)$ of the single interactions that