

Antiresonance in the excitation spectrum for Raman scattering in proustite

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Antiresonances are observed near the fundamental absorption edged in the excitation spectrum of resonant Raman scattering of valence vibrations in proustite. The antiresonances are attributed to an interference of partial scattering amplitudes.

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The cross section (σ) for Raman scattering in a medium increases near excitation frequencies corresponding to resonant states of the medium, so that measurements of the excitation spectrum of the cross section for resonant Raman scattering constitute an extremely sensitive new spectroscopic method. Particularly interesting are the cases in which the cross section is affected by more than one resonant term, so that interference effects may result from the addition or subtraction of the partial scattering amplitudes.^{1,2} Analysis of the spectrum $\sigma(\omega)$ in this case not only identifies the resonant states of the medium but also yields the parameters of the electronic–vibrational interaction.^{3,4}

In this letter we are reporting the first observation of interference minima in the excitation spectrum for resonant Raman scattering of valence vibrations in a proustite (Ag_3AsS_3) crystal near the fundamental absorption edge. Proustite holds promise for nonlinear frequency conversion in the infrared region, but its electronic states have received little study.⁵ We will discuss these states here, working from an analysis of the frequency spectrum of resonant Raman scattering.

The grown proustite crystals were oriented and cut with respect to the crystallographic axes of the trigonal phase¹⁾ ($z \parallel c, y \perp m$ plane). The measurements were

carried out at 69 ± 0.5 K in the $x(zx)y$ and $x(zz)y$ arrangements. The excitation source was a laser which used a mixture of the dyes R101 and R6G and which operated in the range 610–680 nm. The parasitic background accompanying the emission line was eliminated with a diffraction grating and a Pellin-Broca prism. The excitation intensity was measured in front of the entrance window of the cryostat. As a reference we measured the integrated intensity at the 656-cm^{-1} line of CS_2 , for which there are no resonant effects with the particular excitation source used, and the dispersion reduces to $\sigma \sim \omega^4$. To determine the cross section $\sigma(\omega)$ of the mode ν_i , we corrected the ratio of the integrated line intensities in the proustite spectrum and the CS_2 spectrum to the same excitation intensity and to the same accumulation time in the analyzer channel. The polarized absorption of the crystal was measured with an Acta MVII spectrophotometer. Excitation at $\omega \geq 2.03$ eV causes damage to the crystal surface, so that measurements could not be carried out deep in the absorption band.

The spectral region which was scanned (Fig. 1) contains four modes (336 , 344 , 358 , and 368 cm^{-1}) which correspond to valence vibrations of the AsS_3^{3-} molecular group.^{6,7} The splitting of the valence vibrations is directly related to the lattice symmetry and will be discussed in a separate paper; here we simply note that the relative intensities of the bands vary with the excitation frequency, indicating that the scattering is resonant scattering.

Figure 2 shows data on the cross section for resonant Raman scattering as a function of the frequency for the ν_3 mode. The change in the absorption coefficient of the crystal in the frequency range of interest here is slight (curve 1 in Fig. 2); the sharp increase begins at $\omega = 2.14$ eV. Near the fundamental absorption edge there is a general increase in the cross section (by a factor of about 3), and there is also a clearly defined minimum at $\omega = 2.01$ eV, which indicates an antiresonance with incomplete cancellation of the partial amplitudes. In the same frequency interval there are minima in the scattering cross sections for the modes ν_1 and ν_4 . In the $x(xz)y$ arrangement we find one intense mode ($\nu_6 = 368\text{ cm}^{-1}$) and one weak one ($\nu_5 = 336\text{ cm}^{-1}$), which also belong to valence vibrations of a molecular group. The cross sec-

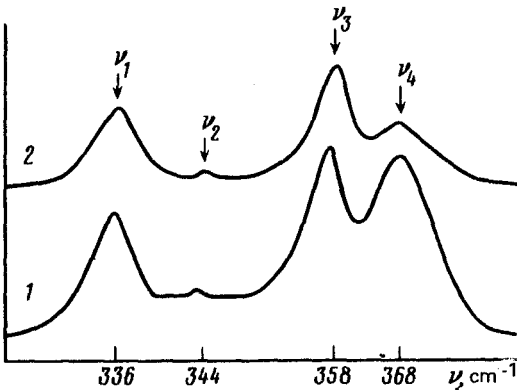


FIG. 1. Valence-vibration Raman-scattering spectrum of proustite at $T=69$ K in the arrangement $x(zx)y$ for two excitation frequencies: 1— $\omega = 613$ nm (2.021 eV); 2— $\omega = 658$ nm (1.885 eV).

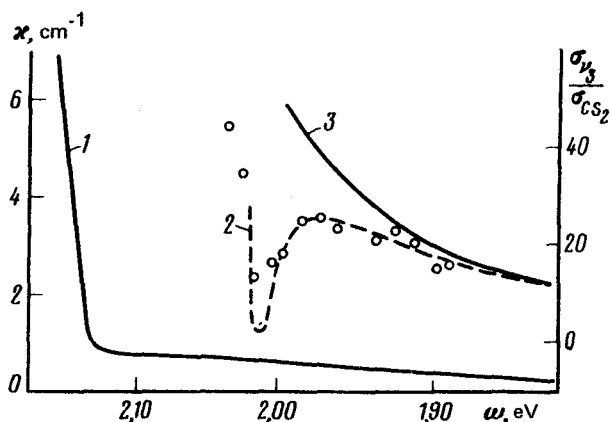


FIG. 2. Experimental data on the scattering cross section for the mode ν_3 [$\sigma_{\nu_3}(\omega)/\sigma_{CS}(\omega)$] at $T = 69$ K (circles). Curves: 1—The absorption coefficient, $\kappa(\omega)$; 2—approximation of $\sigma(\omega)$ for the mode ν_3 by Eq. (1) (the parameters of the approximation are given in the text); 3—the function $|A_1(\omega)|^2 + \gamma^2$.

tion for the mode ν_6 far from the resonance is much larger than that for the mode ν_3 (by a factor $\sim 10^3$) and increases by a factor of about 3 toward the fundamental absorption edge. It does not exhibit any noticeable interference structure.

Let us examine the possible contributions to the cross section for resonant Raman scattering in the proustite crystal. Toward the fundamental absorption edge, possible resonant terms in the polarizability may arise from transitions to the conduction band and from transitions involving the excitation of excitons. Nonresonant scattering may also have an effect and must be taken into account. We write the amplitude for scattering by electrons in the band without damping as $A_1(\omega) = \alpha(\omega_g - \omega)^{-1}$, where ω_g is the width of the energy gap. Scattering by an exciton state (or by some other local electronic state) contributes an amplitude $A_2(\omega) = \beta(\omega_0 - \omega)^{-2}$. Adding a constant amplitude γ to represent the nonresonant effect, we find the expression

$$\sigma(\omega) = [\alpha(\omega_g - \omega)^{-1} + \beta(\omega_0 - \omega)^{-2}]^2 + \gamma^2, \quad (1)$$

which gives a good approximation of the experimental data (curve 2 in Fig. 2). A computer-assisted visual fit of the theoretical curve to the experimental data yielded the parameter values $\omega_g = 2.14$ eV, $\omega_0 = 2.035$ eV, $\alpha = -1.02$, $\beta = 0.00500$, and $\gamma^2 = 2.0$. Setting $A_2 = 0$ in (1), we find curve 3 in Fig. 2, which is a reasonable approximation of the scattering cross section far from the interference minimum. Curve 3 satisfactorily described the experimental dependence of the cross section for mode ν_6 . We can take the approximation parameter ω_g as a reasonable value for the energy corresponding to the bottom of the conduction band. If we assume that $\omega_g = 2.25$ eV (found from the absorption edge⁵), we will be unable to find a correct description of the rise of the curve in front of the minimum. We note that there is no weaker ω dependence of the amplitude A_2 , which reproduces the observed behavior $\sigma(\omega)$ and the width of the minimum. In $\sigma(\omega)$ for the mode ν_6 , the partial amplitudes in

(1) have the same sign (the scattering-tensor elements α_{zx} and α_{zz} are opposite in sign), and no antiresonance is observed.

Since an absorption maximum is not observed at a frequency near ω_0 , the second term in (1) may be due to a resonance with indirect transitions. Transitions involving phonons have been observed⁵ at the fundamental absorption edge of proustite, and the energy of the transition for the case $\mathbf{E} \parallel z$ has been estimated to be 2.083 eV, which is near ω_0 . Theoretically, there may be an interference of Condon and non-Condon contributions to the cross section for resonant Raman scattering.⁴

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