the transition discovered in antimony by Bridgman[4] from a jump in volume at 83.3 kbar, and with the triple point reported by Klement et al.[2] Since the Sb I—Sb II transition was not discovered in[1,2], it seemed interesting to carry out a more thorough study of the phase diagram of antimony by a thermal analysis method. The description of the experimental method will be published later. The accuracy of the pressure measurements was ± 75 kg/cm². The reproducibility of the thermocouple readings in one experiment amounted to 0.15 deg C. The scatter of the data from different tests did not exceed 0.5 deg C. It is evident from Fig. 1 that the melting point of antimony (our sample of which was 99.999% pure) is depressed by pressure to a point with the coordinates: P = 3900 kg/cm², T = 627.8°C. Above this pressure, the melting curve rises and reaches a maximum at the point P = 6700 kg/cm², T = 628.6°C, and then it again begins to drop.

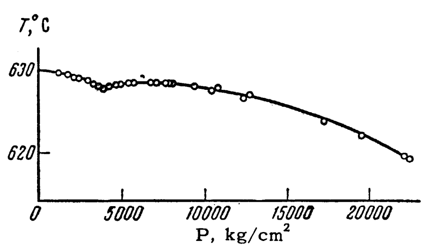

FIG. 1. Melting curve of antimony up to 20 000 kg/cm².

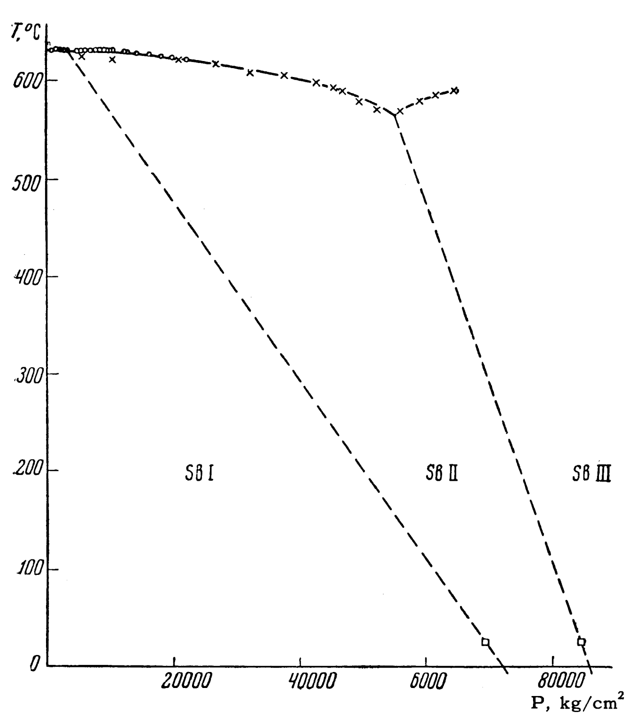

FIG. 2. Unified phase diagram of antimony: ● – data of the present study; × – data of Klement et al.[2]; ■ – data of Vereshchagin and Kabalkina.[3]

In the region above 10 000 kg/cm², our data agreed, in general, with the data of Klement et al. The minimum at P = 3900 kg/cm², T = 627.8°C, was obviously the triple point but we were unable to observe the thermal effects associated with the solid-state transformation anywhere in the range of investigated pressures. Most probably, the thermal effect of this transformation is very small. We assumed that the observed triple point was the point of intersection of the melting curve with the Sb I—Sb II equilibrium curve.[3] Vereshchagin and Kabalkina assumed that the Sb I—Sb II transition is a second-order phase transition, but the properties of the melting curve of antimony in the region of the triple point indicated quite definitely a phase transition with a finite change in volume. In our opinion, this contradiction is not serious, since the change in volume should be very small and may not have been noticed. Figure 2 shows the unified phase diagram of antimony. It is seen that this phase diagram is another example of diagrams with a maximum in the melting curve.

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STIMULATED RAMAN SCATTERING IN THE ANTI-STOKES REGION

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THE present paper deals with the explanation of the mechanism of the appearance and of the properties of the anti-Stokes component in stimulated Raman scattering (SRS). The conditions under which this scattering may appear have been formulated in the paper of Garmire, Pandarese, and Townes.[1] The same authors have derived, from indirect considerations, an expression for the angle (with respect to the direction of the incident wave) at which the scattered component should be emitted. Their derivation was based only on a consideration of the interaction of plane waves in a medium without reference to the sources exciting these waves. The real sources of the scattered radiation waves are, as in normal Raman scattering, individual molecules of the substance. The difference in the SRS case is that the (pumping) light wave incident on a substance (and scattered by it) is sufficiently intense to alter considerably the electrodynamic properties of the substance. The problem of the radiation of a molecular dipole in such a medium is discussed in the present communication. It is established that the anti-Stokes component is emitted only in the close vicinity of a certain angle (about the direction of the incident wave) and that this angle differs from the value given by Garmire, Pandarese, and Townes.[1]

The material equation for a medium in which SRS occurs has been given in a number of papers.[1-3] According to these studies, the response of the polarization P to an external field E is given by the equations

$$m\ddot{x} + R_0\dot{x} + fx = \frac{1}{2}\frac{d\alpha}{dx}E^2, \qquad \mathbf{P} = N\frac{d\alpha}{dx}x\mathbf{E}. \qquad (1)$$

The coordinate x describes the molecular vibrations and α represents the polarizability of a molecule for a given (in general, nonequilibrium) distribution of nuclei, N is the density of molecules in the substance. We shall consider below only the case when the intensity of the wave emitted by a dipole is considerably less than the pumping intensity. Then, the dipole (of Stokes frequency ω_S) excites only the Stokes and anti-Stokes components in the medium (this represents a certain approximation):

$$\mathbf{E}_S(t) = \mathrm{Re}\,\{\mathbf{E}_S e^{-i\omega_S t}\}, \qquad \mathbf{E}_a(t) = \mathrm{Re}\,\{\mathbf{E}_a e^{-i\omega_a t}\},$$

where $\omega_a = 2p - \omega_S$, $\omega_S \approx p - \omega_0$, and p is the pumping frequency, representing a given wave $\omega_0 = \sqrt{f/m}$. To simplify the problem, we may replace the vector quantities $\mathbf{E}_S$ and $\mathbf{E}_a$ with the scalar quantities $u \to E_S$ and $v \to E_a^*$, satisfying, in the absence of the pumping field, the usual three-dimensional wave equations, which, in the presence of pumping, acquire additional terms fully analogous to the material equations which follow from Eq. (1). As a result, we obtain the following system of equations for the quantities u and v:

$$-\nabla^2 u - \varepsilon_S k_S^2 u = \nu\frac{4\pi\Gamma}{\Delta+i}k_S^2\mathbf{e}^2 v\exp(2i\mathbf{K}_p\boldsymbol{\rho}) + 4\pi k_S^2\delta(\boldsymbol{\rho}),$$

$$-\nabla^2 v - \varepsilon_a^* k_a^2 v = \nu\frac{4\pi\Gamma}{\Delta+i}k_a^2\mathbf{e}^{*2}u\exp(-2i\mathbf{K}_p\boldsymbol{\rho}), \qquad (2)$$

where

$$\varepsilon_S = \varepsilon(\omega_S) + \frac{4\pi\Gamma}{\Delta+i}\mathbf{e}\mathbf{e}^*, \qquad \varepsilon_a = \varepsilon(\omega_a) + \frac{4\pi\Gamma}{\Delta-i}\mathbf{e}\mathbf{e}^*,$$

$$\Gamma = \frac{N}{4R_0\omega_0}\left(\frac{d\alpha}{dx}\right)^2,$$

$$\Delta = \frac{2m}{R}(\omega - p + \omega_0), \qquad K_p = k_p n_p, \qquad n_p = \sqrt{\varepsilon(p)} > 0,$$

$$k_p = \frac{p}{c}, \qquad k_S = \frac{\omega_S}{c}, \qquad k_a = \frac{\omega_a}{c},$$

$$d(\boldsymbol{\rho}, t) = \mathrm{Re}\,\{d\delta(\boldsymbol{\rho})e^{-i\omega_S t}\}, \quad \mathbf{E}_p(\boldsymbol{\rho}, t) = \mathrm{Re}\,\{\mathbf{e}e^{i(\mathbf{K}_p\rho - pt)}\}, \qquad (3)$$

d is the dipole moment of the radiating source, $E_{\rho p}$ is the electric field of a plane traveling pumping wave. Equation (2) includes a dipole factor ν for reasons which are explained below.

Let us assume that the z-axis is directed along the pumping-wave vector $\mathbf{K}_p$ and that the values of the vector ρ are expressed in spherical coordinates ρ, θ, φ. Then, the required solution (at sufficiently high values of ρ) is given by the following expressions:

$$u(\rho) = dk_S^2\rho^{-1}\exp(ik_S\sqrt{\varepsilon_S}\rho),$$

$$v^*(\rho) = \nu d^* k_S^2 k_a^2\frac{4\pi\Gamma}{\rho(\Delta - i)}\mathbf{e}^2$$

$$\times\frac{\exp[i(2k_p n_p\cos\theta - k_S\sqrt{\varepsilon_S^*})\rho]}{[k_S^2\varepsilon_S^*\sin^2\theta + (2k_p n_p - k_S\sqrt{\varepsilon_S^*}\cos\theta)^2 - k_a^2\varepsilon_a]}$$

$$-\frac{\exp[-ik_a\sqrt{\varepsilon_a}\rho]}{[k_a^2\varepsilon_a\sin^2\theta + (2k_p n_p + k_a\sqrt{\varepsilon_a}\cos\theta)^2 - k_S^2\varepsilon_S^*]}, \qquad (4)$$

($\mathrm{Re}\sqrt{\epsilon_S} > 0$, $\mathrm{Re}\sqrt{\epsilon_a} < 0$). If we allow for the conditions realizable in practice

$$|\varepsilon_S''| \ll \Delta n \ll n, \qquad \varepsilon_S'' = [-4\pi\Gamma/(1+\Delta^2)]\mathbf{e}\mathbf{e}^* < 0,$$

$$\Delta n = (k_a n_a + k_S n_S - 2k_p n_p)/k_p,$$

$$n_a = \sqrt{\varepsilon_a'} > 0, \qquad n_S = \sqrt{\varepsilon_S'} > 0,$$

it then follows from Eq. (4) that the most interesting is only the range of angles $\theta^2 \ll 1$. In this range, Eq. (4) simplifies to:

$$n(\rho) = dk_S^2\rho^{-1}\exp\left[-\frac{\varepsilon_S''}{2n}k_S\rho\right]\exp[ik_S n_S\rho],$$

$$v^*(\rho) = \nu\frac{d^* k_S^2 k_a^2}{2nk_p\rho}\frac{4\pi\Gamma}{\Delta - i}\mathbf{e}^2$$

$$\times\left\{\exp\left[-\frac{\varepsilon_S''}{2n}k_S\rho\right]\frac{\exp[i(2k_pn_p\cos\theta-k_Sn_S)\rho]}{k_a[(k_s/k_a)n\theta^2-\Delta n+i\varepsilon_S''/n]}\right.$$
$$\left.-\exp\left[\frac{\varepsilon_S''}{2n}k_a\rho\right]\frac{\exp[ik_an_a\rho]}{k_S[(k_a/k_S)n\,\theta^2-\Delta n+i\varepsilon_S''/n]}\right\}. \quad (5)$$

It follows from Eqs. (4) and (5) that in the case of practical interest—$\epsilon_S''k_S\rho/2n \gg 1$—the anti-Stokes component is emitted only over a narrow range (total width $\Delta\theta \ll \theta_0$) of the angles θ_0, where

$$\theta_0^2=\frac{\omega_a}{\omega_S}\frac{\Delta n}{n}, \qquad \Delta\theta=\frac{\omega_a}{\omega_S}\frac{|\varepsilon_S''|}{n^2}\frac{1}{\theta_0}. \quad (6)$$

We note that Eqs. (4) and (5) for values $\nu \sim 1$ are valid only for the angles θ outside the immediate vicinity of θ_0. The same equations are valid for arbitrary θ (including θ_0) if $\nu^2 \ll 1$. If $\nu = 1$ the Stokes component field becomes distorted in the vicinity of θ_0 [compared with the expression (5)] and the form of the maximum of the anti-Stokes component also becomes slightly distorted.

The angle θ_0 is determined by the first term in the braces of the expression for v^*. The second term also has a sharp maximum at $\theta = \tilde{\theta}_0 = (\omega_S\Delta n/\omega_a n)^{1/2}$. However, the value of this term is negligibly small even at the maximum. On the other hand, the angle $\tilde{\theta}_0$ is equal to the angle in which, according to [1], the anti-Stokes component should be emitted. The reason for this disagreement is as follows. According to Eq. (5), the wave vector $\mathbf{K}_a'$ of the radiated anti-Stokes component is $\mathbf{K}_a' = 2\mathbf{K}_p - \mathbf{K}_S$, where $\mathbf{K}_S = k_Sn_S$ (the direction of the vector $\mathbf{K}_S$ coincides with the direction of the $\theta = \theta_0$ ray of the anti-Stokes component). It can easily be seen that the vector $\mathbf{K}_a'$ is directed at an angle to this ray and, consequently, it makes an angle different from θ_0 with the direction of the vector $\mathbf{K}_p$ (we shall denote this angle by β). Direct calculations show that $K_a' = k_an_a$, $\beta = \tilde{\theta}_0$.

Thus, the reason for the disagreement is this: the direction of the anti-Stokes component ray does not coincide with the direction of its wave vector, but is at an angle $\theta_0 + \tilde{\theta}_0$ to it.

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