Optical anomalies in proustite resulting from a first-order structural phase transition

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A diffraction of light by the space lattice of a proustite crystal formed as a result of a first-order phase transition was observed for the first time. The diffraction occurs with the rotation of the polarization plane and without the rotation, depending on the polarization of the incident light and the orientation of the crystal.

Crystalline proustite (Ag_3AsS_3), a synthetic material which has semiconducting, ferroelectric, and nonlinear optical properties[1–3] and which has a promising future as a material with practical applications, is continuing to amaze investigators by its unusual properties and the effects it exhibits. One such effect was observed when a proustite single-crystal wafer was exposed to an incoherent white light from a 100-W incandescent lamp and to a coherent monochromatic light from a 5-mW He-Ne laser at a temperature T below the first-order structural phase transition ($T_c \sim 22$ K).

The test sample was cut out from a block in the shape of a plane-parallel wafer (the deviation from parallel direction was no greater than 30′), so that the C axis of the crystal lied in the wafer's plane. The thickness of the wafer was $\sim 100\ \mu$m. During the experiment, the crystal was positioned in space in such a way that the wafer's plane was perpendicular to the horizontal plane and the C axis was parallel to it. The experimental arrangement is shown in Fig. 1.

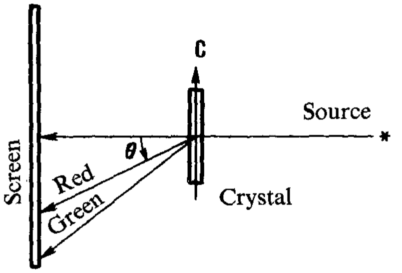

FIG. 1. Experimental arrangement.

When a crystal, whose temperature is below T_c, is subjected to a white light, the main transmitted beam of light is accompanied by a second beam which is deflected from the main beam at an angle θ. Both beams of light lie in the plane that passes through the C axis of the crystal. If the transmitted beam of light remains a white light, then the deflected beam separates into a spectrum extending from red light to green light (the crystal absorbs the shorter wavelengths). The deflection angle θ turned out to be inversely proportional to the wavelength of light ($\theta \sim 1/\lambda$).

Since the cryostat we used had only one window, whose axis formed a 45° angle with the incident beam, we had no way of knowing whether a beam was deflected symmetrically from the transmitted beam on the opposite side. We noticed, however, the presence of a second deflected beam after rotating the crystal 180° around the axis perpendicular to the crystal plane.

The same beam was observed again after exposing the sample to a coherent monochromatic light with a wavelength $\lambda = 632.8$ nm. Each of these beams had a three-dimensional periodic structure consisting of a principal maximum and additional maxima arranged symmetrically on either side of the principal maximum and directed along the C axis of the crystal (Fig. 2). The angle of deflection of the second beam was $40 \pm 0.5^\circ$ at the indicated wavelength and increased to 70° at $\lambda = 514.5$ nm. The intensity of the principal transmitted beam was approximately 60% of the original intensity after the deflected beams were formed (before the phase transition).

The polarization of transmitted and deflected beams depends on the polarization of the incident light and on the orientation of the crystal (Fig. 3). As can be seen in Fig. 3, a deflected beam forms in the case of polarization of the incident light and in the case of a 90° rotation of polarization.

The dispersion surprisingly turns out to be different from the dispersion by an ordinary diffraction grating but the same as the dispersion by a prism. Because of this

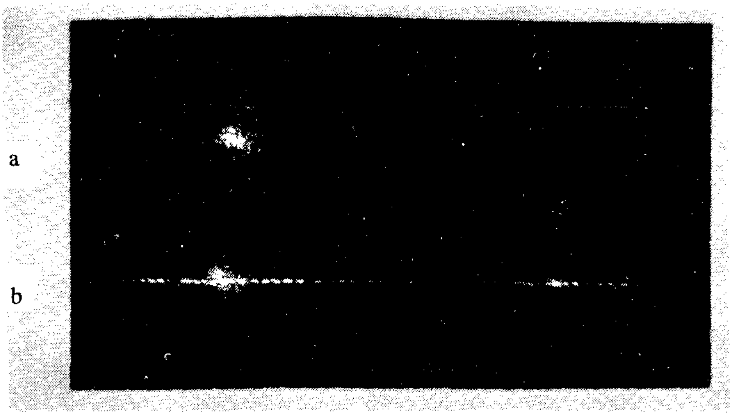

FIG. 2. Arrangement of the light maxima of the laser beam transmitted through the crystal ($\lambda = 632.8$ nm): (a) before the phase transition ($T > T_c = 22$ K); (b) after the phase transition ($T < T_c = 22$ K).

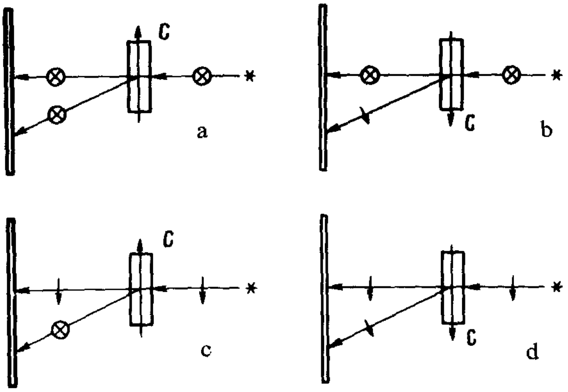

FIG. 3. Polarization of the transmitted and deflected beams as a function of polarization of the incident light and the orientation of the crystal (⊗ —light is polarized perpendicular to the *C* axis of the crystal;→ — light is polarized parallel to the *C* axis of the crystal).

situation, we can justifiably call the diffraction grating in proustite an extraordinary grating.

The experimental results, taken collectively, suggest that a proustite crystal forms a supergrating as a result of a first-order structural phase transition. The spacing of this supergrating is estimated to be on the order of 500 nm. Since the silver ions, Ag^+, are highly mobile in proustite, a grating may be formed as a result of a phase transition in which these ions are rearranged and ordered. We can accordingly expect that at temperatures below the first-order phase transition such crystals can be used to generate waves in the submillimeter frequency range.

It is conceivable, however, that because of the phase transition, proustite forms ferroelectric domains that are perpendicular to the *C* axis of the crystal. Upon exposure of the sample to light, the sample will produce photoelectric charges which are captured by the traps at the domain walls. This process accounts for the periodically changing internal electric field. As a result of the electro-optical effect,[4] this process, in turn, leads to a modulation of the refractive index, i.e., to the formation of a phase grating which accounts for the diffraction of light.

Further experiments, which will furnish data upon which a definitive explanation of the unusual effect occurring in proustite can be based, are in progress.

In conclusion we wish to point out that the beam deflection is so strong and sharp that this effect could be used to control a laser beam.

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