EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part II. Crystals (*Contd.*)

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1. Introduction

IN a previous communication[1] the author has studied the effect of temperature on the intensities of Raman lines in some typical crystals like quartz, mercuric chloride and sodium nitrate. The frequencies chosen for study in those three cases are 465 cm.$^{-1}$, 315 cm.$^{-1}$, and 1065 cm.$^{-1}$, respectively. It has been observed that while according to Placzek's theory the intensities should increase with temperature both for the Stokes and the anti-Stokes lines, experimental results show that there is a marked decrease in intensity for the Stokes lines with increase of temperature. The rate of decrease is almost the same for all the three cases even though the frequencies studied are distinctly different. It has also been observed that the rate at which the intensity increases in the case of the anti-Stokes lines is not in conformity with that expected on the basis of Placzek's theory. The ratio of intensities between the Stokes and the anti-Stokes lines is, however, in agreement with the expected result.

From the study made by the author in those three cases, two important questions arise, namely, what will be the effect of temperature on different Raman frequencies in the same crystal and will there be any difference between the rate of variation of the intensities for the internal and for the lattice lines. Ornstein and Went[2] studied the effect of temperature on the different Raman lines in calcite and they concluded that the theoretical considerations of Placzek are applicable only for the proper frequencies of the crystal and not to the deformation frequencies very near the exciting line. Their results show no change in intensity for the 1085 line whereas the 710 line and the two lattice lines rapidly decrease in intensity with increase of temperature. This result is contrary to what has been obtained by the author in the case of the 1065 line in $NaNO_3$ which is quite similar to the 1085 line in calcite. In view of the discrepancies and with a view to get a coherent account of the effect of temperature on different Raman lines both internal and lattice in the same crystal and different crystals, the author is making a detailed study of this problem and this paper describes the results obtained in calcite.

2. *Experimental Arrangements*

The experimental arrangements are the same as those described in the previous communication. Light from a quartz mercury arc lamp condensed by a glass condenser is allowed to fall on one face of a nearly one-inch cube of calcite crystal and the scattered light emerging from one of the other faces is focussed on to the slit of a Fuess spectrograph. With an exposure of about 20 hours, intense and clear spectrograms have been obtained. The crystal is heated by means of a specially constructed electrical heater and a thermometer kept in contact with the crystal indicated the temperature with an accuracy of $\pm$ 5° C. Extreme care has been taken to see that the time of exposure and the intensity of the source are maintained constant while obtaining different spectra. The Raman spectra at various temperatures along with a set of intensity marks given by the method of varying slit-widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source are recorded on the same plate. The plate is run through a Moll micro-photometer and the intensities of the various Stokes and the anti-Stokes lines are computed in the usual way.

As the lines studied do not show any appreciable broadening in the temperature range employed, as can be seen from the Plate and also from the micro-photometric records which are not reproduced here, only the peak intensities have been compared.

3. *Results and Discussion*

The results given in the following tables are the mean of several observations. Table I contains the results relating to the effect of temperature on the intensities of the Stokes lines (155, 280, 710 and 1085) in calcite. The calculated results given in the table are obtained with the help of Placzek's relation quoted in Part I.

TABLE I

Temperature °K.	ν_j = 155 cm.$^{-1}$			ν_j = 280 cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·77	1·15	1·50	0·75	1·11	1·48
423	0·59	1·26	2·14	0·61	1·19	1·95
493	0·48	1·42	2·96	0·49	1·31	2·67

TABLE I—(*Contd.*)

Temperature °K	ν_i = 710 cm.$^{-1}$			ν_i = 1085 cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·81	1·04	1·28	0·86	1·01	1·17
423	0·66	1·06	1·60	0·72	1·02	1·42
493	0·58	1·11	1·91	0·62	1·04	1·68

In the above table, the ratio of the intensity of the Raman line at different temperatures to the intensity at 305° along with what is expected from the Placzek's theory are given. It is clear from the table that the quotient of the theoretical value by the value observed is much larger for the low frequency lines. This may be due to the fact that for low frequencies the elastic forces between the nuclei will be small. It is, therefore, evident that Placzek's theory in respect of the temperature dependence of the intensity of the vibrational Raman lines is not applicable for the vibrational Raman lines. The failure appears to be much more prominent in the case of lattice lines than for the internal oscillations in crystals.

Table II contains results relating to the effect of temperature on the anti-Stokes Raman lines ν_i being − 155 and − 280. The calculated results given in the table are obtained with the help of Placzek's relation already quoted in Part I.

TABLE II

Temperature °K.	ν_i = − 155 cm.$^{-1}$			ν_i = − 280 cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·91	1·31	1·44	0·92	1·40	1·52
423	0·85	1·54	1·81	0·85	1·70	2·00
493	0·78	1·86	2·38	0·80	2·16	2·70

It is clear from the above table that the intensities of the anti-Stokes lines decrease with temperature. In all cases previously studied by the author it has been observed that the anti-Stokes lines increase in intensity with temperature though not to the expected extent, but the present investigation provides us with a new case where the intensities of the anti-Stokes lines also decrease with temperature. The discrepancy between the theoretical and the observed values is shown diagrammatically in Figs. 1 (*a*) and 1 (*b*).*

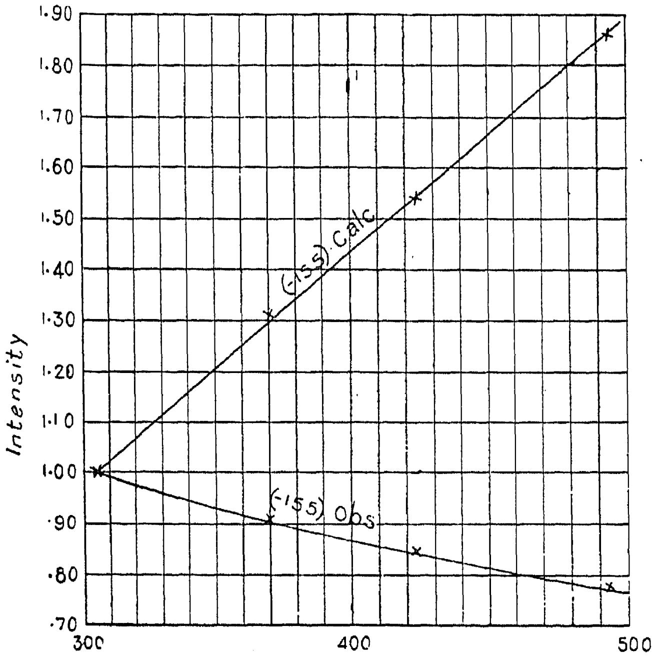


FIG. 1 (*a*)

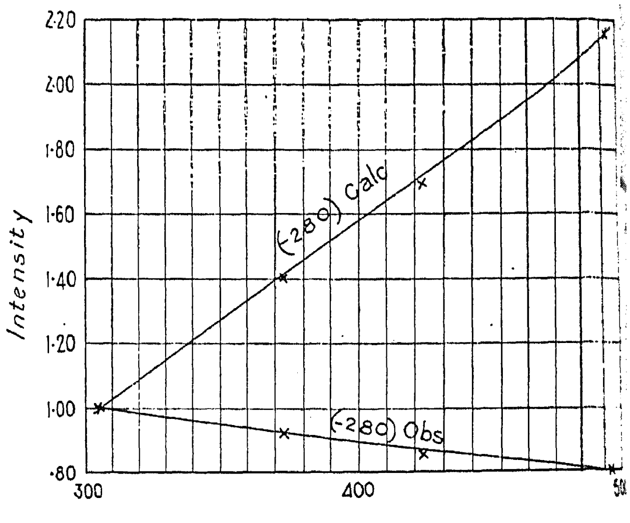


FIG. 1 (*b*)

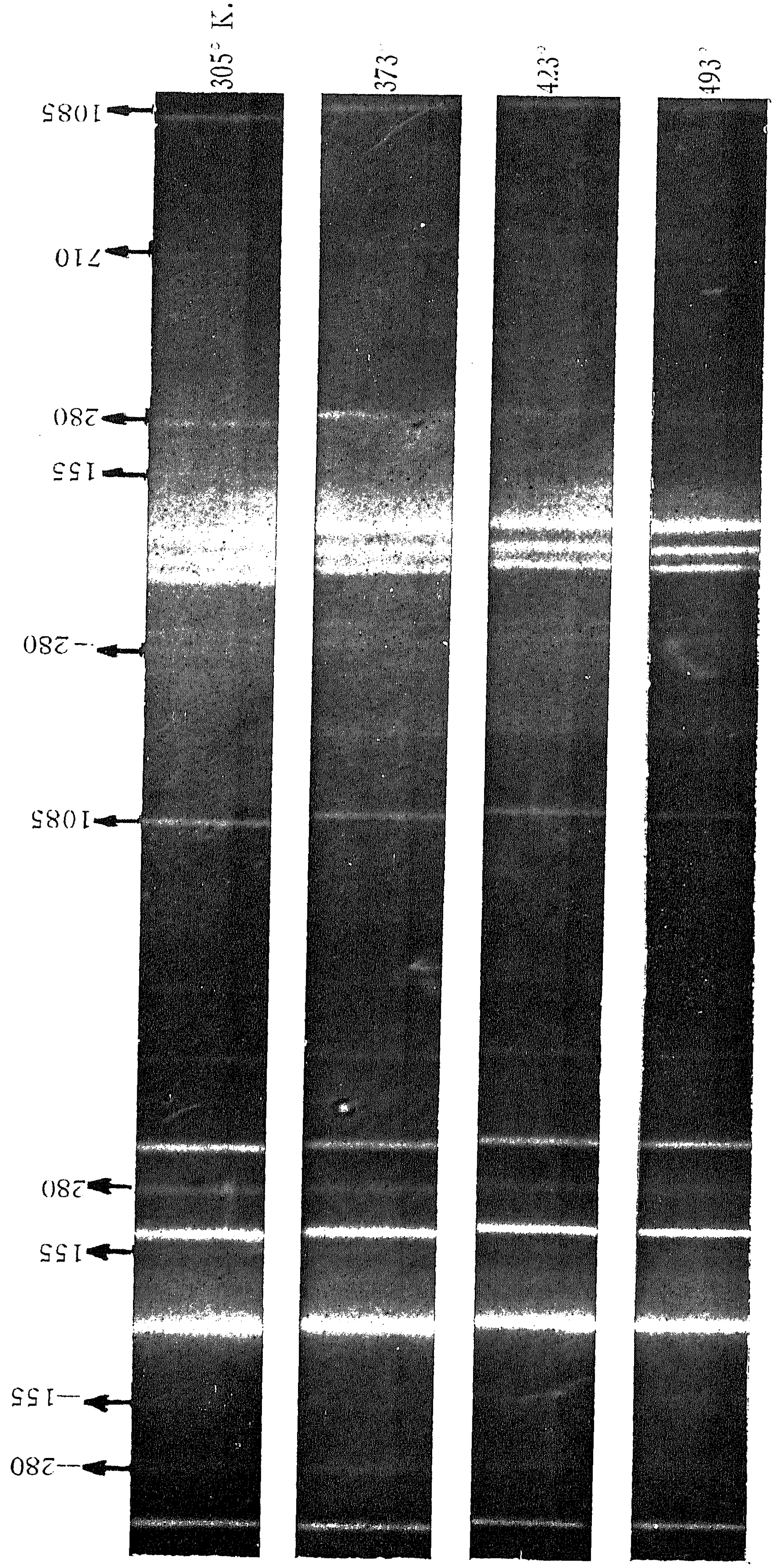
Table III contains results relating to the effect of temperature on the ratio of intensities of the Stokes and the anti-Stokes Raman lines.

TABLE III

Temperature °K.	$\nu_j = 155$ cm.$^{-1}$			$\nu_j = 280$ cm.$^{-1}$		
	$e^{\frac{h\nu_j}{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 . e^{\frac{h\nu_j}{kT}}$	$\frac{I_S}{I_{A.S.}}$ obs.	$e^{\frac{h\nu_j}{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right) . e^{\frac{h\nu_j}{kT}}$	$\frac{I_S}{I_{A\ S.}}$ obs.
305	2·07	1·96	2·00	3·73	3·38	3·30
373	1·81	1·72	1·69	2·93	2·66	2·69
423	1·69	1·60	1·39	2·58	2·34	2·37
493	1·57	1·49	1·26	2·26	2·05	2·02

It can be seen from the above table that the ratio or the intensities of the Stokes and anti-Stokes lines agrees fairly well with the expected result at all temperatures.

* Diagrams showing the rate of fall for Stokes lines are not reproduced. As this is the first instance recorded where the intensity of the anti-Stokes lines also decreases with temperature, this diagram is reproduced with a view to bring out the discrepancy clearly.



Raman spectra of calcite at different temperatures

Table IV contains the results relating to the effect of temperature on the Raman frquencies or the positions of the Raman lines in calcite.

TABLE IV

Temperature °K.	Raman Frequencies			
305	156	282	708	1083
373	151	278	708	1083
423	148	272	710	1084
493	144	268	709	1083

It is obvious from the above table that the lines 710 and 1085 of calcite do not show any shifts whatsoever whereas the lines 155 and 280 show appreciable shifts towards the exciting lines between the temperature interval studied. These results are in agreement with the earlier observations of Ornstein and Went.

4. *Summary*

The effect of temperature on the intensities of Raman lines at 155, 280, 710 and 1085 cm.$^{-1}$ in calcite has been studied. It has been observed that for all the four lines, there is a decrease in intensity with increase of temperature but the rate of decrease is more rapid in the case of lattice lines than in the case of the internal lines. The intensities of the anti-Stokes lines (155, 280) also are found to be decreasing with increase of temperature but the ratio of the intensities of the Stokes and the anti-Stokes Raman lines at different temperatures is found to be in agreement with the expected result. It has been concluded that Placzek's theory regarding the dependence of the intensities of the vibrational Raman lines on temperature is not in agreement with experimental results. The disagreement is more prominent in the case of low frquency lines than in the case of high frequencies. It has also been observed that the two lattice lines in calcite exhibit a marked shift with increasing temperature towards the exciting line whereas the other lines remain in the same positions at different temperatures.

In conclusion, the author takes great pleasure in expressing his grateful thanks to Prof. S. Bhagavantam, HON. D.SC., Principal and Head of the Physics Department, under whose guidance the present investigation has been taken up.

REFERENCES

1. Venkateswarlu, K. .. *Proc. Ind. Acad. Sci.*, 1941, **15**, 529.
2. Ornstein, L. S., and Went, J. J. *Physica*, 1935, **2**, 503.