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THE EFFECT OF PRESSURE AND TEMPERATURE ON THE ABSORPTION EDGES OF THREE SILVER HALIDES*

by

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Abstract

The effect of pressure to 160 kilobars, combined with temperature to 400°C has been measured on the absorption edge of AgCl, AgBr, and AgI. The behavior of AgCl and of AgBr is nearly identical. In the low pressure (fcc) phase there is a red shift with pressure at low temperature. At high temperature the edge shifts blue with increasing pressure. A possible explanation in terms of the defect structure is proposed. The high pressure phase shows a normal red shift with pressure at all temperatures. The behaviour of AgI in the fcc phase is anomalous both at room temperature and at elevated temperature.

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The continued effects of pressure to 160 kilobars and temperature to 400°C on the absorption edges of silver chloride, bromide, and iodide, was determined. The experimental techniques have been previously described(1,2,3); the latest revised pressure calibration(4) was used. The silver halides used were from the same crystals used in the room temperature work(2). The results for both the NaCl (fcc) and CsCl (sc) phases of the three compounds are illustrated in Figures 1, 2 and 3. The room temperature shift of the edge in all cases was obtained from the data of Slykhouse(2).

In the cases of the chloride and bromide, the results are quite similar. At room temperature, the edge in both phases showed a shift toward lower energy with increasing pressure. At higher temperatures, the pressure shift in the sodium chloride phase of the bromide and chloride exhibited a reversal in sign, the magnitude of the reversal increasing with increasing temperature. The shift of the iodide in the sodium chloride phase was to higher energies with increasing temperature, with little or no trend toward reversal of the pressure shift.

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[1] Fitch, R. A., Slykhouse, T. E., and Drickamer, H. G., J. Opt. Soc. Am. 47, 1015 (1957).

[2] Slykhouse, T. E. and Drickamer, H. G., J. Phys. Chem. Solids 7, 210 (1958).

[3] Balchan, A. S. and Drickamer, H. G., Rev. Sci. Inst. 31, 511 (1960).

[4] Drickamer, H. G., Rev. Sci. Inst. (in press).

In all silver halide "isobars", when a certain temperature was reached, an irreversibility was noticed, the displacement of the room remperature edge (upon cooling) from the initial value being greater than that due to a simple pressure loss on heating. In the case of the iodide, the effect was quite severe, and a temperature of 165°C was the highest that could be reached reversibly. The irreversibility was probably associated with the flow of the sodium chloride from the center of the pellet, and subsequent reduction in effective cross-section of the sample, as it was noticed that the degree of irreversibility was directly proportional to the pressure loss at a given temperature and pressure. The effect on the iodide may have been due in part to the phase transition at 145°C.

The results given here are measurements after which the edge upon cooling of the sample was found to return to its value at room temperature; in short, all reversible results.

The shifts observed were relatively independent of wavelength, over a range of about 3000 cm.$^{-1}$, but the data for all runs on a particular compound were taken at one value of wavelength (corresponding to an absorption coefficient of about 30 cm^{-1}).

The results of Urbach$^{(5)}$ show that in the long wavelength region of the edge (up to about 450 mu in AgBr and 385 mu in AgCl) the logarithm of the absorption coefficient is a linear function of wavelength (with a slope of - 1/kT in the case of the bromide. From this Urbach concludes that the

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[5] Urbach, F., Phys. Rev. 92, 1324 (1957).

absorption in this region is directly related to the thermal energy. Further measurements (6,7) indicate that this absorption is not an impurity effect. (8)

The large effect of high temperature on the pressure shift of the bromide and chloride in this work also leads to the conclusion that the absorption processes are due to a thermally-controlled mechanism.

Two possible reasons for the unusual behavior of the NaCl phase of the chloride and bromide at high temperatures can be proposed:

1. Let it be assumed that the long wavelength absorption consists primarily of the indirect transition u, that is, a transition from the valence band at the zone boundary to the conduction state at $\overline{k} = o$. Then the blue shift with pressure at high temperatures would occur if either the conduction band shifted toward higher energies and the valence band remained relatively fixed, or the valence band became narrower faster than conduction band shifted toward lower energies. Both of these alternatives seem improbable in view of results obtained in this laboratory on the fundamental absorption of other simple lattices. These invariably show a broadening of the bands with pressure.

2. The absorption at high temperature is caused by the defect structure of the crystal. As it has been proposed that the absorption is not associated with impurities, the defects concerned are probably thermally induced. Work in this laboratory on the effect of pressure on the optical absorption of imperfections has shown that a shift

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[6] Moser, F. and Urbach, F., Phys. Rev. 102, 1519 (1956).

[7] Gilleo, M. A., Phys. Rev. 91, 534 (1953).

[8] Brown, F. and Seitz, F., Photographic Sensitivity, Vol. 2 (1957).

toward higher energies of this absorption with pressure is not unusual. In addition it has been shown that the equilibrium concentration of vacancies (predominantly Frenkel defects)(9,10,11,12) in the silver halides is quite high as the melting point is approached (about 2 atomic percent).

In the high pressure (presumably CsCl) phase of the chloride and bromide, the pressure shift appeared quite regular with increasing temperature, the direction being toward lower energies with increasing temperature. There is no indication here of the reversal in sign of the pressure shift as exhibited by the NaCl phase. The data on the bromide in the high pressure phase is of necessity sparse, because of the difficulties in controlling the amount of sodium chloride extrusion, and hence the center pressure, at the higher temperatures. Data in the high pressure phase of the chloride were fortunately less erratic.

The regularity in the high pressure phase lends weight to the second hypothesis above. In the close-packed simple cubic phase, the energy required to produce a Frenkel defect would be quite high, and a much lower concentration of these defects would be expected than in the NaCl structure.

The shift of the edge with increasing temperature toward higher energies in the NaCl phase of silver iodide is anomalous with respect to the other halides, as is the room temperature shift. These facts appear

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[9] Teltow, J., Ann. Physik. <u>5</u>, 61, 71 (1949).

[10] Berry, C. R., Phys. Rev. <u>82</u>, 422 (1951).

[11] Strelkow, P. G., Physik. Z. Sowjetunion <u>12</u>, 77 (1937).

[12] Zieten, W., Z. Physik. <u>145</u>, 125 (1956).

to indicate that a different transition is occurring in the low-wavelength tail than in the other halides. In the high pressure phase, however, the pressure shifts at all temperatures resemble those in the bromide and chloride, with a steady desplacement toward lower energy with increasing temperature. The anomalous blue shift across the high pressure transition shows a decrease in magnitude as the temperature is increased, and it is likely that the shift will reverse sign at about 300-350°C. Because of the large irreversibility accompanying the heating of the iodide in the NaCl phase to greater than 165°C, this effect could not be observed. It appears that the unusual blue discontinuity at room temperature may indeed be simply due to an oddity in the band structure, which becomes resolved at a high temperature.

Acknowledgment

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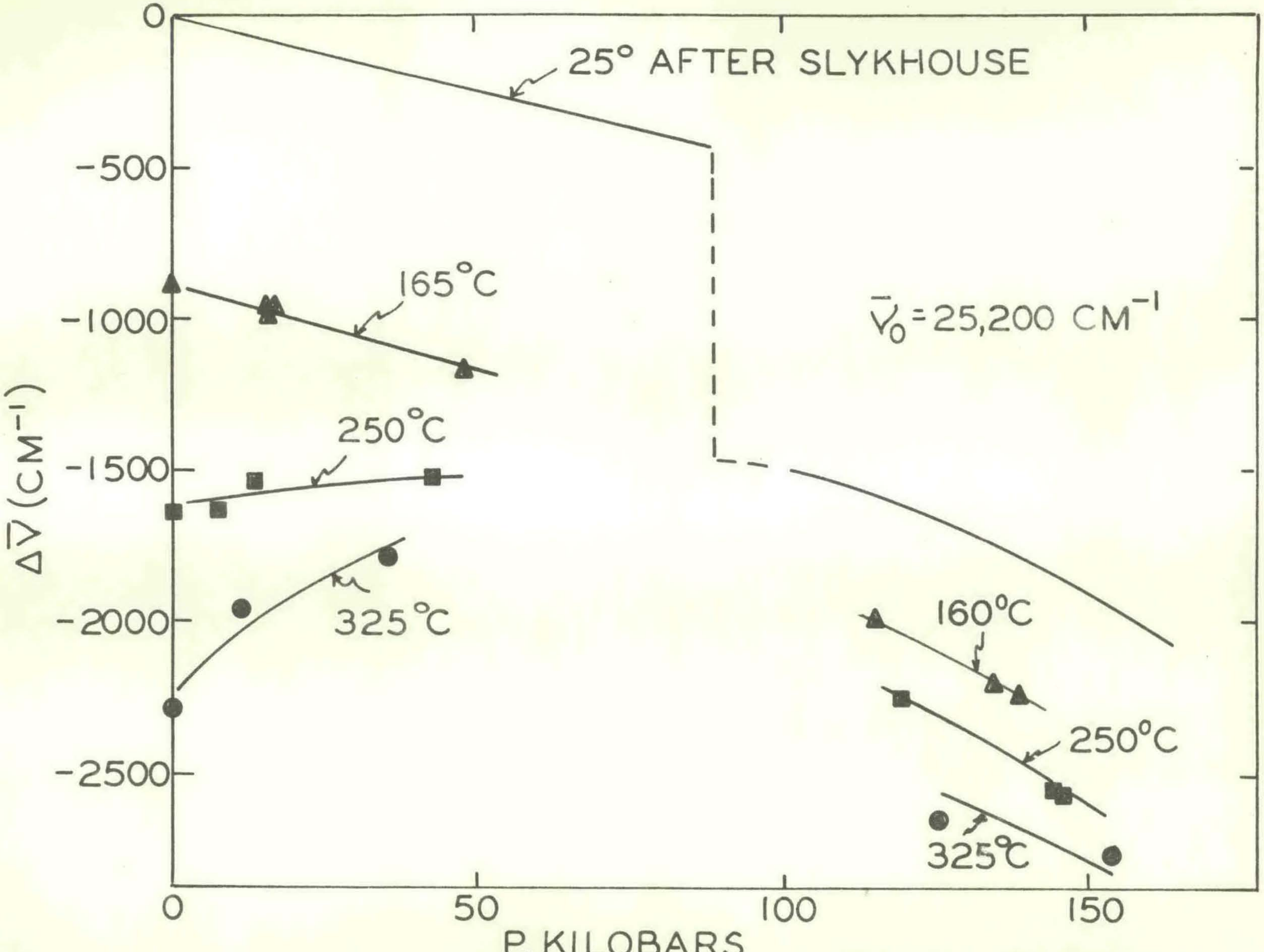

FIG. I SHIFT OF ABSORPTION EDGE OF AgCl AT HIGH PRESSURE & TEMP.

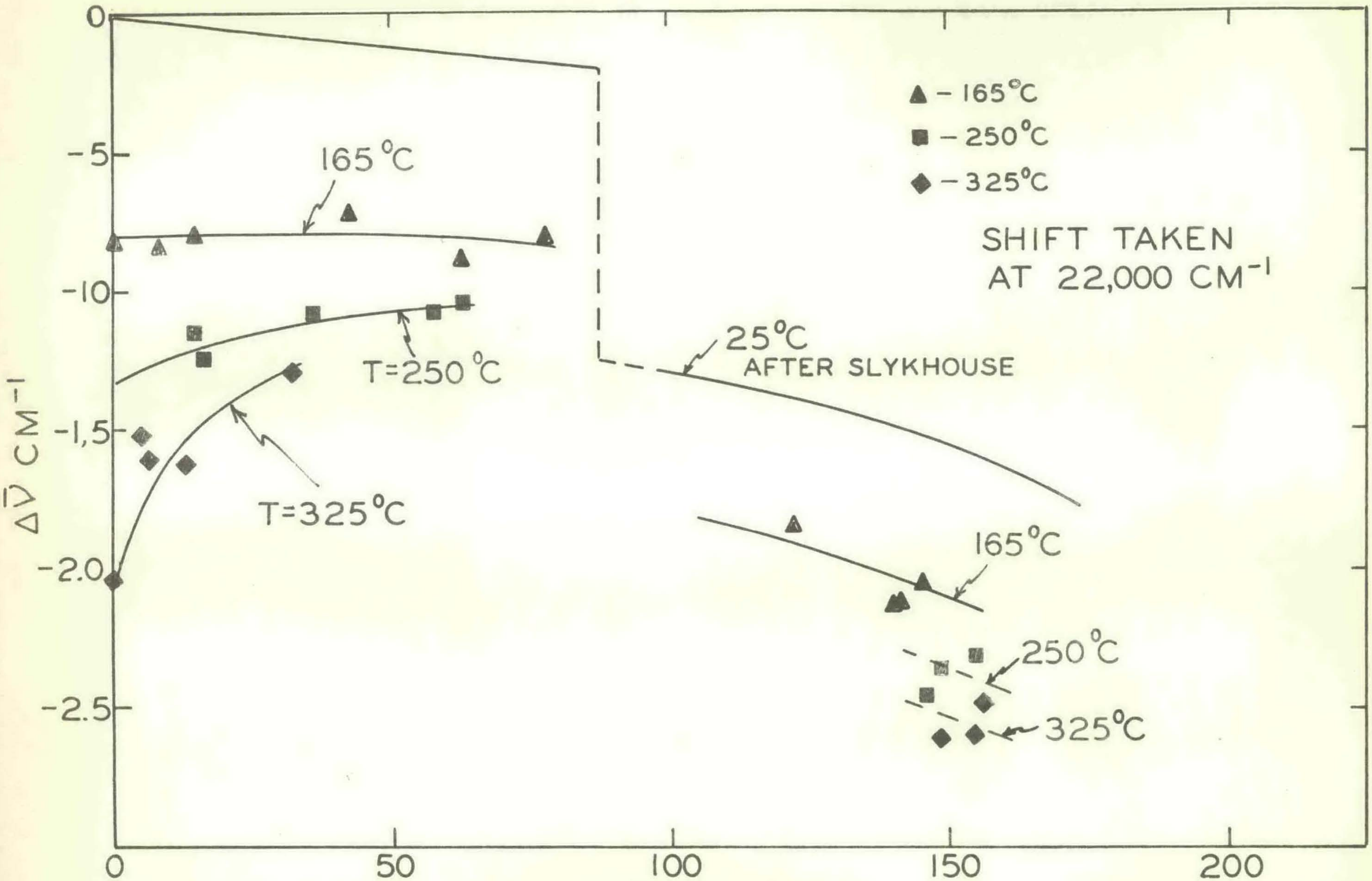

FIG. 2 SHIFT OF ABSORPTION EDGE OF AgBr AT HIGH PRESSURE AND TEMPERATURE

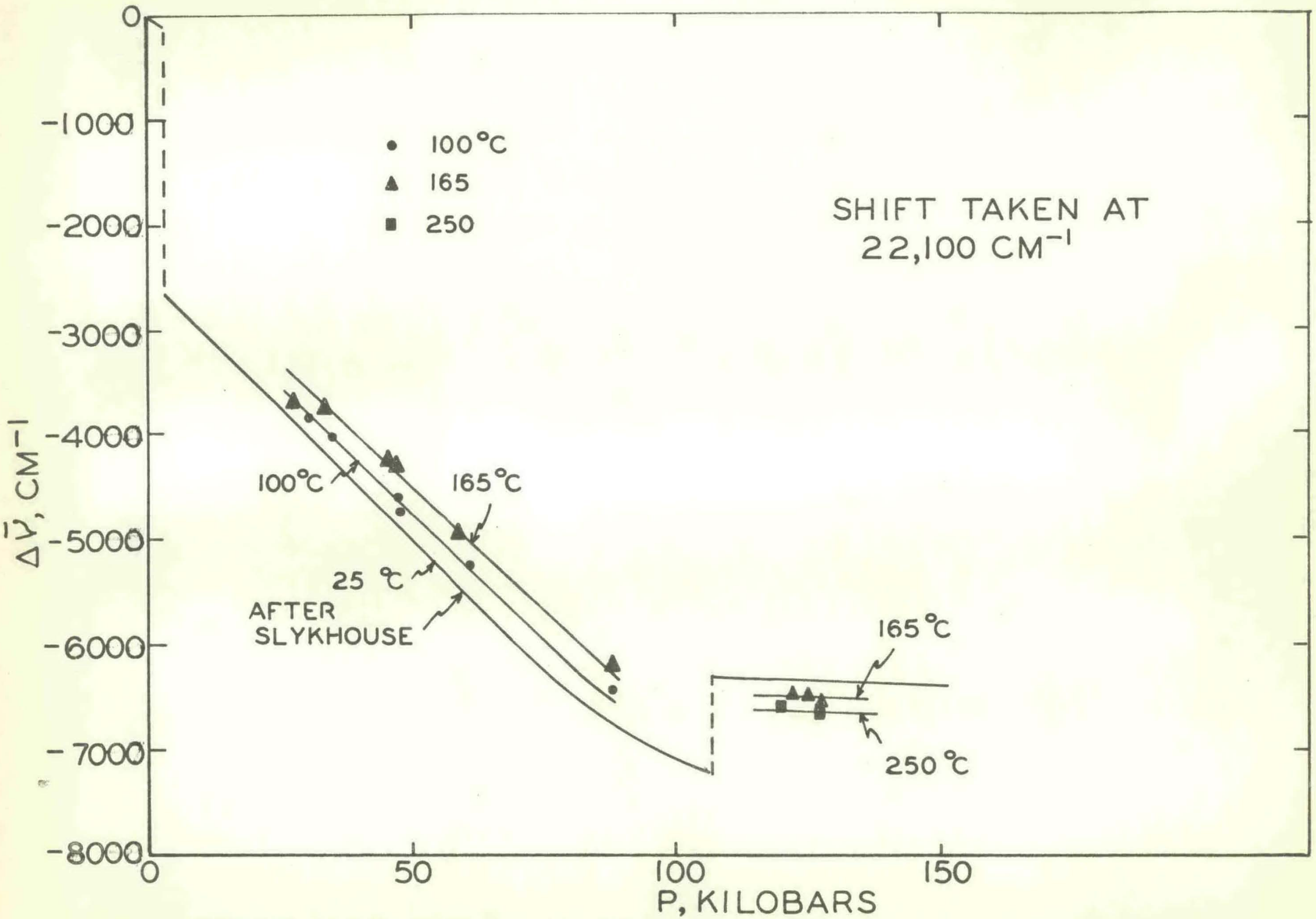

FIG.3 SHIFT OF ABSORPTION EDGE OF AgI AT HIGH PRESSURE AND TEMPERATURE