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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: 3
2. GOVT ACCESSION NO.: AD-A103913
3. RECIPIENT'S CATALOG NUMBER: P/S
4. TITLE (and Subtitle): ⑥ Raman scattering spectra of $TmPO_4$
5. TYPE OF REPORT & PERIOD COVERED: Tecnical ~~Report~~ #3,1981
6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): ⑩ Soumyendu Guha
8. CONTRACT OR GRANT NUMBER(s): ⑮ N00014-80-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS:

Chemistry Department
Howard University
Washington D.C. 20059

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 051-733
11. CONTROLLING OFFICE NAME AND ADDRESS:

Office of Naval Research
Arlington, Va 22217

12. REPORT DATE: ⑪ Jun[illegible]981
13. NUMBER OF PAGES: ⑫ 15
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): ⑭ TR-3
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:
16. DISTRIBUTION STATEMENT (of this Report):

Approved for public release : distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):
18. SUPPLEMENTARY NOTES:

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

Raman scattering, $TmPO_4$

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Raman scattering spectra of $TmPO_4$ have been studied between 5^0 K and room temperature. We have observed four electronic transitions between the crystal field split levels of the Tm^{3+} ion ($^3H_6$) which is at the D_{2d} site symmetry of the lattice. In addition to electronic transitions, we have observed eleven phonon peaks which we assign to the internal and external vibrations of the PO_4^{3-} ion in the irreducible representation of D_{4h}.

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Raman Scattering Spectra of $TmPO_4$

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Abstract

Raman Scattering spectra of $TmPO_4$ have been studied between 5^0 K and room temperature. We have observed four electronic transitions between the crystal field split levels of the Tm^{3+} ion ($^3H_6$) which is at the D_{2d} site symmetry of the lattice. In addition to electronic transitions, we have observed eleven phonon peaks which we assign to the internal and external vibrations of the PO_4^{3-} ion in the irreducible representation of D_{4H}.
Like several other rare earth phosphates and vanadates, no phase transition has been observed in this crystal.

PO4(3-)

Introduction

Laser Raman scattering from the electronic states has been found to be a useful method to determine the low lying electronic energy states of rare earth ions in various complexes. In addition, a great deal of information regarding the phase transition in rare earth complexes[1] has alwo been obtained from electronic and one phonon Raman scattering. This paper reports Raman scattering studies of $TmPO_4$ crystal between 5^0 K and room temperature.

The free ion ground electronic state $(^3H_6)$ of the Tm^{3+} ion is split into ten energy levels $(2A_1 + A_2 + 2B_1 + 2B_2 + 3E)$ in the irreducible representation of D_{2d} which is the site symmetry of rare earth ion in the lattice. Our Raman scattering data at 5^0 K have revealed four sharp peaks in the low frequency region (< 300 cm^{-1}) which we identify as the $A_1^1 \rightarrow E^1$ (29 cm^{-1}), $A_1^1 \rightarrow B_2^1$ (84 cm^{-1}), $A_1^1 \rightarrow E^2$ (138 cm^{-1}) and $A_1^1 \rightarrow E^3$ (280 cm^{-1}) electronic transitions. The assignments of these levels are in accord with the optical absorption data of Knoll et al[2] and ultrasonic sound scattering data of Harley et al.[3] Why the transitions between the ground and other excited electronic states were not observed is not understood. It is presumably due to the weak intensities of these peaks or overlapping frquencies with the phonon spectra in the low frequency region (< 500 cm^{-1}).

We have observed at least twelve sharp phonon peaks at room temperature. The two $TmPO_4$ molecules per primitive cell in the D_{4h} zircon structure have thirtysix branches in the phonon spectrum. At $q = 0$, there are thirteen even parity modes $(2A_{1g}^{I} + 2B_{1g}^{I} + B_{2g}^{I} + 2E_{g}^{I} + A_{2g}^{Ex} + 2B_{1g}^{Ex} + 3E_{g}^{Ex})$ and all except A_{2g} are Raman active. We have also labelled the internal and external vibrations of the PO_4^{3-} ion with superfixes I and Ex respectively. The positions and intensities of these peaks vary between room temperature and liquid helium temperature. As will be discussed in the following sections, we attribute it mostly to an anharmonic effect arising due to thermal contraction of the crystal at low temperature.

2. Experimental

Our Raman scattering experiment includes an argon ion laser, a spex 1400 double monochromator and conventional photon counting detection which is directly connected to a PDP 11 computer. This enabled us to store our data on magnetic tapes and then to plot it with the computer plotter. Most measurements were made with the 5145 Å line at 40 mw power level to avoid local heating of the sample. Slits employed were 80-150-80 which is equivalent to a resolution of ~1 cm^{-1}. The sample was mounted inside a cryogenic dewar and was surrounded by helium exchange gas. Temperatures were measured with gold-iron-chromel thermocouple and were controlled by a PAR 152 cryogenic temperature controller. The dimension of the sample was 3x3x4 mm with the c axis parallel to the longest direction and was obtained from the laboratory of Dr.S.H.Smith at Oxford, England. Four independent components of Raman tensors which transform as the $A_{1g}(\alpha_{xx}+\alpha_{yy}, \alpha_{zz})$, $B_{1g}(\alpha_{xx}-\alpha_{yy})$, $B_{2g}(\alpha_{xy})$, and $E_g(\alpha_{xz}, \alpha_{yz})$ irreducible representations of D_{4h} were measured by suitable combinations of incident and scattered polarisations. The conventional 90° scattering geometry were employed to observe the Raman data.

3. Experimental Results and Discussion

3.1. Electronic Raman Spectra

Strong electronic peaks appear between 0 and 300 cm^{-1} below 77° K. The electronic peak at 84 cm^{-1} (Figure 1a) in the B_2 spectrum is as strong (6300 counts/sec or 5 mv dc) as some strong phonon peaks. We identify this peak as the $A_1^1 \to B_2^1$ electronic transition. The choice of the ground state singlet as A_1 is purely arbitrary. At 77° K, a peak at 108 cm^{-1} also appears in the B_2 polarisation (Fig. 2) which we identify as the $E^1 \to E^2$ electronic transition. This 108 cm^{-1} peak also appears in the $A_1 + B_1$ polarisation at 77° K which justifies our assertion to this peak to the $E \to E$ transition.

We have also observed three electronic peaks at 5° K in the E polarisation geometry which we identify as the $A_1^1 \to E$ (29 cm^{-1}), $A_1^1 \to E^2$ (138 cm^{-1}) and $A_1^1 \to E^3$ (280 cm^{-1}). The intensities of these peaks are either comparable or an order of magnitude less than the weaker phonon lines(~ 200 counts/sec or 1 mv dc). A considerable amount of leakage from all polarisation geometries has been observed. We have associated the observed peaks to different polarisation by carefully monitoring the intensities of these peaks. For example, the strong peak at 84 cm^{-1} in the B_2 polarisation (Figure 1) appears as a weak line in the E polarisation and therefore,we regard this peak as a leakage to the E spectrum from the B_2 spectrum.

According to group theory,there are six singlets ($2A_1 + 2B_1 + 2B_2$) in the ground state manifold of the Tm^{3+} ion at the D_{2d} site symmetry. Electronic transitions between these energy levels are all Raman allowed; except the $A_1 \to B_2$ transition, we were unable to observe any other electronic transitions among these singlets. Crystal field calculations on Tm^{3+}: YVO_4(2) indicate that the energy levels arising due to the crystal field splitting of the ground state of Tm^{3+} extend over to 365 cm^{-1}. Although the crystal fields at the rare earth site in the phosphate differs from the vanadates, it is unlikely that the crystal field parameters would change the energy levels significantly in these two systems. We have arrived at this conclusion by comaring the energy level schemes in Eu^{3+}: YVO_4, YPO_4(4) and Er^{3+}: YVO_4, YPO_4(5). For both of these rare earth ions, the energy levels of the ground state manifold do not differ substantially from the phosphates to vanadates as regards to the spread of the energy states i.e. the separation between the ground and final excited state of the ground state manifold. The failure to observe the other singlets is probably due to the weak intensities of these electronic transitions. Another possible explanation is that the frequencies of these singlets lie close to the low lying phonon frequencies which are probably masking them. The observed energy levels are shown in Table 1.

3.2. Phonon Spectra

The Raman active phonon modes can be classified as the internal vibrations of the phosphate ion and external modes in which the phosphate moves as a unit relative to rare earth. The identification of the observed phonon peaks (Figure 2) is achieved by carefully monitoring the intensiti of these peaks in different polarisations. As can be seen in Figure 2, a leakage (labelled as L) from one polarisation geometry to the other has been a considerable problem in assigning the observed phonon frequencies to a particular polarisation geometry. The Table 2 in reference 6 has been a considerable help to us. We have also quoted the corresponding phonon frequencies in $DyPO_4$(6) in Table 2 for comparison. The symmetric stretching mode of free phosphate ion occurs around 980 Cm^{-1}. This is also the most intense peak. We assign the 1057 Cm^{-1} peak to the symmetric stretching mode (A_{1g}) although it is not clear why it has been shifted to higher frequency in $TmPO_4$. Moreover, we have observed a change in frequencies for all external and internal modes as compared to $DyPO_4$. It is possible that the particular crystal we have used may have internal strains; alternatively a strong electron lattice coupling may be reponsible for such a large shift in the observed frequencies in these two systems. Another anomalous trend that we have observed is the temperature dependency of the phonon frequencies. Usually, a decreased temperature results in lattice contraction which leads to increased force constants and higher frequencies. It has been reported (3) that the elastic constant c_{66} in $TmPO_4$ exhibits a marked softening at 20°K. It is probable that a combined effect of the anharmonicity due to thermal contraction and softening of the force constant due to electron lattice coupling is responsible for the anomalous trend of phonon frequencies as a function of temperature.

Finally, we would like to mention that we have not observed any phase transition in this crystal till 5°K. We have carefully investigated the phonon and electronic peaks in the vicinity of this temperature and have not noticed any splitting or significant change in the spectrum, although both phonon and electronic peak started becoming sharper at lower temperature.

4. Conclusion

We have observed four sharp electronic transitions in the low frequency Raman spectra at 5.5° K which we have identified as the transitions between the ground state manifold of the Tm^{3+} ion. Although the group theory predicts ten electronic energy levels, we were able to observe only five of them. In addition, we have also observed eleven Raman active one phonon scattering modes.

Acknowledgements

The author expresses his gratitude to Prof.L.L.Chase of Indiana University for providing the laboratory facilities where most of the low temperature (5° K) work was done. Thanks are due to Dr.R.Prater of Indiana University for computational help with the PDP 11 computer. The author also wishes to thank Prof.R.S.Katiyar of University of Campinas,Brasil for providing the sample. This work is partially by an ONR laser chemistry grant at Howard University.

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Table 1. Frequencies in cm^{-1} of the observed electronic transitions between the energy levels of the ground state manifold of the Tm^{3+} ion.

A_1^1	E^1	B_2^1	E^2	E^3
0	29	84	138	280

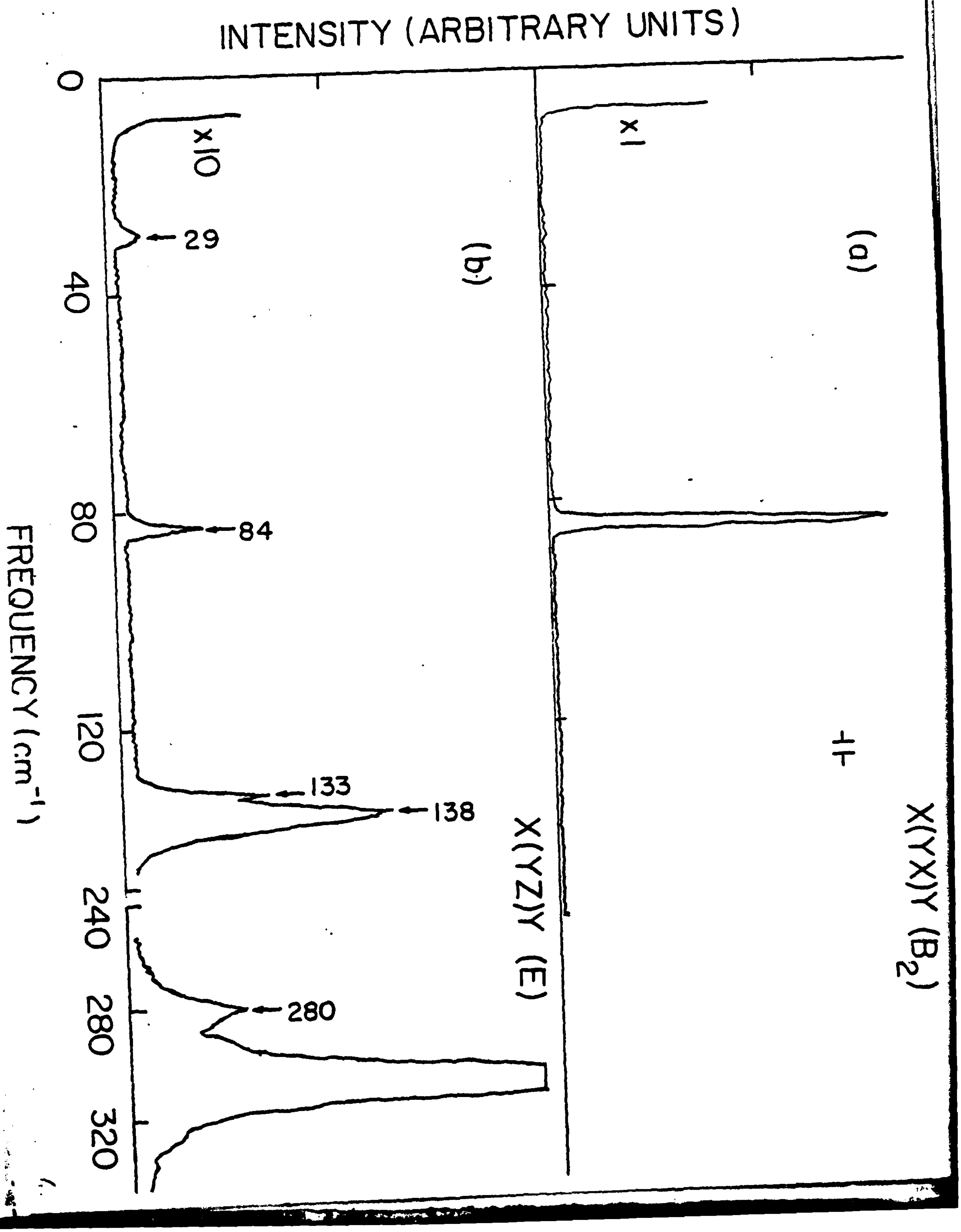
Table 2. Frequencies in cm^{-1} of the Raman active phonon modes of $TmPO_4$ (Accuracy of measurements is ± 2 cm^{-1}). For comparison, the corresponding frequencies of internal and external modes of $DyPO_4$ in reference 6 are also listed.

		A_{1g}	E_g	B_{1g}	B_{1g}	E_g	A_{1g}	B_{2g}	B_{1g}	E_g	E_g	B_{1g}	E_g
$TmPO_4$	300 K	1057	1086	1123	678	597	499	336	-	308	188	141	134
	77 K	1055	1077	1125	683	593	498	334	-	312	185	139	132
	5 K	1051	1075	1117	678	591	497	336	-	309	188	135	133
$DyPO_4$(6)	300 K	997	1017	1053	653	576	485	330	-	294	184	140	130
	77 K	998	1019	1057	655	577	488	330	-	297	186	140	132
	4.5 K	999	1021	1060	656	578	491	328	-	296	-	138	132

Figure Captions

Figure 1. Low frequency spectra at 5° K. (a) The B_2 (xy) spectrum shows a strong peak at 84 cm^{-1} which is identified as the $A_1^1 \rightarrow B_2$ electronic transition. (b) The E (xz) spectrum shows three electronic transitions which are identified as the $A_1^1 \rightarrow E^1$ (20 cm^{-1}), $A_1^1 \rightarrow E^2$ (138 cm^{-1}) and $A_1^1 \rightarrow E^3$ (280 cm^{-1}) transitions. The peak at 84 cm^{-1} is a leakage from the B_2 polarisation, while the peaks at 133 cm^{-1} and 308 cm^{1} are phonon lines.

Figure 2. One-phonon Raman spectra at 77°K. Different polarisation geometry spectra are shown in (a), (b), (c) and (d). Here L indicates the leakage from one geometry to the other, while e indicates the electronic Raman transitions which are described in Figure 1. The most intense lines are observed in A1g (c) and A_{1g}, B_{1g} (d) spectra. The intensity of the 1057 cm^{-1} is about 6300 counts/sec, while that of 1125 cm^{-1} peak is 5000 counts/sec.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FREQUENCY (cm^{-1})
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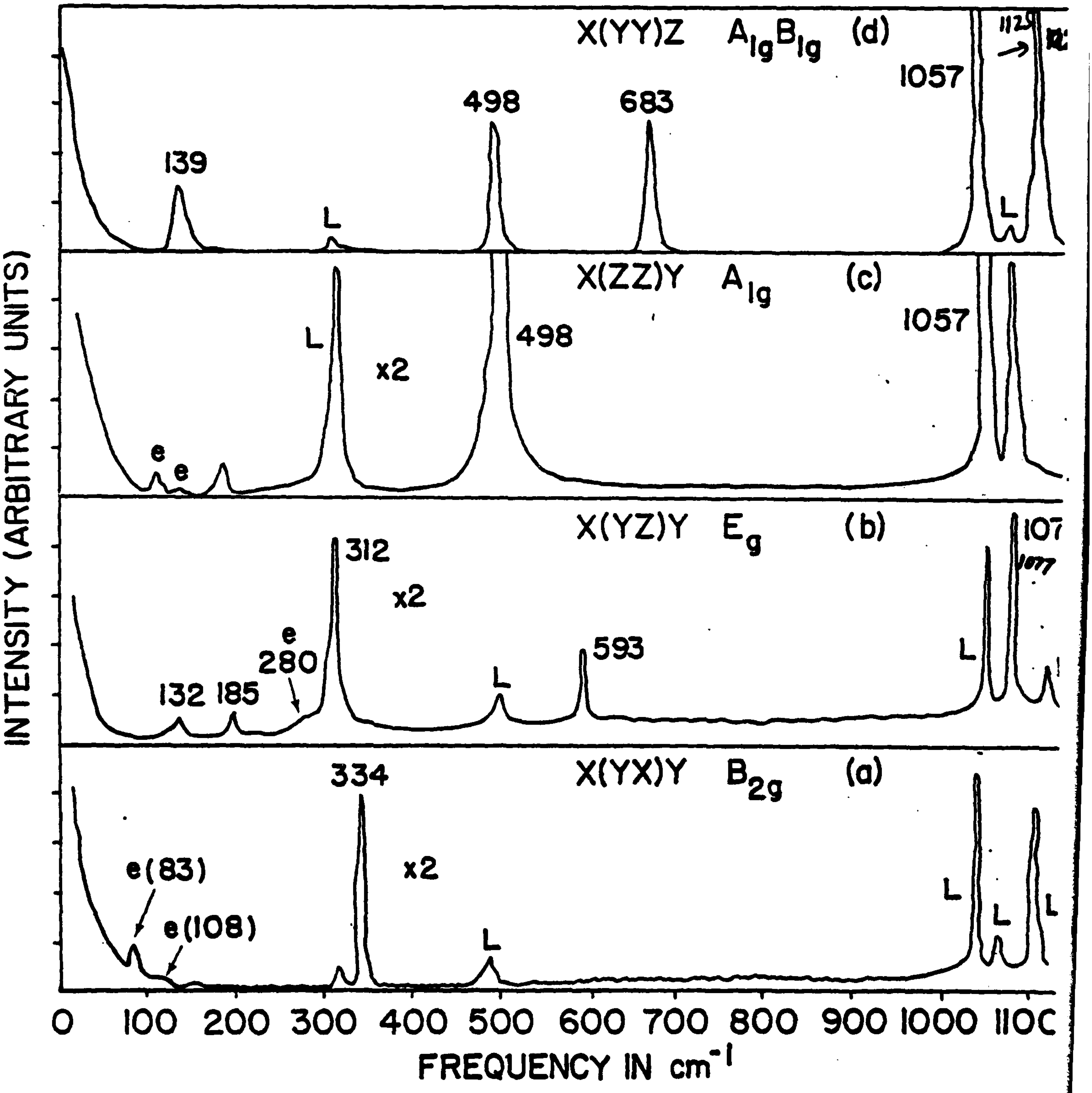
X(YZ)Y (E)

12



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L
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683
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112
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X(YZ)Y E$_g$ (b)
132
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