Changes in the ultrasonic attenuation of proustite at the photoinduced phase transition near 210 K

LETTER TO THE EDITOR

Changes in the ultrasonic attenuation of proustite at the photoinduced phase transition near 210 K

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Abstract. The ultrasonic attenuation in proustite has been measured in the vicinity of 210 K. The results provide further evidence for a photoinduced phase transition at this temperature. A possible mechanism for the increase in attenuation induced by illumination is discussed.

1. Introduction

There has been considerable dispute about the existence of a phase transition in proustite (Ag_3AsS_3) at 210 K since Smolenskii *et al* [1] reported the splitting of the doubly degenerate, lowest frequency E-phonon modes in the Raman scattering spectrum. Since that time, several other investigations have been carried out in this temperature region [2–6], which show conflicting evidence for this transition, although the photodielectric studies in our own laboratory [7] clearly demonstrate the presence of photoinduced changes at temperatures around 210 K.

In the past, observations of the ultrasonic properties have formed an important element of the study of proustite. Measurements of the attenuation of dilatational waves [8] have indicated distinct anomalies at 26 and 51 K, which are the temperatures at which the first- and second-order phase transitions occur. Similar anomalies were also observed when the samples were irradiated with white light at these temperatures [9]. At 210 K, Gorin *et al* [3] reported anomalies in the temperature dependences of ultrasonic velocities, but Belyaev *et al* [5] failed to observe any such effects in either the velocity or the attenuation coefficient. Further investigations, such as thermal expansion [6] and photodielectric measurements [7, 10], have been interpreted in terms of a broad, photoinduced phase transition at about 210 K.

The present paper reports preliminary investigations of the effect of light on the ultrasonic attenuation in proustite in the region of this transition.

2. Experimental apparatus and techniques

Ultrasonic attenuation was measured in a proustite crystal, cut in the form of a prism of dimensions $8.8 \times 8.5 \times 9.8$ mm aligned with its edges parallel to the crystallographic

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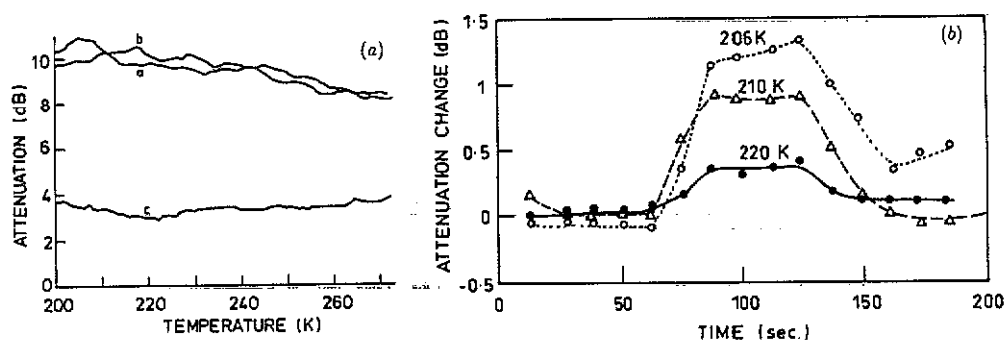
Figure 1. (*a*) Acoustic attenuation at 5.5 MHz in a single crystal of proustite as a function of temperature. The different curves relate to measurements along the three crystallographic axes *a*, *b* and *c*. (*b*) Changes in the attenuation caused by exposure to light at different temperatures close to 210 K. In all cases, the illumination was switched on at 62.5 s and off at 125 s.

axes, denoted by *a*, *b* and *c* selected in the usual way for the trigonal system, i.e. the axis c_3 parallel to *c*, and the *b* axis in the *m* symmetry plane. A small ultrasonic transducer with resonant frequency 5.5 MHz was attached to the sample, using salol as a coupling agent, together with a thermocouple to measure its temperature.

The sample was placed in a special optical cryostat with a quartz window to permit illumination of the sample. The electrodes of the transducer and the thermocouple were connected through leads fitted into the bottom of the cryostat. Low temperatures were obtained by means of 'slush' baths produced by using a freezing mixture of liquid nitrogen and chloroform (melting point 209.7 K).

The attenuation measurements were carried out in a conventional manner using a computer-controlled pulsed ultrasonic test system. The system could complete one measurement in about 12 s.

A low pressure mercury vapour lamp and a sodium vapour lamp were used to illuminate the sample to give a general indication of any spectral variation effects. The light from each source was focused onto the sample in the cryostat through the quartz window using a convex lens. The intensities of the focused illuminations were first measured using a Spectra-Physics 404 Power Meter and found to be 2.0 mW for the mercury light and 1.0 mW for the sodium light.

The sample of proustite was placed in the cryostat in selected orientations and stored in darkness at room temperature for at least 24 hours. The acoustic attenuation of the sample was then measured at temperatures around 210 K in this initial 'dark' condition. Light from either source was then focused on the proustite and the attenuation was measured repeatedly for a period of about 2–5 min, after which the light was extinguished and measurements continued. The sample temperature was monitored to establish whether heating occurred during the illumination, but no changes were observed.

3. Results and discussion

The results of some typical measurements of acoustic attenuation in the proustite sample before, during and after irradiation are shown in figure 1. Figure 1(*a*) shows the absolute attenuation, measured in the dark, in the sample in all three directions and figure 1(*b*)
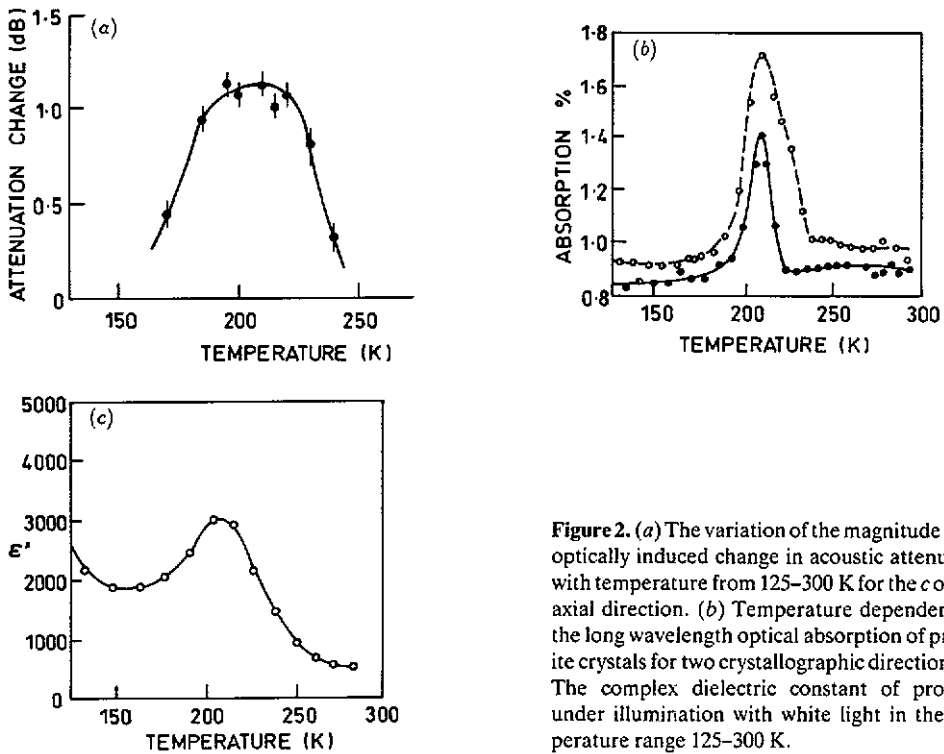
Figure 2. (a) The variation of the magnitude of the optically induced change in acoustic attenuation with temperature from 125–300 K for the *c* optical axial direction. (b) Temperature dependence of the long wavelength optical absorption of proustite crystals for two crystallographic directions. (c) The complex dielectric constant of proustite under illumination with white light in the temperature range 125–300 K.

shows the observed attenuation changes associated with illumination for short times at different temperatures.

As may be seen, all of the results indicate an increase in attenuation in the proustite during exposure to light. The major part of the increase in attenuation occurs within 12 s, after which the effect saturates. When the illumination was removed, the attenuation dropped rapidly to its 'dark' value. Surprisingly, there was no observable change in the propagation velocity corresponding to these photoinduced effects on the attenuation.

The same effects were noted for light from either the intense blue (mercury) or yellow (sodium) vapour lamps. Differences in the magnitude of the changes were consistent with the different intensities produced by the two light sources suggesting that there is little or no wavelength dependence of the effect in the blue–orange region (400–600 nm) of the visible spectrum.

The increase in the attenuation following irradiation with light was found to be quite sensitive to temperature, the effect being maximum over the range 190–210 K and barely measurable for temperatures below 170 or above 230 K, as shown in figure 2(a). The photoinduced changes were also observed in all three crystallographic orientations, although the absolute values of the changes varied from one orientation to the other.

These results are in agreement with our earlier observations on the temperature dependence of other photoinduced phenomena in proustite—the shift of the indirect absorption edge [11], the increase in long wavelength mean absorption level [2], and dielectric absorption behaviour [10]. This agreement is illustrated in figure 2(b), which shows the temperature dependence of long wavelength optical absorption in proustite, and figure 2(c), which shows the dependence of dielectric loss constant on temperature.

In contrast to the earlier work, the relaxation times for the appearance and disappearance of the increased ultrasonic attenuation due to illumination were essentially the same and relatively short (about 10 s) while the dielectric observations revealed time constants of up to several hours. In this latter case, the observed effects are associated with changes in the charge distribution in the sample as the mobile Ag^+ ions are shifted away from their equilibrium configuration, while in the former it is necessary to search for an origin of the observed effect in terms of an increase in the acoustic scattering centres.

It seems reasonable to suggest that the two effects are closely related, and consequently that the enhanced acoustic attenuation induced by the light results from the charge carriers being maintained in a non-equilibrium mobile state before being trapped in metastable sites from which they eventually relax after the radiation is removed. Since the trapping sites are likely to be atomic positions in the lattice, it is to be anticipated that their changing occupancy will have only a small effect on the atomic periodicity; indeed they may simply be unoccupied sites left empty as a result of previous thermal treatment. In that case, while the charge distribution (and hence the dielectric properties) will change significantly, the acoustic attenuation will be only slightly affected. In the dynamic conditions during excitation, however, the mobile silver ions will lead to local structural perturbations due to charge compensation, which will act as scattering centres for the ultrasonic radiation.

4. Conclusions

An increase in the acoustic attenuation frequencies has been observed in proustite during illumination. The amplitude of this change shows a broad peak at about 210 K and provides further evidence for an optically induced phase change at this temperature. It is suggested that the observed effect is related to the changes in the dielectric behaviour at this temperature, which have been associated with atomic displacements of the Ag^+ ions.

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