



INSTYTUT FIZYKI JADROWEJ
W KRAKOWIE
INSTITUTE OF NUCLEAR PHYSICS
CRACOW

REPORT No 791/PS

LOW FREQUENCY MOTIONS
OF WATER MOLECULES
IN CRYSTALLINE $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

E. MIKULI, J. M. JANIK, G. PYTASZ, J. A. JANIK, J. ŚCIESIŃSKI,
E. ŚCIESIŃSKA, A. MAZURKIEWICZ

142

KRAKÓW

1972

This report has been reproduced directly from
the best available copy

Распространяет:
ИНФОРМАЦИОННЫЙ ЦЕНТР ПО ЯДЕРНОЙ ЭНЕРГИИ
при Уполномоченном Правительства ПНР
по Использованию Ядерной Энергии
Дворец Культуры и Науки
Варшава, ПОЛЬША

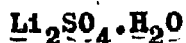
Available from:
NUCLEAR ENERGY INFORMATION CENTER
of the Polish Government Commissioner for Use
of Nuclear Energy
Palace of Culture and Science
Warsaw, POLAND

Drukuje i rozprowadza:
OŚRODEK INFORMACJI O ENERGII JĄDROWEJ
Pełnomocnika Rządu d/s Wykorzystania Energii Jądrowej
Warszawa, Pałac Kultury i Nauki

Wydaje Instytut Fizyki Jądrowej

Nakład 590 egz., Objętość ark. wyd. 0.7, Ark. druk. 1.13, Data
złożenia maszynopisu przez autora 8.2.72, Oddano do druku
16 II 1972, Druk ukończono III. 1972, SP-09/250/66, Zam. nr 57/72

LOW FREQUENCY MOTIONS OF WATER MOLECULES IN CRYSTALLINE



DRGANIA SIECIOWE DROBIN WODY O NISKICH CZĘSTOŚCIACH



НИЗКОЧАСТОТНАЯ ДИНАМИКА МОЛЕКУЛ ВОДЫ В КРИСТАЛЛИЧЕСКОМ



E. MIKULI, J.M. JANIK, G. PYTASZ

Chemical Institute of the Jagiellonian University, Kraków,

J.A. JANIK, J. ŚCIESIŃSKI

Institute of Nuclear Physics, Kraków,

R. ŚCIESIŃSKA, A. MAZURKIEWICZ

Physica' Institute of the Jagiellonian University, Kraków

С р а с о в

February, 1972

II

Low frequency lattice vibrations in lithium sulphate monohydrate were obtained using the INS, IR and RS methods. They were interpreted as lattice acoustic vibrations of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal.

We suppose that it was possible to obtain acoustic vibrations by optical methods owing to the existence in the crystal lattice of an orientational disorder of water molecules. (auth)

Niskie częstotliwości drgań sieciowych monohydratu siarczanu litu uzyskano metodami: INS, IR i RS. Zostały one zinterpretowane jako związane z drganiami akustycznymi sieci krystalicznej $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

Wysunięto hipotezę, że ewidencja drgań akustycznych metodami spektroskopii optycznej stała się możliwa dzięki istnieniu orientacyjnego nieuporządkowania molekuł wody w kryształach.

Низкие частоты решеточных колебаний моногидрата сульфата лития были получены методом НРН, ИК, КР и интерпретированы как акустические колебания кристаллической решетки.

Предполагается, что выявление акустических колебаний методами оптической спектроскопии, стало возможным благодаря существованию ориентировочного беспорядка молекул воды в кристалле.

1. Introduction

Among crystals containing water of crystallization, ice and lithium sulphate monohydrate occupy exceptional position, because of the specific situation of water molecules in both crystals. Namely, there exist chains of hydrogen bonds between water molecules and also two types of lattice defects - orientational and ionic (Fig. 1a and b). These facts are of primary importance for the lattice dynamics and also for the electrical and relaxational properties of both crystals.

In this paper we show the possibility of obtaining by infra-red and Raman spectroscopy information concerning acoustic vibrations in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals. This possibility arises because of the disordered structure which cancels the forbiddance of detection of the acoustic type of motion in optical spectroscopy. It is also possible that two quasi-particles are involved in the photon absorption or scattering process, thus enabling a penetration of the whole Brillouin zone, not only of the $q=0$ region.

2. Experimental

The main part of the experimental material for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ was obtained on the far infra-red Grubb-Parsons interferometer IRIS belonging to the Institute of Nuclear Physics in Kraków. The wave number range covered by the measurements was $50 - 300 \text{ cm}^{-1}$. Samples were prepared in the form of a Nujol mull and placed between polyethylene plates. Measurements with various concentrations of monohydrate in Nujol were made, but only at room temperature. Interferograms were transformed to absorption vs. wave number dependence by using a fast Fourier transformation programme^{/1/} and the ODRA-1204 computer. Several experimental runs were made and a good reproducibility of results was obtained. Additionally, two measurements of absorption in far infra-red, for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ with two independent samples, were made for us by Mr. A. Baise at the Edward Davies Chemical Laboratories in Aberystwyth, U.K. on a Grubb-Parsons cube interferometer, also at room temperature. A comparison of absorption spectra of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ at roughly the same concentration in Nujol (ca. 0.22 g/ml) is presented in Fig. 2. Figure 3

presents absorption spectra of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ at various concentrations. Figure 4 presents the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ spectrum measured at the Edward Davies Chemical Laboratories.

The second part of the experimental material (only for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) was obtained from a previously made neutron inelastic incoherent scattering experiment (IINS) ^{12/}. These results, however, were now transformed into the phonon density spectrum $g(\omega)$. Its comparison with far infra-red data is presented in Fig. 5.

The third part of the experimental material may only be treated as complementary to the two preceding ones. It consists of Raman spectra which were measured on the Cary Model 81 spectrometer with a He-Ne laser light source, belonging to the Chemical Institute of the University of Oslo (Fig. 6).

3. Discussion of results

As may be seen from Fig. 5 the two spectra, the far infra-red one and the IINS one, are very similar, especially in their lower frequency parts. The two spectra have similar numbers of peaks and their positions coincide. We believe that the peaks correspond to maxima of phonon density connected with translatory

motions of water molecules. Arguments for such an interpretation come from the relatively high intensity of neutron peaks, which must certainly be attributed to the motions of hydrogen atoms, and also from the near identity of the $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4\cdot\text{D}_2\text{O}$ spectra, as seen from Fig. 2.

A great similarity of neutron and infra-red spectra in the $50 - 120 \text{ cm}^{-1}$ region leads us to the conclusion that the corresponding peaks are connected with acoustic phonons. This interpretation is at first sight shocking. It is a very well known fact that infra-red and Raman spectroscopy are unable to give information concerning acoustic phonons because in the scattering process only the $q=0$ phonons may be involved. The IINS method may on the other hand penetrate the whole Brillouin zone.

Before we try to solve this paradox, we should note that in a number of papers /3/, /4/, /5/, /6/, /7/, the possibility of detection of acoustic phonons in interaction with photons was discussed. In all cases this possibility was connected with various types of disorder in the crystal. Whalley et al., /7/, /8/, /9/, for instance, explain IR evidence of what they interpret as acoustic phonons in ice as being caused by the

existence of an orientational disorder of H_2O molecules in the ice lattice. The authors present a theory of infra-red absorption by orientationally disordered crystals, and prove that there are no selection rules forbidding photon interactions with acoustic phonons.

We now stress the fact that in lithium sulphate monohydrate there exists a similar open chain of mutually connected water molecules as in ice^{/10/,/11/}. It is therefore natural to assume in the $Li_2SO_4 \cdot H_2O$ crystal a similar orientational disorder of H_2O molecules. We are tempted to express this fact in terms of the Gosar^{/12/} idea of correlated rotational interactions in ice. According to this idea there exists a quasi-particle connected with correlated proton shifts. This quasi-particle may also be treated as a transport of a Bjerrum defect through the lattice, (Fig. 1a). If such a quasi-particle indeed exists it may interact both with photons and with acoustic phonons, thus leading to two quasi-particle light absorption (or light scattering), not necessarily limited to the $q=0$ region. A similar picture could appear in connection with the transport of the ionic defect through the lattice (Fig. 1b).

4. Conclusion

In summing up, we stress the fact of a great similarity between the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal and ice. In both crystals there exist orientational disorders of H_2O molecules leading to a violation of the restriction which forbids the acoustic vibrations to be seen in infra-red and Raman spectroscopy. It remains an open problem whether such orientational disorders may be correlated, thus leading to the existence of a specific quasi particle in both crystals. Support for such a picture may be the fact of a preferred proton conductivity in the direction of the 2_1 - axis in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal, as measured by Thomas and Clark^{/13/}.

Acknowledgements

Our thanks are due to Professor Mansel Davies and to Mr. A. Baise from the Edward Davies Laboratory in Aberystwyth for their measurements on the cube interferometer. We also thank Doc. P. Klæbøe from the Chemical Institute of the University of Oslo for his kind help in enabling us to use the CARY 81 Model Raman Spectrometer.

Literature

- 1/ M. Sudnik-Hryniewicz, private communication.
- 2/ A. Bajorek, J.A. Janik, J.M. Janik, I. Natkaniec, K. Parlinski, Yu.N. Pokotilovsky, M. Sudnik-Hryniewicz, V.E. Komarov, R.P. Ozerov, S.P. Solovov; "Neutron Inelastic Scattering", vol. II, p.143, IAEA, Vienna 1968.
- 3/ K. Dransfeld, J.Phys., 28 (1967), C 4-157.
- 4/ L. Genzel, K.F. Renk, R. Weber, Phys.Stat.Sol., 12 (1965) 639.
- 5/ E.M. Amrhein, Phys.Lett. 29A (1969) 329.
- 6/ E.M. Amrhein, F.H. Mueller, Trans.Faraday Soc. 64 (1968) 666.
- 7/ E. Whalley, J.E. Bertie, J.Chem.Phys. 46 (1967) 1264, 1271.
- 8/ E. Whalley, J.E. Bertie, H.J. Labbé, J.Chem.Phys., 50 (1969) 4501.
- 9/ E. Whalley, H.J. Labbé, J.Chem.Phys., 51 (1969) 3120.
- 10/ N.W. Rannev, R. Ozerov, I.D. Datt, A.B. Tovbis, Kristallografiya (USSR) 10, (1966) 914.
- 11/ H.G. Smith, S.W. Peterson, H.A. Levy, J.Chem.Phys., 48 (1969) 5561.
- 12/ P. Gosar - "Proton-Proton and Proton-Lattice Interactions in Ice", Ljubljana, Yugoslavia (to be published).
- 13/ J.M. Thomas, T.A. Clarke, Trans. Faraday Soc., 65 No. 562 (1969) 2718.

Figure captions

- Fig. 1a Transport of a Bjerrum defect through the chain. Proton 1 is shifted by rotation as shown by the arrow and a hole remains in its previous position. This hole will soon be occupied by proton 2 shifted rotationally from the next hydrogen bond etc.
- Fig. 1b Transport of an ionic defect through the chain. Proton 1 is shifted to the second equilibrium position of the hydrogen bond. This causes a shift of the proton in the next hydrogen bond to a similar shift etc.
- Fig. 2. A comparison of infra-red absorption spectra of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ measured on the IRIS instrument. $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ spectrum is elevated by one $\ln \frac{I_0}{I}$ unit in respect to $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ one. Resolution 4 cm^{-1} .
- Fig. 3. Far infra-red absorption spectrum of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ at different concentrations measured on the IRIS instrument.
- Fig. 4. Far infra-red absorption spectrum of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ measured with two different samples on the cube instrument.
- Fig. 5. A comparison of far infra-red data and neutron incoherent inelastic scattering data for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.
- Fig. 6. Raman spectrum of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in the low frequency region. Arrows are pointing the peaks connected with acoustic phonons.

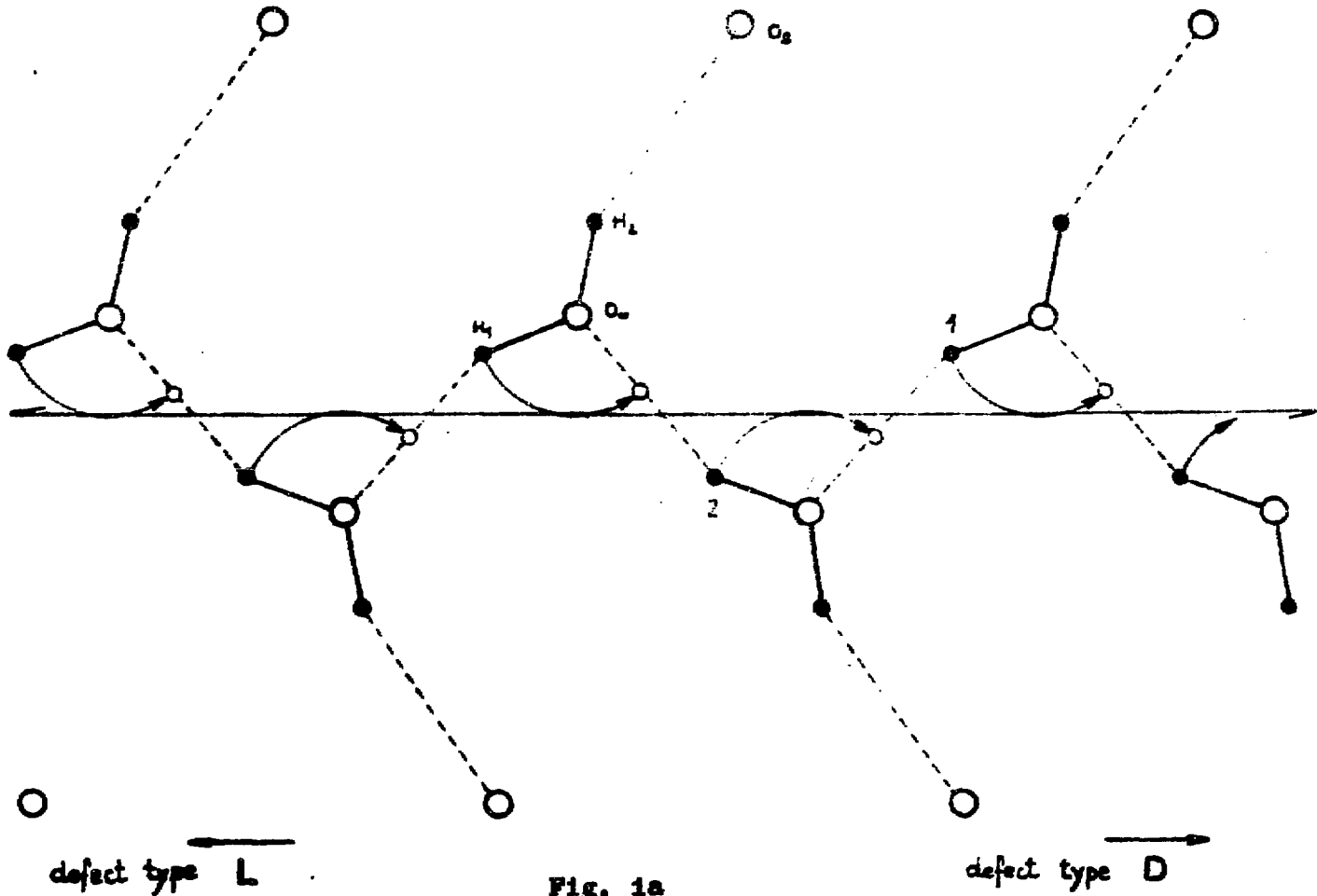


Fig. 1a

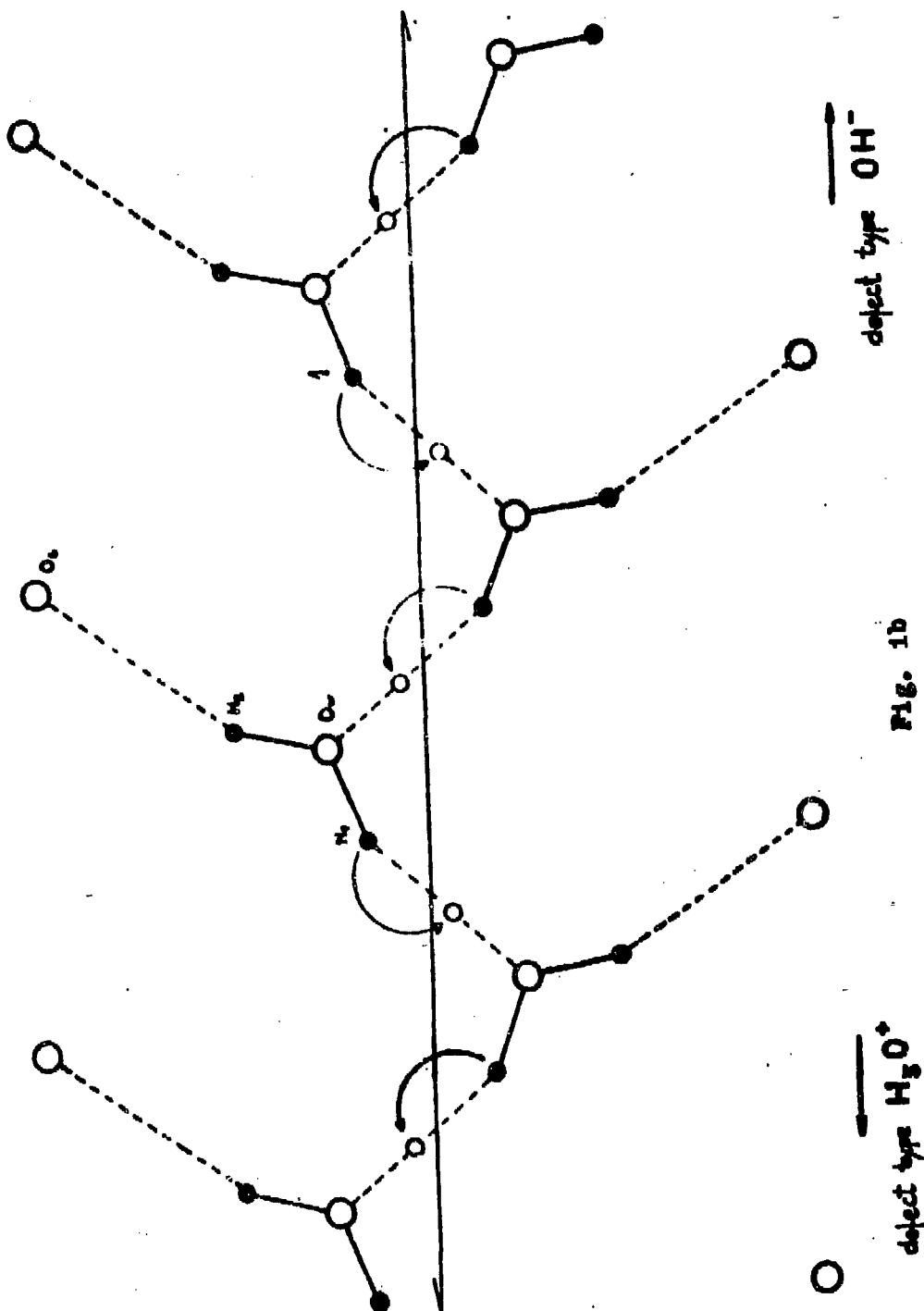
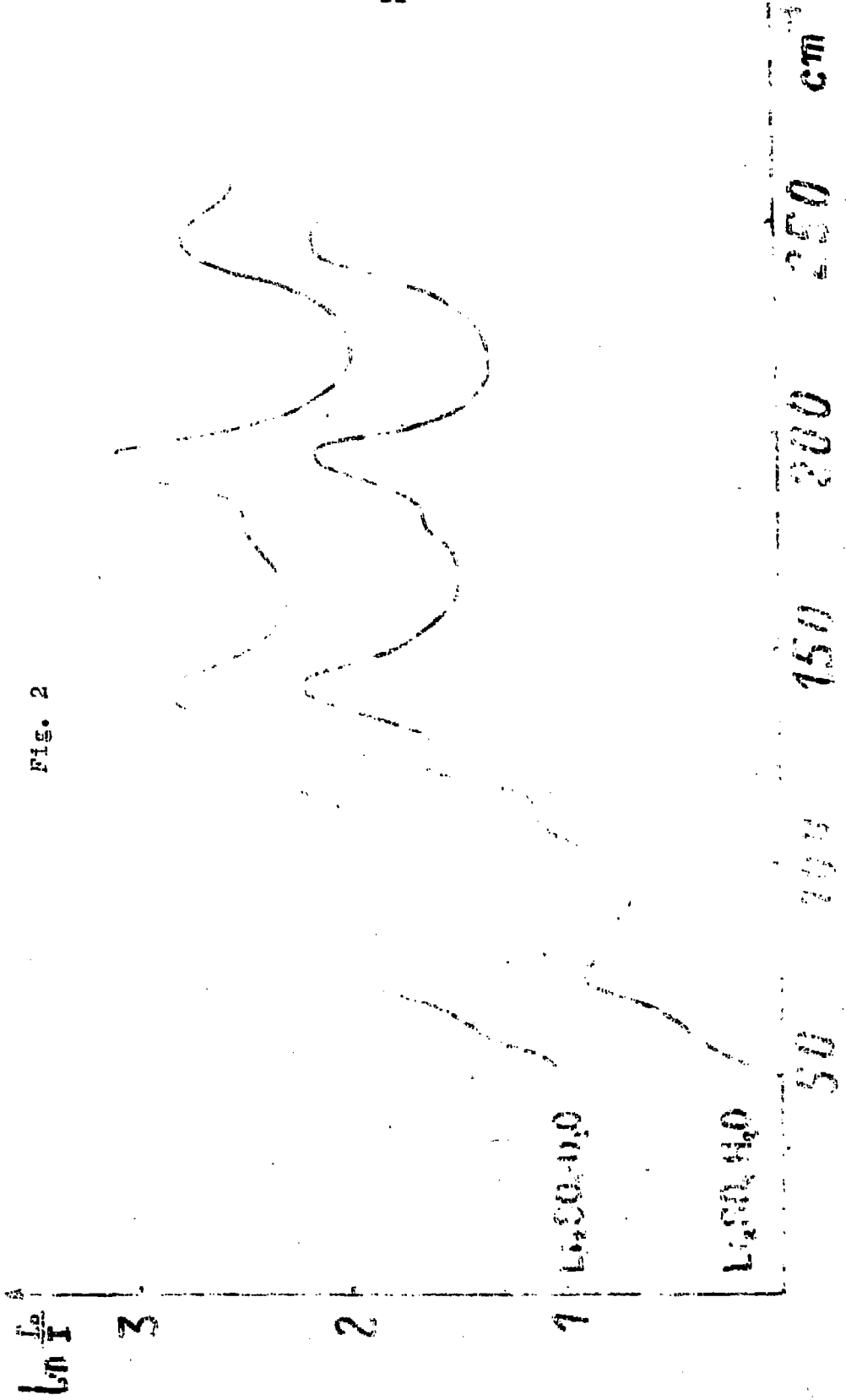


FIG. 1b

FIG. 2



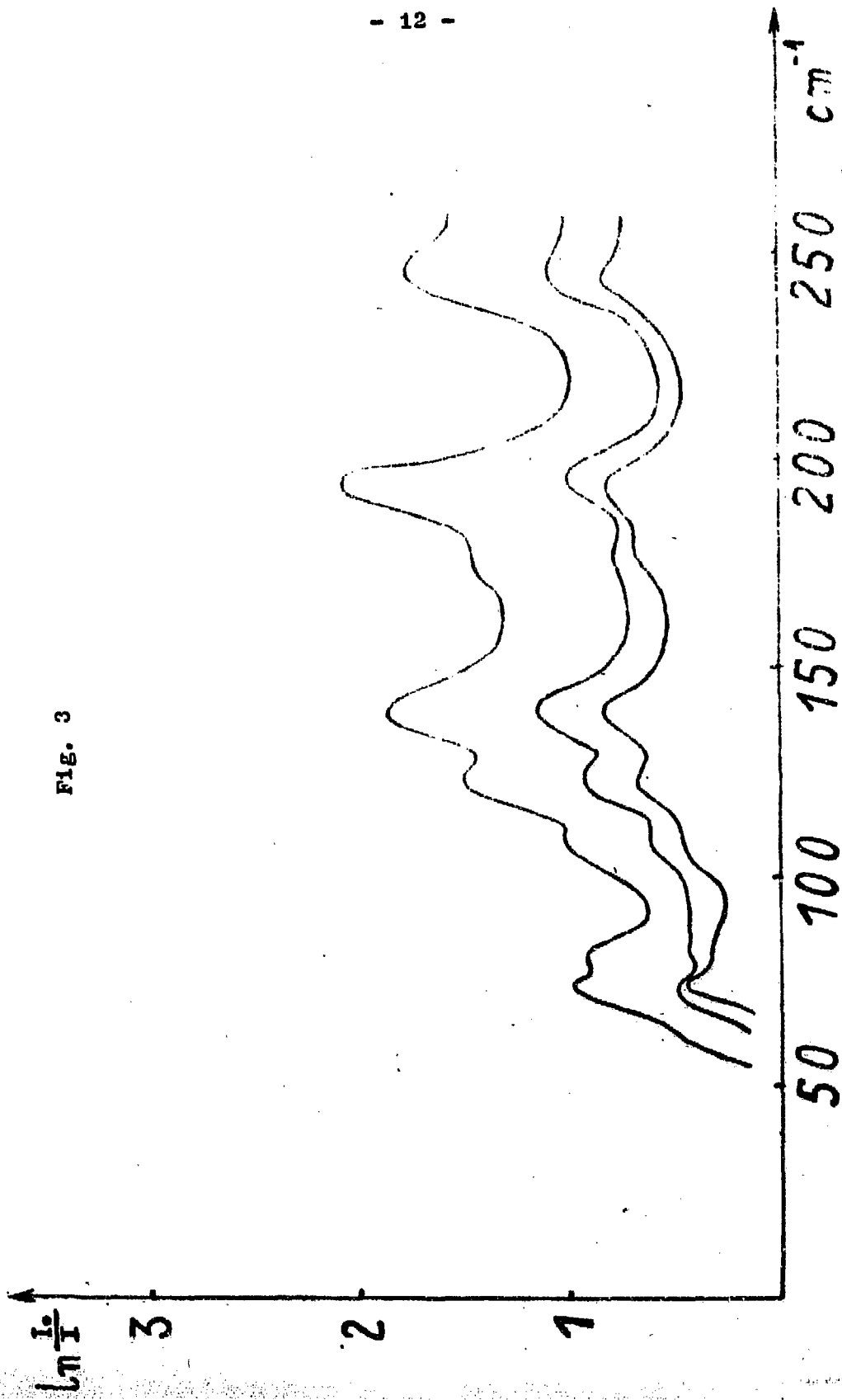
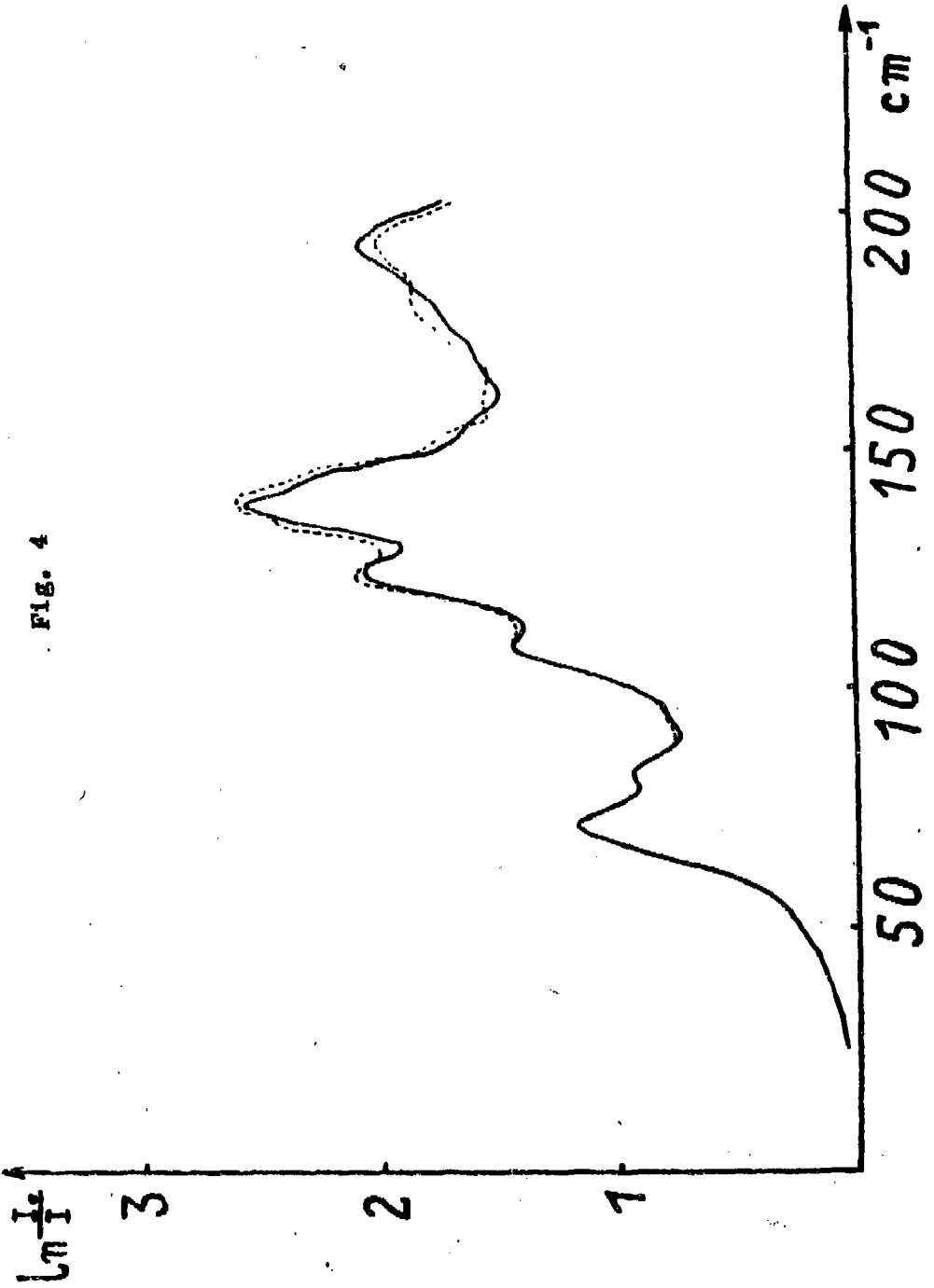


FIG. 3

FIG. 4



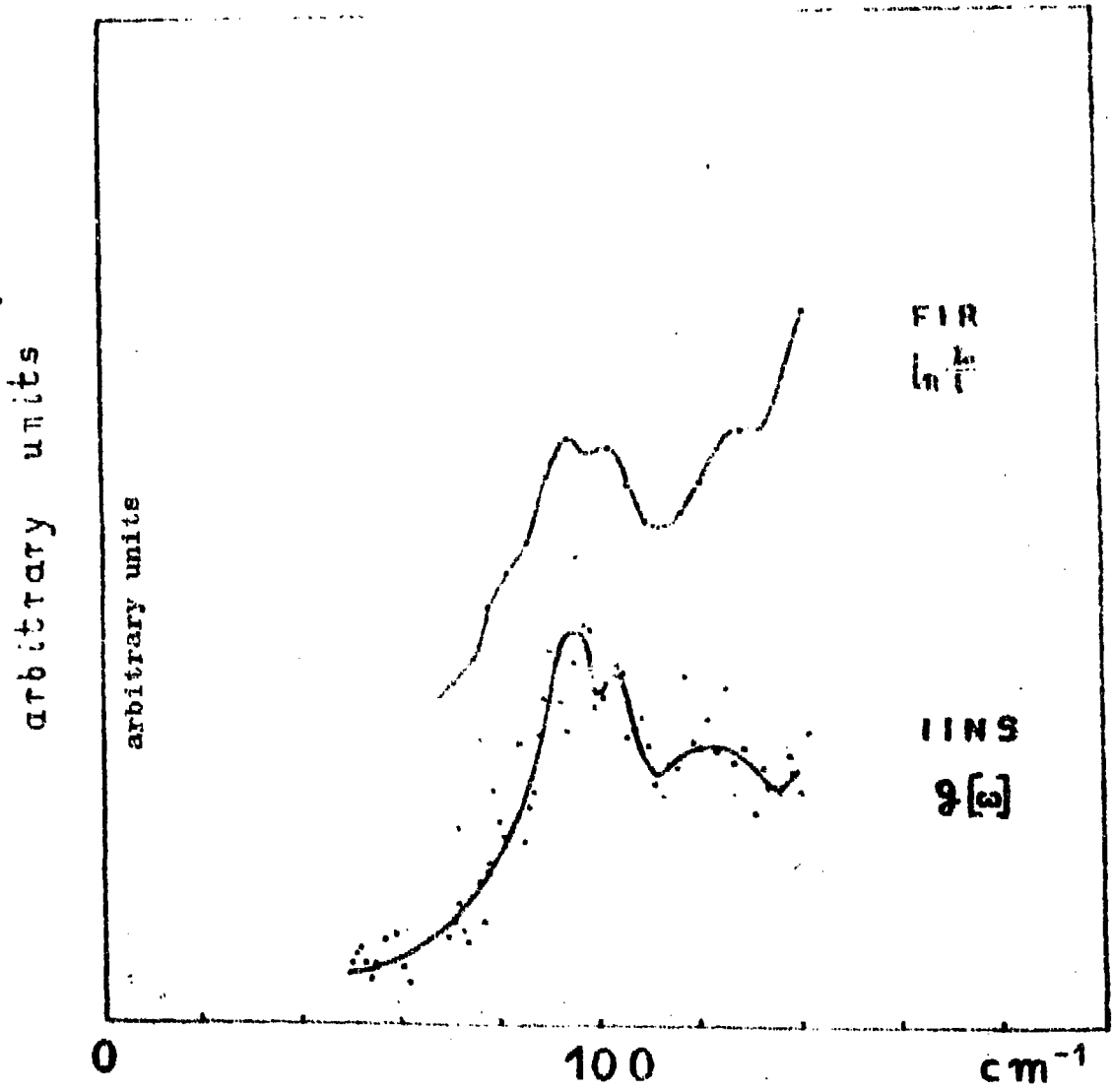
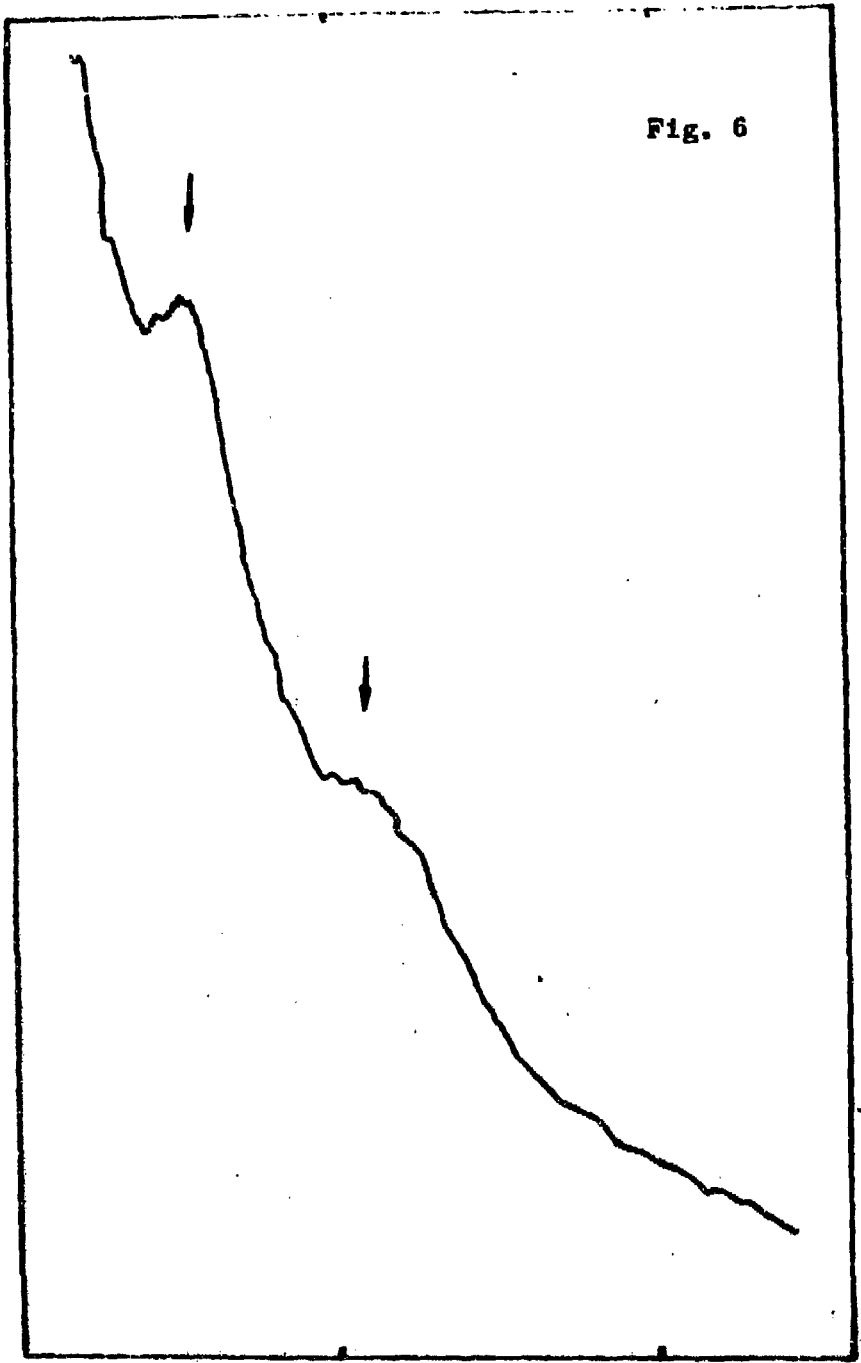


Fig. 5

lacet.

Fig. 6

arbitrary units



50

100

150

cm⁻¹

