AD637256

THE JOHNS HOPKINS UNIVERSITY

DEPARTMENT OF PHYSICS

D D C
RECEIVED
JUL 28 1966

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION

Hardcopy	Microfiche		
$2.00	$.50	31 pp	

ARCHIVE COPY

LASER RAMAN SCATTERING

STUDIES OF CRYSTALS

Annual Technical Report
Nonr 4010 (06)

Sponsored By:
Advanced Research Projects Agency
Project DEFENDER

ARPA Order Number 306-63

JULY 1, 1966

Baltimore, Maryland 21218

Laser Raman Scattering Studies of Crystals

Annual Technical Report
15 June 1965 - 15 June 1966

ARPA Order No. 306-63
Program Code 3730
Contract No. Nonr 4010(06)

Prepared By:

Dr. Herman Z. Cummins, Principal Investigator
Department of Physics
The Johns Hopkins University
Baltimore, Maryland 21218

June 1966

This research is part of PROJECT DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, Department of Defense, and the Office of Naval Research.

ABSTRACT

Laser excited Raman scattering has been explored as a technique for studying crystals containing impurities, particularly the rare-earth doped crystals widely used as laser materials. Spectra obtained with both an A^+ 4880 Å laser and a He-Ne 6328 Å laser are given for CaF_2 and $CaWO_4$ crystals, both pure and doped with various rare earths. To date, the doped crystals studied have either produced strong fluorescence or else given spectra which are indistinguishable from those of the pure crystals.

Modification of the instrumentation is discussed which is currently in progress. With the improved apparatus, further efforts are planned to look for electronic Raman structure of the rare earth ions as well as modification of the vibrational Raman structure due to perturbation of the lattice by the impurities.

Project Personnel

Research Contract Director

Dr. G. H. Dieke (Deceased August 25, 1965).
Dr. Herman Z. Cummins (Since September 9, 1965).

Research Associate

Dr. A. R. Gee (Terminated 15 October, 1965).

Graduate Assistants

Donald C. O'Shea
Stephen Shapiro

Crystal Grower (Part Time)

Earl Williams

Secretary (Part Time)

Mrs. Ruth Rapoport

PUBLICATIONS

1) "Raman Scattering and Fluorescence in Calcium Fluoride", A. Roger Gee, Donald C. O'Shea and Herman Z. Cummins, Solid State Communications, 4, 43 (1966).

2) "Dewar For Use in Crystal Raman Spectroscopy" A. Roger Gee and Donald C. O'Shea Review of Scientific Instruments, 37, 670 (1966).

Contents

		Page
I	Introduction	1
II	Instrumentation	2
III	Calcium Fluoride	4
IV	Calcium Tungstate	8
V	Electronic Raman Effect	10
VI	Impurity Induced Raman Effect	12
VII	Second Order Raman Effect	14
	Appendix A: Raman Dewar Design	18

I. Introduction

This program was initiated by Professor Gerhard H. Dieke to explore the applicability of laser Raman scattering techniques to the study of crystals -- both through electronic Raman scattering by individual ions, and through cooperative Raman scattering by lattice phonons. In particular, it was hoped that this technique would provide a new source of spectroscopic information about crystals containing dilute rare-earth impurities which are widely used as laser materials.

During the past year, the apparatus has undergone a series of modifications which has permitted us to improve our sensitivity by several orders of magnitude. We are currently further modifying the system to suppress instrumental scattering which is now the principal difficulty in the observation of weak signals. The instrumentation is discussed in section II.

Raman spectra of CaF_2 and $CaWO_4$ both pure, and doped with Er, Ho and Nd are presented and discussed in sections III and IV. The result for these crystals are not very encouraging. In general the rare-earth ions have profuse fluorescence spectra, and even slight fluorescence tends to mask the much weaker Raman effect. For those crystals not exhibiting fluorescence the Raman spectra observed were found to be identical to those of the pure crystals. Further work on this problem has been postponed pending the installation of our new tandem spectrometer which will suppress instrumental scattering and permit a more thorough search for weak Raman lines associated with the impurities.

In addition to the generation of electronic Raman lines, the presence of impurities in crystals may give rise to additional vibrational Raman structure due to the destruction of the translational symmetry of the lattice by the impurities. In some cases this will give rise to new localized modes, and in others will permit first order Raman scattering interaction with normal lattice modes. Work on this problem is just beginning and is discussed in section VI. The related problem of second order Raman scattering in pure crystals is discussed in section VII and for CaF_2 in section III. Second order Raman scattering is generated by simultaneous interaction with two phonons and therefore permits, in principle, a mapping of the two phonon density of states function.

II. Instrumentation

All work performed prior to September 1, 1965 utilized a Spectra Physics model 115 helium-neon laser with maximum output power of 6.5mw at 6328 Å as the light source, and a 75 cm Ebert spectrograph with photographic detection for analysis of the scattered light.

Since September 1965 we have acquired a Spectra Physics model 125 He-Ne laser with approximately 80 mw output, and constructed a small argon-ion laser with 30 mw output at 4880 Å. We have also acquired a Jarrell-Ash one meter Czerny-Turner photoelectric spectrometer which we have used with both EMI 9558 and RCA 7265 photomultiplier tubes. Most of the spectra discussed in this report were obtained with this instrumentation.

When the photomultipliers were cooled in order to reduce the dark-current, it was found that a significant part of the residual noise current consisted of large pulses, between 5 and 100 times larger than the normal photoelectric pulses. This noise, which is assumed to arise from some combination of residual gas breakdown, cosmic ray events and surface conduction, interfered with attempts to study very weak Raman structure. In March 1966, we modified the electronic instrumentation by adding a photon counting section consisting of a linear amplifier, single channel analyzer and ratemeter manufactured by Canberra Industries - Sturrup Nuclear Division.

The analyzer baseline and window height can be set so that photoelectric pulses and true dark current pulses are passed while undersize and oversize noise pulses are blocked. This modification improved our signal-to-noise level by approximately 10 times.

It was found that the search for weak Raman structure was being blocked by scattering of the Rayleigh line within the spectrometer. We have, therefore, acquired a tandem grating spectrometer (Spex 1400) which consists of two identical grating spectrographs coupled to the same drive mechanism. This instrument should reduce instrumental scattering by at least three orders of magnitude from the level encountered with the present instrument. This instrument will be equipped with a new I. T. T. "Star Tracker" phototube whose cathode is electrically masked to match the spectrometer exit slit. With this tube, thermal dark current can presumably be reduced to several counts per minute.

Finally, a special Dewar has been built which permits rapid sample changes for survey work at liquid nitrogen temperature (this Dewar is described in appendix A), and a commercial double Dewar has been ordered which will permit us to extend our measurements down to liquid helium temperatures. The apparatus in its present form is shown schematically in figure I.

III. Calcium Fluoride

CaF_2 is a cubic crystal with a single first order Raman line of 322 cm^{-1} at 300^oK. The Raman spectrum of pure CaF_2 was first reported by Rasetti[1] in 1931 and his results have subsequently been reproduced by other workers.[2-3] The second order Raman spectrum of CaF_2 has never been observed.

Early in 1965 Russell[4] published data on the first and second order spectra of CaF_2. An unsuccessful attempt was made in this laboratory to reproduce his results with a pure CaF_2 crystal. However, a 0.1% doped Er^{3+} crystal gave a spectrum which strongly resembled Russell's data (see Table I). When this crystal was cooled to 77^oK, the broad structure observed in the room-temperature spectrum disappeared and several groups of sharp lines appeared (see Figure 2). Comparison of our results with absorption spectra of $CaF_2(Er^{3+})$ taken by Dr. Charles Rector of this Department led to the identification of these lines as transitions between excited states (D_1, D_2) of the erbium ion and its ground states (F_1, F_2, F_3).[5] It was determined that the structure Russell had identified as second order Raman spectrum was, in fact, fluorescence radiation from

TABLE I

Observed Stokes Spectrum

Russell	Present Data on $CaF_2:Er^{3+}$		
300°K	300°K	77°K	Transitions*
157			
218			
254	253	237	
		250	
275	275	261	
322		289**	
		328	
337	337	340	
		349	
		363	
		368	
386	385	377	$D_2 \rightarrow Z_1$
		392	
		399	$D_2 \rightarrow Z_2$
408	406	406	$D_1 \rightarrow Z_1$
	416 (shoulder)	411	$D_2 \rightarrow Z_3$
		427	$D_1 \rightarrow Z_2$
467	468	439	$D_1 \rightarrow Z_3$
		474	
		488	
543		498	
		541	
572	547	558	
		570	
		578	
603	614	595	
635	628	610	
		639	

TABLE I, Cont'd.

Russell	Present Data on $CaF_2:Er^{3+}$		
300°K	300°K	77°K	Transitions*
670	676	670	
714			
744	751	747	
787	787	785	
		833 (Shoulder)	
838	843	846	
		898	
		944	

Present Data on Pure CaF_2	
300°K	77°K
322	328

*Empirical notation of levels and absorption lines. In LS coupling Z corresponds to the $^4I_{15/2}$ level of Er^{3+} and D to the $^4F_{9/2}$.

Rector, C. W., Pandy, B. C. and Moos, H. W., J. Chem. Phys. (to be published).

**First order CaF_2 line.

an Er^{3+} impurity in his sample. These results were published in Solid State Communications.[6]

Our subsequent attempts to find a true second order Raman spectrum of CaF_2 have been unsuccessful. At present, we can find no Raman scattering greater than 1% of the first order line intensity.

We have been limited by instrumental scattering from searching for weaker structure, but will renew the attempt once the new experimental setup is complete.

Because CaF_2 has only one first order Raman line, and because it is an acceptable host crystal for many rare earth ions, it might be expected that this crystal would provide an excellent candidate for the observation of either electronic Raman transitions between the ground state levels of a rare earth ion or of induced first order Raman modes which might result from breaking the translational symmetry of the lattice.

Thus far there has been no indication of the electronic Raman effect in CaF_2 doped with 0.1% Er^{3+}. We were not able to observe the ground state electronic Raman lines of Er^{3+} in CaF_2, which should lie within 40 cm^{-1} of the exciting line because of the strong instrumental scattering, while intense Er^{3+} fluorescence has prevented any observation of possible impurity induced Raman modes.

The Raman spectrum of pure CaF_2 is shown in Figure 3. The upper trace (C) was recorded with ten times the sensitivity of the lower trace (B). From these spectra the upper limit on

second order Raman scattering (less than 1% of the first order line) was determined by comparison of the height of the first order line in B to the variation in the background in C. The ratio of the intensities of the anti-Stokes line to the Stokes line in the lower trace, (about 0.23) is in agreement with the theoretical ratio:

$$\frac{I_a}{I_s} = \left(\frac{\nu + \nu_{nk}}{\nu - \nu_{nk}}\right)^4 e^{-h\nu_{nk}/kT}$$

IV. Calcium Tungstate

Most of the early work in this project was performed with calcium tungstate, a crystal which can readily be doped with rare earths and which has proven extremely important as a laser material. Our Raman spectra of pure $CaWO_4$ (shown in Figure 4) were found to agree substantially with results published by Russell and Loudon[8] (see Table 2). Direct intensity comparisons were not possible due to an ambiguity in the description of their crystal orientation. Raman spectra of $CaWO_4$ samples doped with Er^{3+}, Ho^{3+} and Nd^{3+} were recorded with both the 4880 Å Ar^+ and 6328 Å He-Ne laser used as exciting sources. The Er and Ho doped samples produced intense fluorescence which completely obscured the Raman spectrum, while the Nd doped crystal (1% nominal) gave a Raman spectrum indistinguishable from that of the pure crystal (see Figure 5).

TABLE 2

Observed $CaWO_4$ Raman Spectrum for Three Orientations of the C-axis

Intensities (nanoamperes)			(Wavelength Shifts (cm^{-1})	
‖ to Spectrometer axis	⊥ to spectrometer axis and slit	‖ to slit	Present	Ref. A
> 10	3.4	0.8	84	86 (140)
3.5	7.0	2.5	114	118 (20)
	0.4		186	180
				196 (1)
0.7		0.4	208	210 (20)
	0.3		270	281 (1)
3.4	1.7	1.2	331	[illegible] (30)
3.2	1.2	0.45	401	403 (15)
0.5	4.0	1.0	796	794 (10)
1.9	0.5	0.1	838	838 (15)
6.0	4.1	2.5	912	922 (70)

Ref. (A) [8] Russell, J. P. and Loudon, R., Proc. Phys. Soc, 85, 1029, (1965). Russell's data appear to correspond to ours for orientation of c-axis to spectrometer axis.

None of these spectra showed any evidence either of electronic Raman structure involving rare-earth ions or of new vibrational structure induced by their presence. In particular, it was hoped that the Raman spectrum of the Nd doped sample would show structure in the region of 1500 Å (displacement from the A^+ 4880 Å line) due to transitions between the $^4I_{9/2}$ ground states and the $^4I_{11/2}$ states [9] of the Nd^{3+} ion, but any such structure, if present, was completely masked by instrumental scattering. After the installation of the new tandem spectrograph we plan to continue the search for electronic Raman lines in this crystal.

V. Electronic Raman Effect

The energy levels of rare earth ions in crystals have been under study in this laboratory for a number of years and constituted one of Professor Dieke's principal interests. The crystal field splits the ion ground state characteristically from a few hundred to a few thousand wavenumbers, and the resultant structure is usually studied by fluorescence or infrared absorption spectroscopy. As Elliott and Loudon[10] pointed out in 1963, however, electronic Raman scattering can provide an additional source of information on the energy level structure since it involves transitions to states frequently not accessible to direct infrared measurements. (In 1930 Rasetti[11] had observed an electronic Raman effect in the molecule NO resulting from the split electronic $^2\Pi$ ground state).

The first reported measurement of the electronic Raman effect for rare earth ions in crystals appeared in 1963. Hougen and Singh[12] observed electronic Raman transitions in Pr^{3+} ions in $PrCl_3$. Recently Chau[13] has reported the observation of several electronic Raman lines of Ce^{3+} ions doped (1% molar) in calcium tungstate.

We have recorded Raman spectra of calcium fluoride and calcium tungstate crystals doped with various rare earths at 300° and $77^{o}K$. (The spectra are discussed in detail in sections III and IV). Generally, the samples studied fell into two categories: most showed fluorescence several orders of magnitude stronger than the normal Raman structure of the pure crystal. For those which did not fluoresce (e. g. Nd in $CaWO_4$) the observed Raman spectrum was identical to that of the undoped crystal. Any electronic Raman structure present was at least ten times weaker than the vibrational structure and was lost in the background produced by instrumental scattering.

We plan to re-examine some of these spectra with the new double spectrograph which will greatly reduce the background thereby facilitating the observation of very weak lines. It appears, however, that the electronic Raman effect of dilute rare earth ions in crystals is in general not easily observable and will therefore probably not provide an important alternative to the presently employed absorption and fluorescence techniques.

VI. Impurity-Induced Raman Effect.

Raman scattering in ideal pure crystals[14] is strictly subject to momentum conservation because of translational symmetry. As a result, phonons participating in first order Raman scattering must have wavevectors comparable to the wavevector of light, while in second order Raman scattering the wavevectors of the two participating phonons must add to form a vector again comparable to the wavevector of light. The inclusion of impurities destroys the translational symmetry thereby permitting Raman scattering in which momentum is not conserved. Classically, if one pictures the individual ion as being modulated by lattice vibrations, then the condition for constructive interference for light scattered by all ions in a perfect lattice requires a specific phase relationship between the motions of adjacent ions which is identical to the choice of a particular phonon wavevector imposed formally by momentum conservation.

The inclusion of randomly spaced impurity ions in the lattice changes the situation since these ions will scatter incoherently thereby eliminating the phase requirement, which is formally equivalent to the lifting of the momentum conservation requirement.

Therefore, the light scattered by impurity ions should exhibit a Raman spectrum characterizing the full dynamic behaviour of the ion. In those cases where the ion "fits" mechanically into the lattice without altering the lattice dynamics (while possessing a scattering cross section significantly

different from that of a normal lattice ion), the Raman spectrum should resemble the normal phonon density of states function $g(\omega)$. This "impurity induced first order Raman effect" is expected to be very weak and has not yet been experimentally observed.

A different result arises if the impurity ion is badly matched to the lattice either in mass or restoring forces. In this case, a localized mode of vibration can occur whose frequency is outside of the band of normal lattice frequencies.[15] The ion will then be very weakly coupled to the lattice modes and will primarily move at the frequency of the localized mode.

This phenomenon has been widely studied in recent years following the original pioneering work of Lifshitz[16]. Stekhanov and Eliashberg have recently reported the observation of Raman lines produced by localized vibrations of Li in KCl[17], and of I, Br and Li in KCl[18].

Experiments of this type are particularly important for laser materials since the optical characteristics of the active impurity ions are strongly effected by the lattice vibrations. However, one needs to know the spectrum of lattice vibrations as seen by the impurity ion and <u>not</u> that of the pure crystal. This information is extremely difficult to obtain by other techniques, but may be found naturally from the impurity induced Raman spectra. A study of the problem is about to be initiated in this laboratory. We have obtained a set of iodine doped KCl crystals ranging from 0.025 to 1.0 mole percent

iodine from the Optovac Company, North Brookfield, Massachusetts. We will first attempt to reproduce (and then refine) the Russian results, and later use the technique in the study of other crystals.

VII. Second-Order Raman Effect

Momentum conservation restricts first order Raman scattering through the requirement that the participating phonon have wavevector $\vec{q}$ equal to $\vec{k}$, the difference between the wavevectors of the scattered and incident light, $\vec{k}_s$ and $\vec{k}_o$. Since the magnitude of $\vec{k}$ for light is less than 0.1% of the maximum $\vec{q}$ in crystals, the phonons observed in first order Raman scattering are essentially at the center of the Brillouin zone and generate Raman shifts equal to the q=o intercept of the optical phonon modes.[14] Thus first order Raman scattering cannot be used to study the phonon dispersion curves except at the zone center.

In 1931, Fermi and Rasetti[19] discovered that rocksalt produces a broad Raman spectrum which they interpreted as a second order effect. In the phonon language, the scattering is produced by a pair of phonons whose wavevectors $\vec{q}_1$ and $\vec{q}_2$ add vectorially to $\vec{k}$. Thus second order Raman scattering is not restricted to the center of the zone. Since phonons from the entire zone participate, the second order spectrum will be proportional to the combined two-phonon density of states function subject to $\vec{q}_1 + \vec{q}_2 \approx 0$ and appropriate selection rules.

Much experimental work has been done on the second order Raman effect in recent years, particularly on the alkali halides. Because the effect is weak, it is ideally suited to the techniques of laser Raman spectroscopy. Recently, Worlock and Porto[20] have reported laser Raman results for NaCl similar to the earlier results of Welsh et al.[21]

We have looked for second order Raman scattering in CaF_2, so far without success. (see Section III). This effort will be continued with our new apparatus and will be discussed in subsequent reports.

References

(1) Rasetti, F., Nature 127, 626 (1931).

(2) Press, D. C., Proc. Indian Acad. Sci. A31, 56 (1950).

(3) Ananthanarayanan, V., Z. Phys. 167, 39 (1962).

(4) Russell, J. P., Proc. Phys. Soc. 85, 194 (1965).

(5) Rector, C. W., Pandy, B. C. and Moos, H. W., J. Chem. Phys. (to be published).

(6) Gee, A. R., O'Shea, D. C., and Cummins, H. Z., Solid State Comm. 4, 43 (1966).

(7) Mizushima, S., "Raman Effect" in Handbuch der Physik, 26, (Springer-Verlag, Berlin, 1958) p. 203.

(8) Russell, J. P. and Loudon, R., Proc. Phys. Soc. 85, 1029 (1965).

(9) Carlson, E. H. and Dieke, G. H., J. Chem. Phys. 34, 1602 (1961).

(10) Elliott, R. J. and Loudon, R., Phys. Letters 3, 189 (1963).

(11) Rasetti, F., Z. Phys. 66, 646 (1930).

(12) Hougen, J. T. and Singh, S., Proc. Roy. Soc. (London) 277, 193 (1964).

(13) Chau, J. Y. H., J. Chem. Phys. 44, 1708 (1966).

(14) Loudon, R., Adv. Phys. 13, 423 (1964).

(15) Maradudin, A. A., Phonons and Phonon Interaction ed. by Bak, T. A. (W. A. Benjamin, Inc., New York, 1964) p. 424.

(16) Lifshitz, I. M., Nuovo Cimento, Suppl. [10] 3, 716 (1956).

(17) Stekhanov, I. A. and Eliashberg, M. B., Sov. Phys. Sol. St. 5, 2185 (1964).

(18) Stekhanov, I. A. and Eliashberg, M. B., Sov. Phys. Sol. St. 6, 2718 (1964).

(19) Fermi, E. and Rasetti, F., Z. Phys. 71, 689 (1931).

(20) Worlock, J. M. and Porto, S. P. S. presented at "Conference on Phonons", University of Edinburgh, Edinburgh Scotland (April 6-7, 1966).

(21) Welsh, H. L., Crawford, M. F. and Staple, W. J., Nature 164, 737 (1949).

APPENDIX A

Reprinted from THE REVIEW OF SCIENTIFIC INSTRUMENTS, Vol. 37, No. 5, 670-671, May 1966
Printed in U. S. A.

Dewar for Use in Crystal Raman Spectroscopy*

A. ROGER GEE† AND DONALD C. O'SHEA‡
Department of Physics, Johns Hopkins University, Baltimore, Maryland 21218

(Received 2 December 1965; and in final form, 17 January 1966)

PROGRESS in the field of crystal Raman spectroscopy has been limited by the lack of a stable, intense, monochromatic light source with a very low background continuum. Recently, with the advent of the cw gas laser, this limitation has been removed and interest in the field has been revived. Some of the information to be derived from the Raman spectra can only be obtained when the crystals are cooled to liquid helium or liquid nitrogen temperatures. One is faced with the problem of cooling the crystals, while assuring that the incident and scattered radiations are attenuated as little as possible since Raman scattering from solids is a weak phenomenon.

Most of the conventional methods of cooling crystals contain certain drawbacks. Direct immersion of the crystal in the cryogenic liquid runs the risk of thermal shock. In some cases the incident radiation must be imaged through the liquid nitrogen, resulting in a changing beam path inside the crystal due to unavoidable bubbling. If the crystal is cooled by attachment to a cold finger, it is difficult to measure the temperature of the sample and guard against thermal gradients. Encapsulation of the crystal followed by immersion in liquid nitrogen overcomes the above difficulties, but it is a time consuming process and can create problems in aligning the crystal and the Dewar simultaneously.

We have designed and built a Dewar (see Fig. 1) which has the advantages of encapsulation without its drawbacks. The crystal is located at the bottom of a central column which is flushed by the nitrogen evaporating in the Dewar. The cold nitrogen gas not only cools the crystal, but also prevents moisture from the atmosphere from condensing on the crystal. Alignment is greatly simplified because the crystal is in contact with the Dewar.

The Dewar is constructed of Pyrex with optical grade windows in the bottom of the tip. The entire Dewar is silvered except a slot at the sides and bottom of the tip. The laser beam is directed vertically into the tip from the bottom and the scattered light is collected from the side. For each crystal an aluminum holder is made to fit snugly inside the central column, permitting rapid removal and replacement of crystals and restricting the motion of the crystals inside the column. The holder consists of an aluminum tube open at both ends with a lip at the bottom. Wide slots in the side permit the scattered light to be collected into a spectrometer. A cotton string is attached to the holder for raising and lowering the crystals.

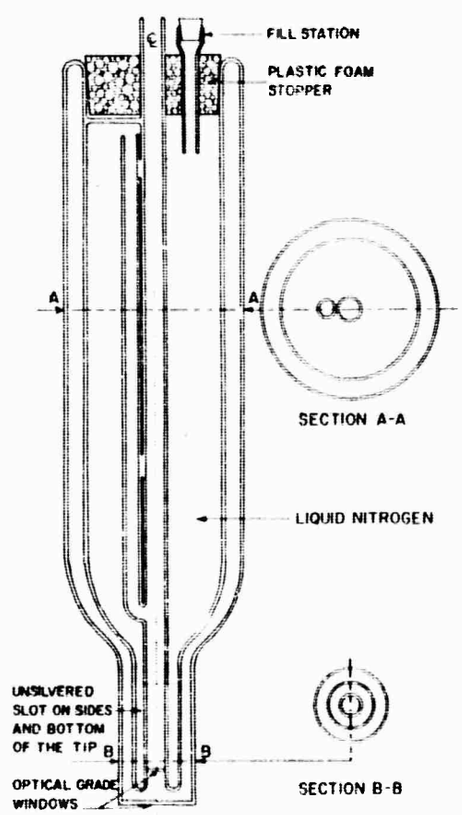

FIG. 1. Section of a Dewar for use in crystal spectroscopy.

NOTES

Imaging the scattering volume on to the slit of the spectrometer is accomplished in the following manner. Before the Dewar is placed in position a white card is held at an angle in the laser beam at the height of the slit, and the spot formed is focused onto the slit by means of an imaging lens. The laser beam is parallel to the slit and aligned on the spectrometer axis when the image of the laser beam moves along the slit as the card is moved in a parallel direction in the laser beam. The Dewar can now be positioned so that the laser beam is in the center of the crystal. With a well cut and polished crystal, and parallel windows on the Dewar, only small adjustments in the laser beam path are required to optimize the amount of Raman scattered radiation received by the spectrometer. When crystals are changed, and when liquid nitrogen is added, there is almost no change in alignment.

Because the dimensions are not critical, they are not included in the figure. Our Dewar is 9 cm in diameter, 44 cm long, and has a capacity of about 1 liter. When the Dewar had been well evacuated, one filling lasted 18 h. Although the central column is open to the atmosphere and the holder sits on a window next to an evacuated space, the nitrogen gas and the aluminum holder act as effective heat transfer media between the crystal and the walls of the column. As a check of the effectiveness of the Dewar for cooling the crystal, a thermocouple in thermal contact with the top of a crystal through a drop of mercury was used to measure the temperature difference between the crystal in position at the bottom of the central column and the liquid nitrogen. The difference was found to be less than 1°C.

One modification which might be considered is the use of square optical cells for the Dewar tip since the imaging of the scattering volume at the slit would be less affected by the addition of liquid nitrogen, and much unwanted scattering would be eliminated. Also, the addition of a nitrogen jacket to the above configuration would permit crystals to be cooled to near liquid helium temperatures.

We would like to thank F. Maiolatesi who built the finished product, and E. Williams for silvering the Dewar.

* Work supported by Project Defender sponsored jointly by ARPA, ONR, and the DOD under Contract Nonr 4010(06).

† Present address: Department of Chemistry, California Institute of Technology, Pasadena, California 91100.

‡ NASA trainee.

FIGURE CAPTIONS

Figure 1. Instrumentation for laser Raman spectroscopy (as of 6/15/66.)

Figure 2. Fluorescence spectra of CaF_2 (Er^{3+}) at 300°K and 77°K (Stokes components only) Full scale photomultiplier currents (Amps.)

A. 2×10^{-6}

B. 5×10^{-7}

C. 2×10^{-8}

D → Z symbols denote identified Er^{3+} fluorescence lines. (Ref. 5)

Figure 3. Raman Scattering Spectra of CaF_2 at 300°K. Full - scale photomultiplier currents (Amps)

A. 3×10^{-6} (S. W. 250 μ)

B. 3×10^{-8} (S. W. 250 μ)

C. 10^{-8} (S. W. 400 μ)

(G denotes spectrometer "ghosts", present when 4880 Å light is directed into the spectrometer).

Figure 4. Raman spectra of $CaWO_4$ for various crystal orientations. 300°K, full scale photomultiplier current: 3×10^{-7} amps.

FIGURE CAPTIONS, Cont'd.

Figure 5. Scattering spectra for doped and undoped $CaWO_4$ at $77^{o}K$.
Full scale photomultiplier current: $3x10^{-7}$ amps,
except section Y-Y of curve A: $3x10^{-6}$ amps.

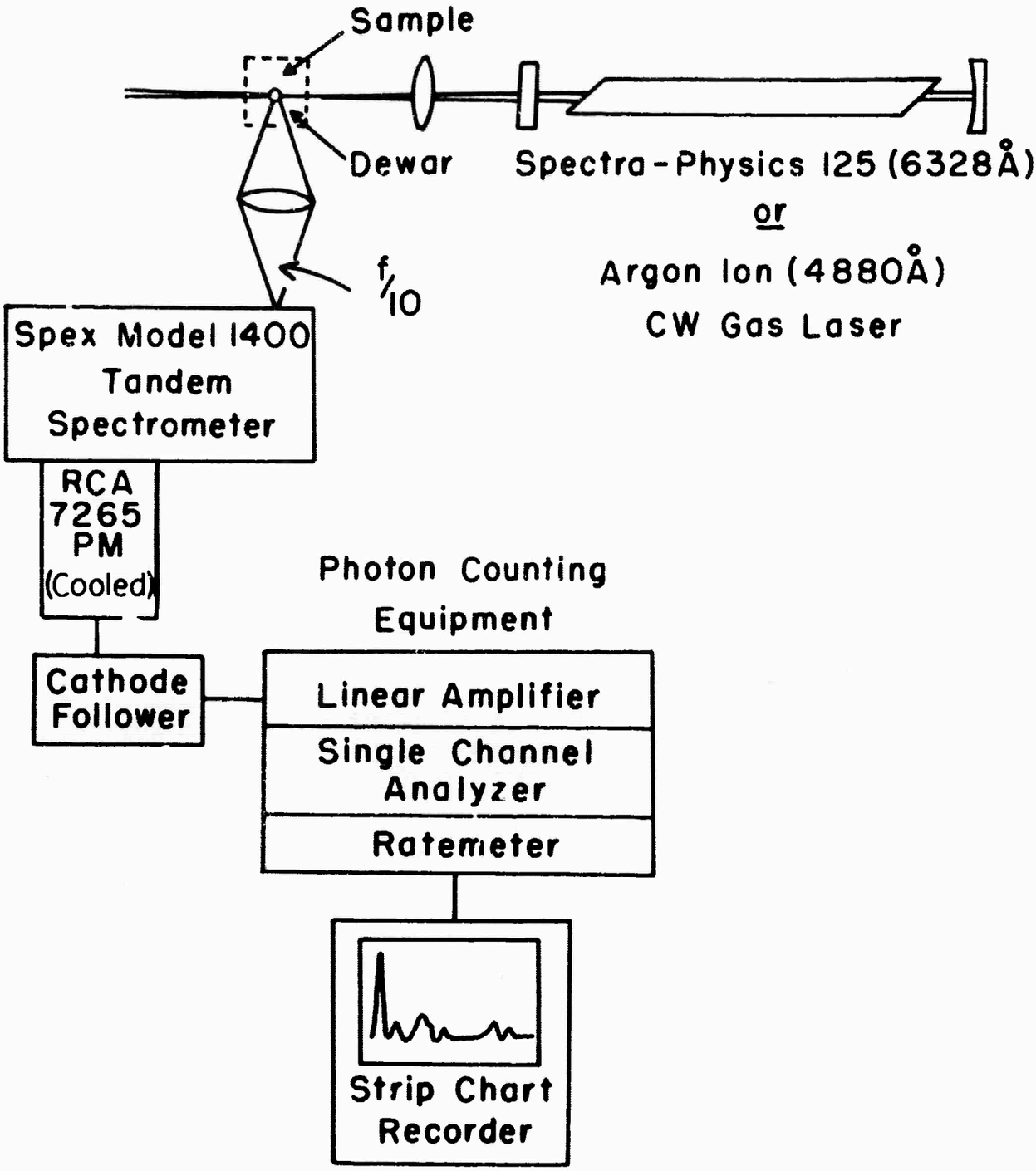
Sample
Dewar
Spectra-Physics 125 (6328Å)
or
Argon Ion (4880Å)
CW Gas Laser
f/10
Spex Model 1400
Tandem
Spectrometer
RCA
7265
PM
(Cooled)
Photon Counting
Equipment
Cathode
Follower
Linear Amplifier
Single Channel
Analyzer
Ratemeter
Strip Chart
Recorder

FIGURE 1

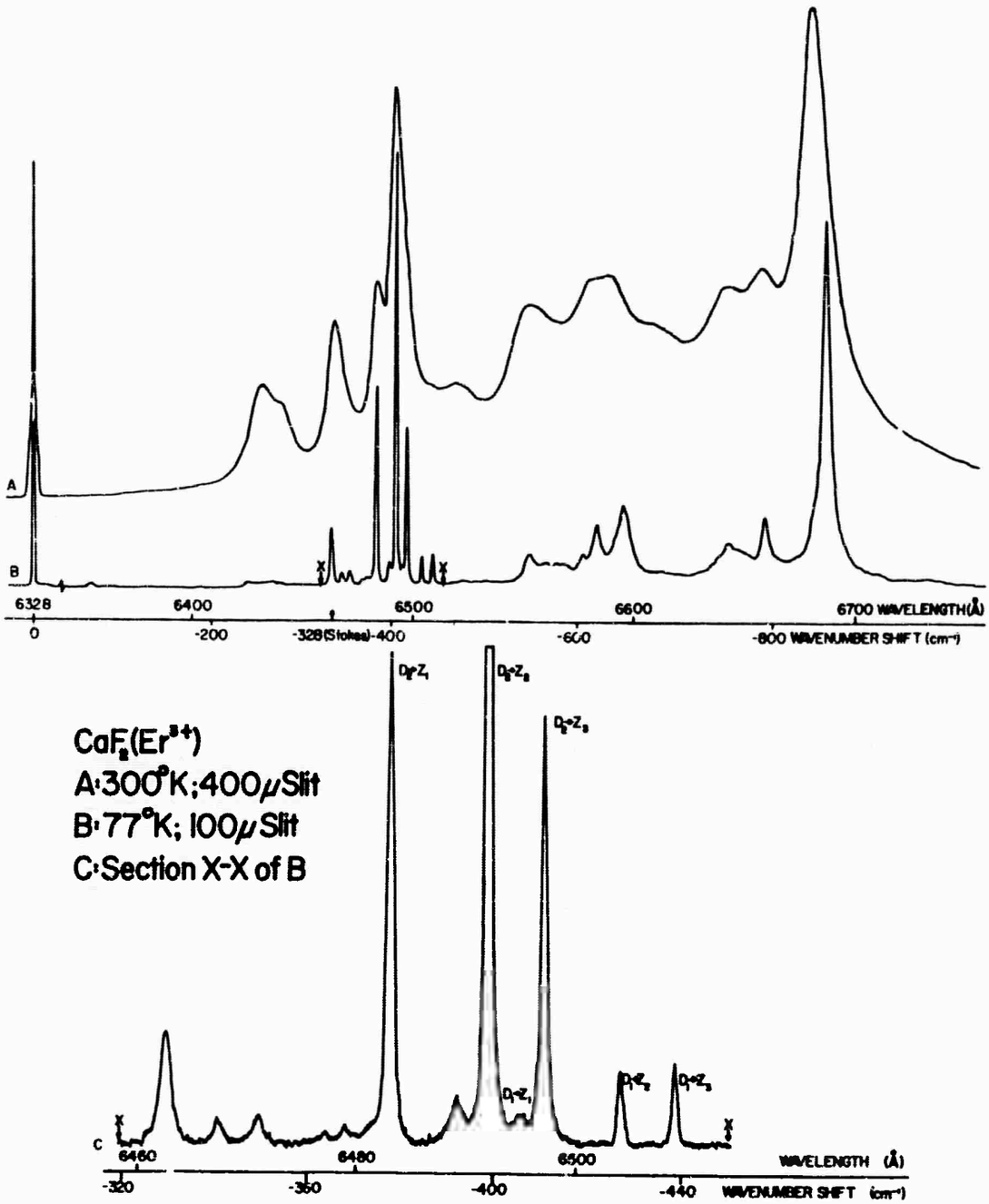
A
B
6328
6400
6500
6600
6700 WAVELENGTH(Å)
0
-200
-328(Stokes)-400
-600
-800 WAVENUMBER SHIFT (cm⁻¹)
CaF₂(Er³⁺)
A:300°K;400μSlit
B:77°K; 100μSlit
C:Section X-X of B
C
6460
6480
6500
WAVELENGTH (Å)
-320
-360
-400
-440
WAVENUMBER SHIFT (cm⁻¹)

FIGURE 2

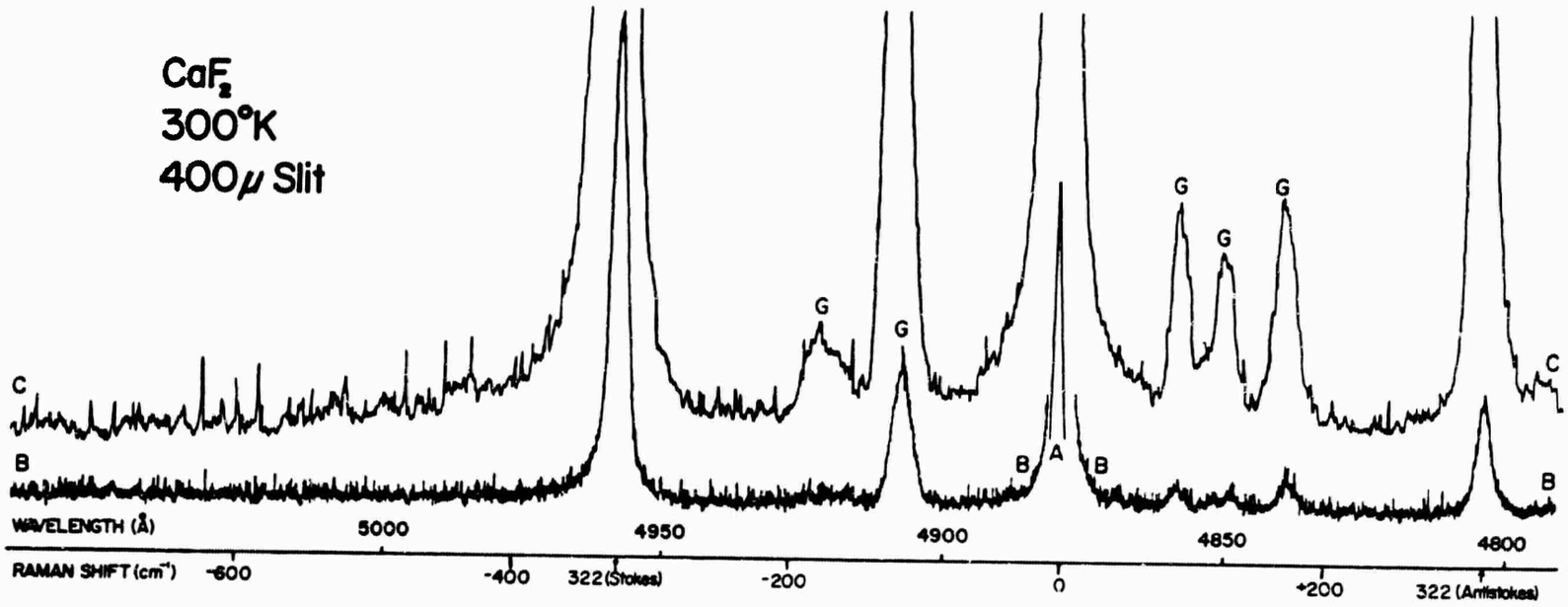
CaF2
300°K
400μ Slit
C
B
G
G
G
G
G
B
A
B
C
B
WAVELENGTH (Å)
5000
4950
4900
4850
4800
RAMAN SHIFT (cm⁻¹)
-600
-400
322 (Stokes)
-200
0
+200
322 (Antistokes)

FIGURE 3

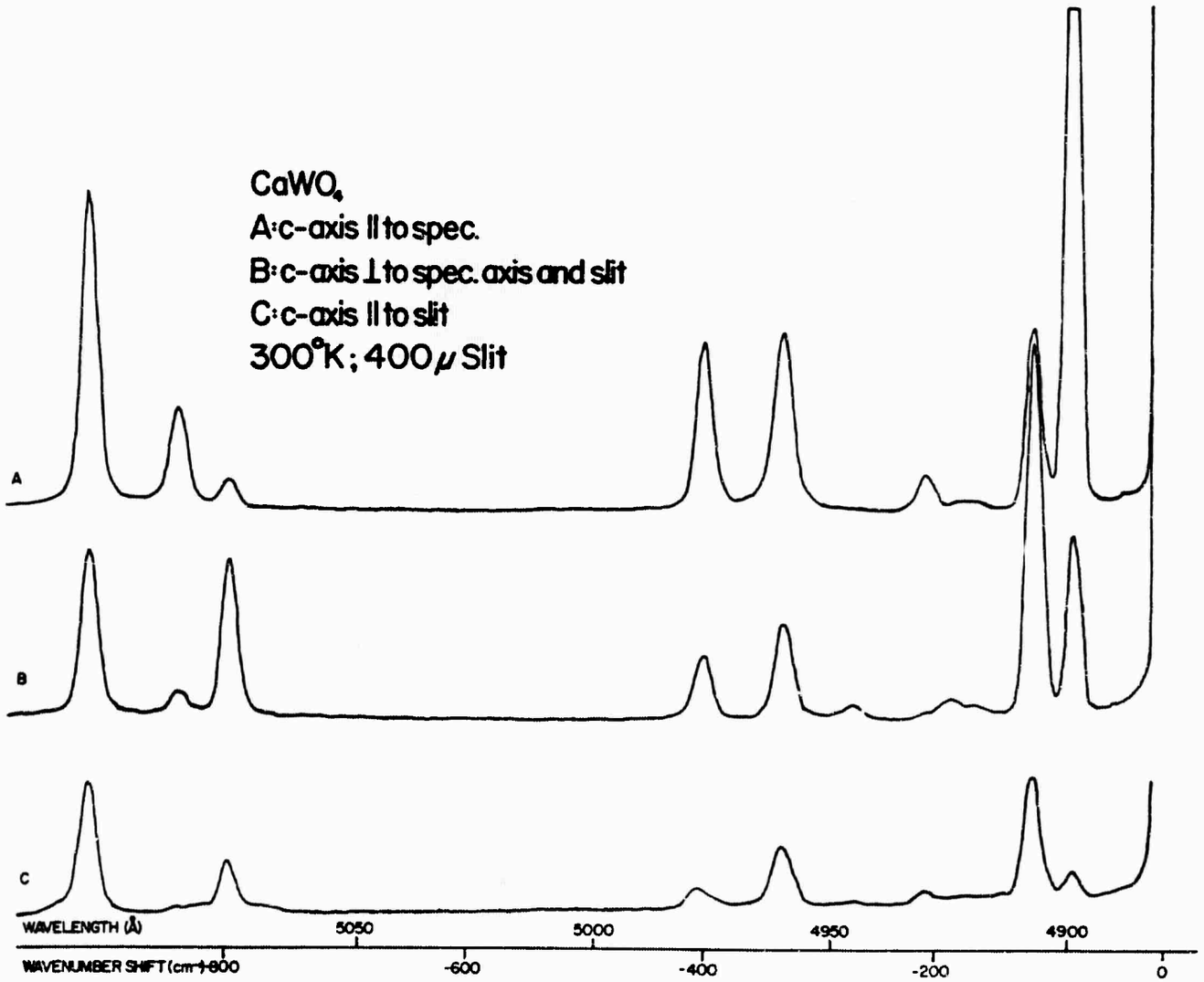
CaWO4
A: c-axis ll to spec.
B: c-axis ⊥ to spec. axis and slit
C: c-axis ll to slit
300°K; 400μ Slit
A
B
C
WAVELENGTH (Å)
5050
5000
4950
4900
WAVENUMBER SHIFT (cm-1)
-600
-400
-200
0

FIGURE 4

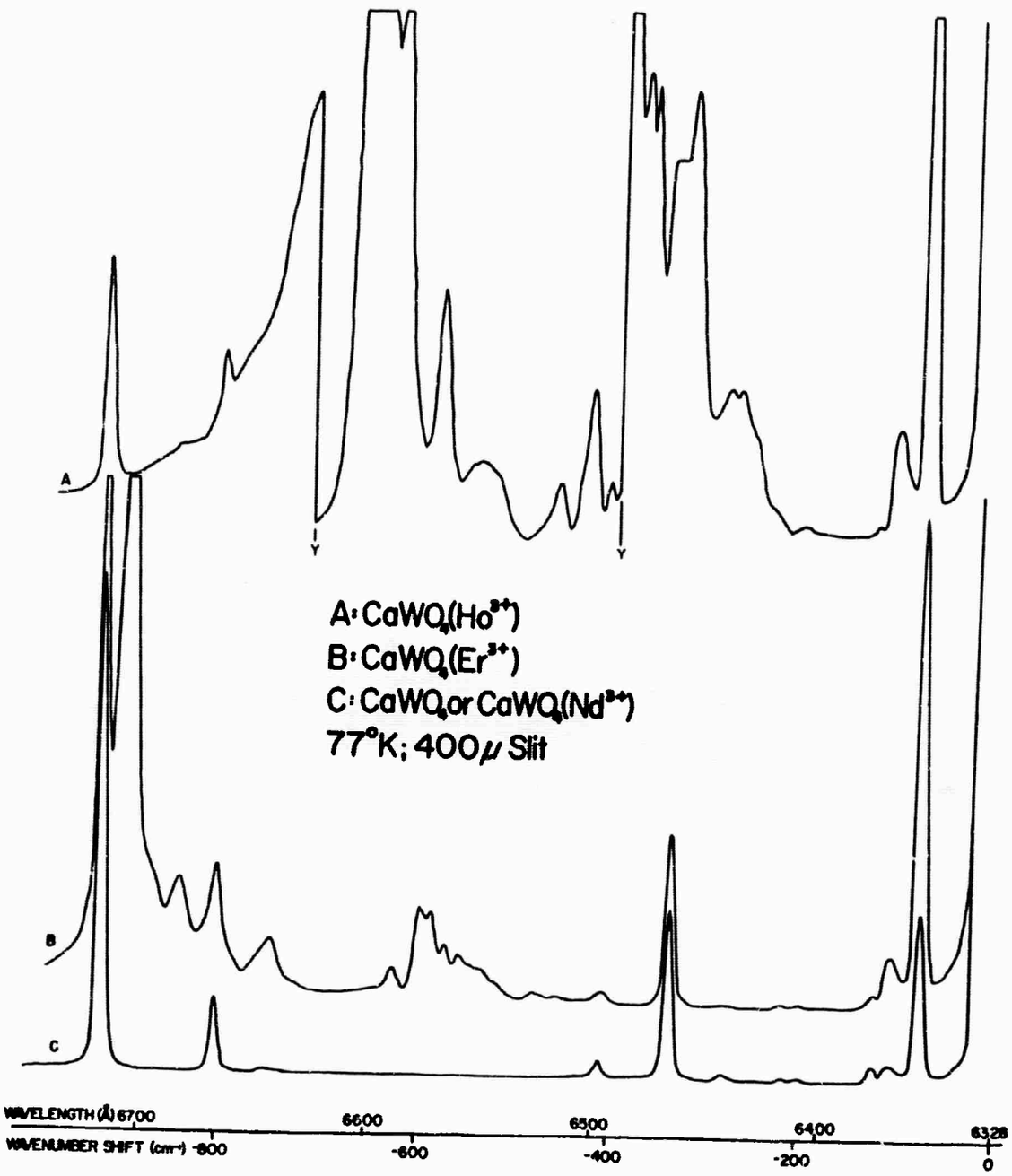
A
B
C
A: $CaWO_4(Ho^{3+})$
B: $CaWO_4(Er^{3+})$
C: $CaWO_4$ or $CaWO_4(Nd^{3+})$
77°K; 400μ Slit
WAVELENGTH (Å) 6700
6600
6500
6400
6328
WAVENUMBER SHIFT (cm⁻¹) -800
-600
-400
-200
0

FIGURE 5