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X-RAY DIFFRACTION IN
RESONANT FLUORESCENCE CONDITIONS

X-Ray Diffraction
in Resonant Fluorescence Conditions

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The semiclassical model is used to describe some important peculiarities inherent in X-ray anomalous diffraction providing that the photon energy lies at (or near) the discrete resonance. The energy linewidth of incident radiation (10-100 meV) is supposed to be smaller than the width of the resonant state (i.e. the case of resonant fluorescence). Although photoabsorption increases in this case, the resonant scattering amplitude should also increase and should be considerably larger than the Thompson scattering amplitude. Another important feature of the resonant fluorescence is strong polarization anisotropy.

In the ultra soft X-ray range (USX, 0.1-1 keV) the discrete resonance strengths are well known to be extremely strong. Moreover, as literature data evidence, when molecular crystals are used as USX radiation analyzers, the effect of a resonance-like increase in the reflectivity of these crystals was observed. The interpretation of this effect is presented in our report. It is theoretically predicted that the anisotropic $\sigma-\pi$ and $\pi-\sigma$ diffraction should be very important in these crystals as the photon energy nears the energy of the discrete resonance. The oscillation dependence of resonant reflectivity as a function of the azimuthal angle in consequence should be observed.

We propose to use resonant scattering by functional groups (>C=O,-C≡N,etc.) of molecules in organic crystals. Since each functional group has the characteristic energy of resonance of its own, one can analyze diffraction on isolated functional groups by tuning the photon energy.

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1. INTRODUCTION

The first theoretical treatment of scattering at the discrete resonance was made by W.Heitler in 1936 [1]. It was shown by him that if the energy linewidth of incident photons is smaller than the width of the resonant state, and the photon energy coincides with the resonance energy, then the spectrum of scattered radiation is equivalent to the spectrum of incident radiation. Moreover, the scattered electromagnetic wave should be coherent to the incident electromagnetic wave. The scattering in the conditions described above is known as resonant fluorescence.

Though the space translation symmetry prohibits the discrete states of the electron in the crystal, the hole creation breaks this symmetry. Moreover, the electron-hole interaction can reduce the energy of the excited electron state below the Fermi level [2]. In this case, the excited electron state should be discrete and localized in the space. For example, in the hard X-ray region this effect is known for d-metals oxyanion [3].

In contrast to the hard X-ray region, where this effect is relatively weak, in the Ultra Soft X-ray (USX) region the oscillator strength of the discrete resonance may be very great. A wavefunction of the core electron state of light element has a large spatial spread ($\sim a_0/Z$), and thus, it better overlaps the wavefunction of the localized excited electron state. Moreover, due to the fact that the light elements have a small number of the electrons, the screening

effect is weaker and the electron-hole interactions are very important. As a consequence, the USX absorption spectra have the strong singular fine structure (the set of discrete resonances) near the absorption K-edge of light elements.

The practical interest to X-ray resonant fluorescence aroused in the 70s. It was connected with the observation of the "re-emission" lines in the USX emission spectra by V.A.Fomichev and his colleagues [4,5]. Though, the energy of such a line was equal to the energy of the pre-edge resonance in the absorption spectrum, it seemed to be difficult to explain these peculiarities of emission spectra of light element compounds by resonant fluorescence. Indeed, in USX emission experiments the fast (1-3 keV) electrons provide the primary excitation of atoms [5]. This excitation is equivalent to the polychromatic X-ray excitation. The emission lines are excited by the extended spectrum of X-rays (~ 1 keV) while the "re-emission" lines are excited by the spectrum which is limited by the width of the resonant state (~ 1 eV due to the band structure). Thus, in order that the intensity of the "re-emission" line becomes comparable to the intensity of the emission spectrum, the cross-section of resonant fluorescence must be very high.

In order to confirm the origin of the "re-emission" peaks, the theoretical quantum examination of the resonant fluorescence was performed by A.V.Kondratenko and his colleagues [6] by using the Kramers-Heisenberg dispersion formulae [7]

$$\frac{d\sigma(\omega',\omega)}{d\Omega} = \alpha^4 \omega \, \omega'^3 \left| \sum_i \frac{(d_{0i} e'^*)(d_{i0} e)}{E_i - E_0 - \omega - i\Gamma_i/2} \right|^2 \delta(\omega - \omega'), \quad (1)$$

where e, e' are the polarization vectors of the incident and scattering waves respectively; ω, ω' are the angular frequencies; E_0 and E_i are the ground and i-th excited state energies, Γ_i is the linewidth, $\alpha=1/137$ and d is an electric moment of the atom. Unlikely, their interest was limited to X-ray emission spectroscopy applications only.

In section 2 the diffraction and scattering in resonant fluorescence conditions are theoretically considered. The main attention will be paid to the resonant scattering by functional groups ($>C=O$, $-C\equiv N$, etc.) of molecules. In this case, the $1s \longrightarrow \pi^*$ transition (transition from 1s orbital to unoccupied π^* valence orbital) leads to the appearance of the strong peak below the continuum of K-edge in USX absorption spectra [8]. The resonant scattering will be shown to have some peculiar features. Firstly, the resonant scattering amplitude can be considerably larger than the Thompson scattering amplitude. Secondly, the resonant scattering by functional groups has strong polarization anisotropy.

The existence of polarization anisotropic effects in X-ray diffraction was first explained theoretically by V.E.Dmitrienko [9] and proved experimentally by D.H.Templeton & L.K. Templeton [10]. It is necessary to note that the experiments were performed in the hard X-ray range, where the strengths of oscillators are weak, and hence these effects are also weak in contrast to the USX region, where, as it will be shown, the anisotropic scattering amplitude may be dominant.

Anomalous scattering is extensively used today in crystallographic research in the middle and hard X-ray ranges. Unfortunately, it is impossible to say the same about anomalous scattering in USX range. This situation is a result of some experimental difficulties in USX range: the UHV limitations and, that is more important, the very expensive and imperfect USX optics. Besides, the USX radiation wavelength is greater than some possible interplanar distances in the crystal as usual. Nevertheless, there is a large and important class of crystals (molecular and liquid crystals) in which some of interplanar distances may be very large.

It is necessary to note that there are only a few quantitative USX diffraction and scattering data which were reported in the literature. Nevertheless, the resonant effects were observed. In section 3 these experiments will be critically reviewed.

The main purpose of our paper is to focus attention on great power of anomalous scattering at the discrete molecu-

lar resonance in USX range for the structural research. We propose to use resonant scattering by functional groups ($>C=O$, $-C\equiv N$, etc.) of molecules in organic crystals. Indeed, in the so-called molecular crystals the band structure effects are negligible. Since each functional group has the characteristic energy of resonance of its own, one can analyze diffraction (or scattering) on isolated functional groups by tuning the photon energy.

Moreover, it is possible to get important information about the space orientation of the resonant complexes (resonant atom and its nearest chemical environment) from the scattering (not diffraction) experimental data analysis.

2. THEORY

The scattering amplitude at the classical oscillator can be written as [11]:

$$f(\omega) = -r_0 \frac{\omega^2}{\omega^2 - \omega_0^2 + i\gamma\omega} , \qquad (2)$$

where r_0 is the classical electron radius, ω, ω_0 are the angular frequencies of the oscillator and electromagnetic wave, γ is the dumping factor. It may be noted that if the dumping factor γ is determined only by the interaction of the electron with the electromagnetic field, then

$$\gamma_r = \frac{2}{3} \frac{1}{c} r_0 \omega^2 , \qquad (3)$$

where c is the velocity of light [12], any absorption (incoherent) processes are impossible. It can be readily tested by using the optical theorem.

If ω is equal to ω_0, then the scattering is very similar to Breit-Wigner scattering of neutrons. In this case, the scattering amplitude becomes great and imaginary, and the cross-section of the coherent scattering becomes very high too [7]:

$$\sigma_{sc} = \frac{3}{2\pi} \lambda^2 , \qquad (4)$$

where λ is the wavelength. The scattering amplitude in this case increases by a factor of $3\lambda/4\pi r_0$ in comparison to the Thompson non-resonant scattering amplitude. This value is $\sim 10^6$ for $\lambda = 4.6$ nm.

Really, it is necessary to reduce strongly the last value by the following reasons. Firstly, in USX range the dumping factor γ is determined by the non-radiative Auger transitions. Secondly, in the quantum theory the probability of any electron excitation can not be equal to unity. Besides, the phonon splitting reduces the strength of the resonance.

We will describe the resonant scattering in terms of a semiclassical model in which the bonded electron is a set of classical oscillators with various excitation capabilities. The suitability of this model to quantum theory is satisfactory [1,11].

For the presentation of the bonded electron as a set of the classical oscillators eq.(2) must be replaced by the following one [11]:

$$f(\omega) = -r_0 \sum_i g_i \frac{\omega^2}{\omega^2 - \omega_i^2 + i\gamma\omega} , \qquad (5)$$

where g_i is the oscillator strength or the excitation probability of the i-th oscillator. If the wave frequency ω is equal to any frequency ω_i of a strong discrete oscillator, then the contribution to the scattering amplitude of other oscillators may be neglected:

$$f(\omega) = ir_0 \frac{\omega}{\gamma_r} (g_i \frac{\gamma_r}{\gamma}) . \qquad (6)$$

The value of $g_i \gamma_r / \gamma$ is evident to be small. For example-

le, if the photon energy lies near the carbon K-edge, γ_r is equal to 8×10^{-4} eV. The value of γ slowly varies from one light element to another in the USX range, and the experimental value 0.05 eV may be used [13]. The value 0.2 of the integrated oscillator strength can be reached [14]. The phonon splitting reduced the value of g_i by several fold, and the value of g_i is equal to 0.02 can be used. Finally, the value of $g_i\gamma_r/\gamma$ is equal to 3×10^{-4}. Nevertheless, in this case the scattering amplitude increases by a factor of 200 in comparison to the conventional scattering amplitude $f=2.1+i0.2$ of atom carbon [15].

According to eq.(6), the coherent scattering cross-section (4) must be replaced by

$$\sigma_{sc} = \frac{3}{2\pi} \lambda^2 g_i^2 \frac{\gamma_r^2}{\gamma^2} . \qquad (7)$$

Thus, the cross-section of the coherent scattering must be $\gamma^2/g_i^2\gamma_r^2$ times smaller as compared to the cross-section (4). On the other hand, according to the optical theorem, the photoabsorption cross-section (proportional to $Im(f(\omega))$) must be only $\gamma/g_i\gamma_r$ times smaller:

$$\sigma_{abs} = \frac{3}{2\pi} \lambda^2 g_i \frac{\gamma_r}{\gamma} \qquad (8)$$

It is easy to interpreter eqs.(7) and (8) in terms of quantum electrodynamics. In the time perturbation theory, while the photoabsorption is described by the first-order term ($\sim g_i$), the anomalous scattering is described by the second-order term ($\sim g_i^2$).

It should be noted that the resonant scattering experiment more attractive than the non-resonant case. Indeed, the value of $(\sigma_{sc}/\sigma_{abs})_{res} = g_i\gamma_r/\gamma$ is equal to 3×10^{-4} for the described above case, whereas $(\sigma_{sc}/\sigma_{abs})_{non-res}$ is equal to 5×10^{-5}.

In the resonant fluorescence conditions, the crystal diffraction in the USX range should have unique properties. Due to the great scattering amplitude it is necessary to use a Darwin-Prins model describing the crystal diffraction. Simultaneously, this great scattering amplitude reduces strongly the number of the scattering planes providing a large rocking curve of the crystal. Using a simple assessment one can obtain that only few hundreds crystal planes take part in diffraction.

Another important feature of the resonant scattering by the functional groups in the USX region is strong polarization anisotropy. Indeed, as a rule, the bonds in the organic molecules are linear. That is why the localized excited state, which is determined by the nearest chemical environment of the resonant atom, should be essentially anisotropic. As compared to the non-organic crystals, in which such effects exist, but its value is very small, the resonant excited state in the functional groups may be extremely anisotropic.

For example, the π^*-orbital of the carboxyl group is depicted in Fig.1. The sp^2-hybridization of the carbon atomic orbitals provides the orthogonal orientation of the π^*-orbital to the plane of the C-O bonds. The orientation of the carbon electric m ment induced by the π^*-resonance is the same.

This phenomena may be described using classical model which allows the electron to move along one direction alone. It leads to the replacing of the usual polarization factor in the following manner

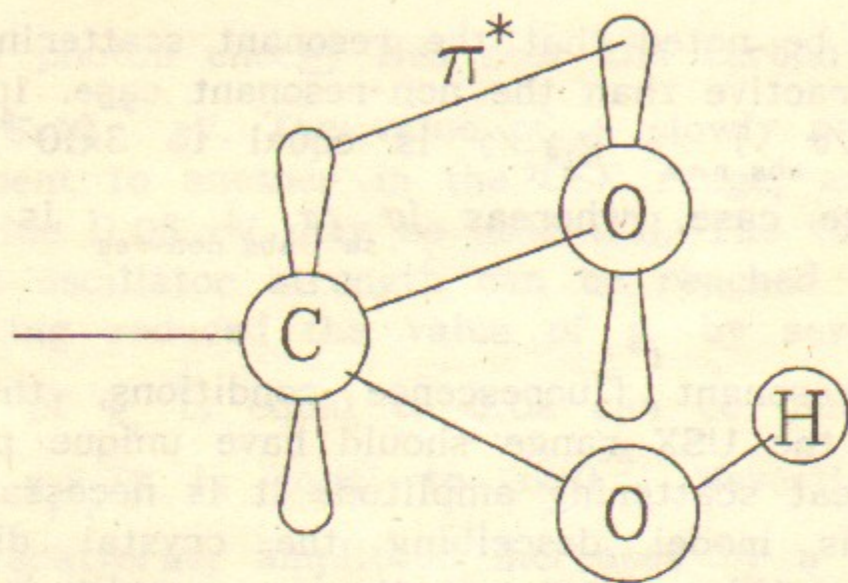$$(e'^* e) \longrightarrow (e'^* s)(s\, e) , \qquad (9)$$

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Fig.1. The molecular antibonded π^*-orbital is depicted [16]. The sp^2-hybridization of the carbon atomic orbitals provides the orthogonal orientation of the π^*-orbital to the plane of the C-O bonds. The orientation of the electric moment induced by the π^*-resonance is the same.

where s is the unit vector along the electron movement. Otherwise, the reason of this replacing is immediately evident from eq.(1). Thus, if the polarization vector e of the incident wave is orthogonal to the orientation of the π^*-orbital, then the scattering and absorption at discrete resonance are impossible. This fact is well known in polarization USX absorption spectroscopy [8,17].

The theoretical examination of X-ray diffraction in crystals with anisotropic X-ray susceptibility was made by V.E.Dmitrienko [9]. He has shown that if this anisotropy is taken into account, then the glide-plane and screw-axis extinction rules are no longer valid. The glide-plane and screw-axis forbidden reflections may be excited and the intensity of these reflections depends on anisotropy of the susceptibility alone. Moreover, a σ-polarized incident beam can give a π-polarized diffracted one and vice versa [9].

These effects may be illustrated by using the described above classical model (eq.(9)). For example, the screw-axis
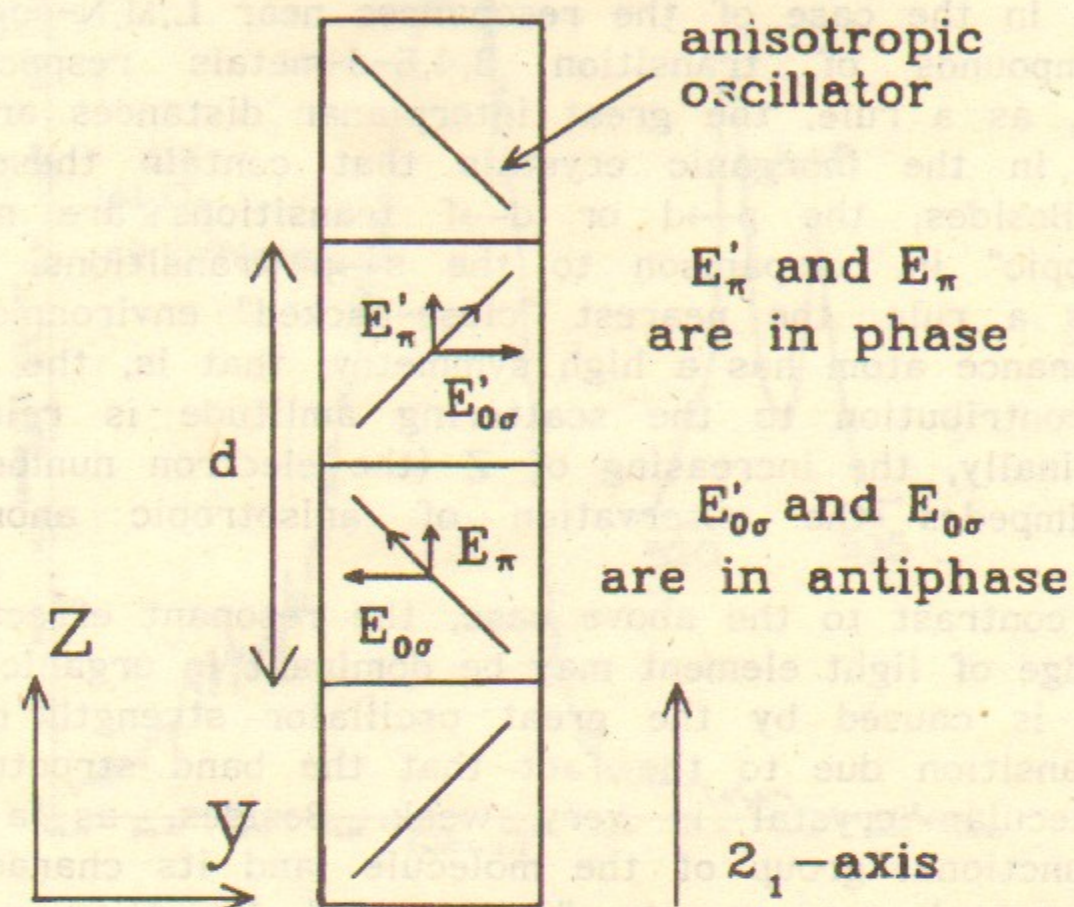
Fig.2 The extinction rule violation due to oscillator anisotropy (see text).

2_1 along z-direction forbids (001) reflection (Fig.2) due to fact that the phase shift between scattered waves of any atom and its image under symmetry operation 2_1 is equal to π (Bragg condition). The extinction rule may be violated for the anisotropic oscillator. Indeed, though the scattered waves of any anisotropic oscillator and its image are in antiphase for the movements of the electron in x- and y-directions (σ-π diffraction, zx is diffraction plane), the phase shift should be equal to zero in the case of z-direction. The situation is similar for π-σ diffraction.

Finally, it is necessary to note that the anisotropic effects are important for both real and imaginary parts of the atomic scattering amplitude.

3. CRITICAL REVIEW OF SOME REPORTED EXPERIMENTS

The resonant diffraction effects in USX region may be observed in the case of the resonances near L,M,N-edges of the compounds of transition 3,4,5-d-metals respectively. However, as a rule, the great interplanar distances are impossible in the inorganic crystals that contain these elements. Besides, the p→d or d→f transitions are not so "anisotropic" in comparison to the s→p transitions. Moreover, as a rule, the nearest "close-packed" environment of the resonance atom has a high symmetry; that is, the anisotropic contribution to the scattering amlitude is relatively weak. Finally, the increasing of Z (the electron number per atom) impedes the observation of anisotropic anomalous effects.

In contrast to the above case, the resonant effect near the K-edge of light element may be dominant in organic crystals. It is caused by the great oscillator strength of the s→p transition due to the fact that the band structure of the molecular crystal is very weak. Besides, as a rule, every functional group of the molecule (and its characteristic resonance) are greatly "anisotropic" (in the extremal case as well as, for example, >C=O).

In accordance with this, we have analysed the literature which are devoted to the diffraction by the organic crystals in USX region. Inspection of the literature revealed that almost no quantitative measurements existed. The salts phtalate crystals are used for X-ray analysis and spectroscopy to be examined best.

As an example of the first experimental evidence of the diffraction in the resonant fluorescence conditions, it is possible to cite the report of W.L.Baun & E.W.White [18]. They have compared (Fig.3) the oxygen K emission spectra from α-Al_2O_3 obtained by using the clinochlore and potassium acid phthalate (KAP) crystals [19]. The anomalous second peak in the case of KAP is evident to be caused by the transition to the π^* unoccupied molecular orbital. This situation is typical for the phthalate crystals. Contrary to the KAP crystal, the clinochlore crystal which is representing
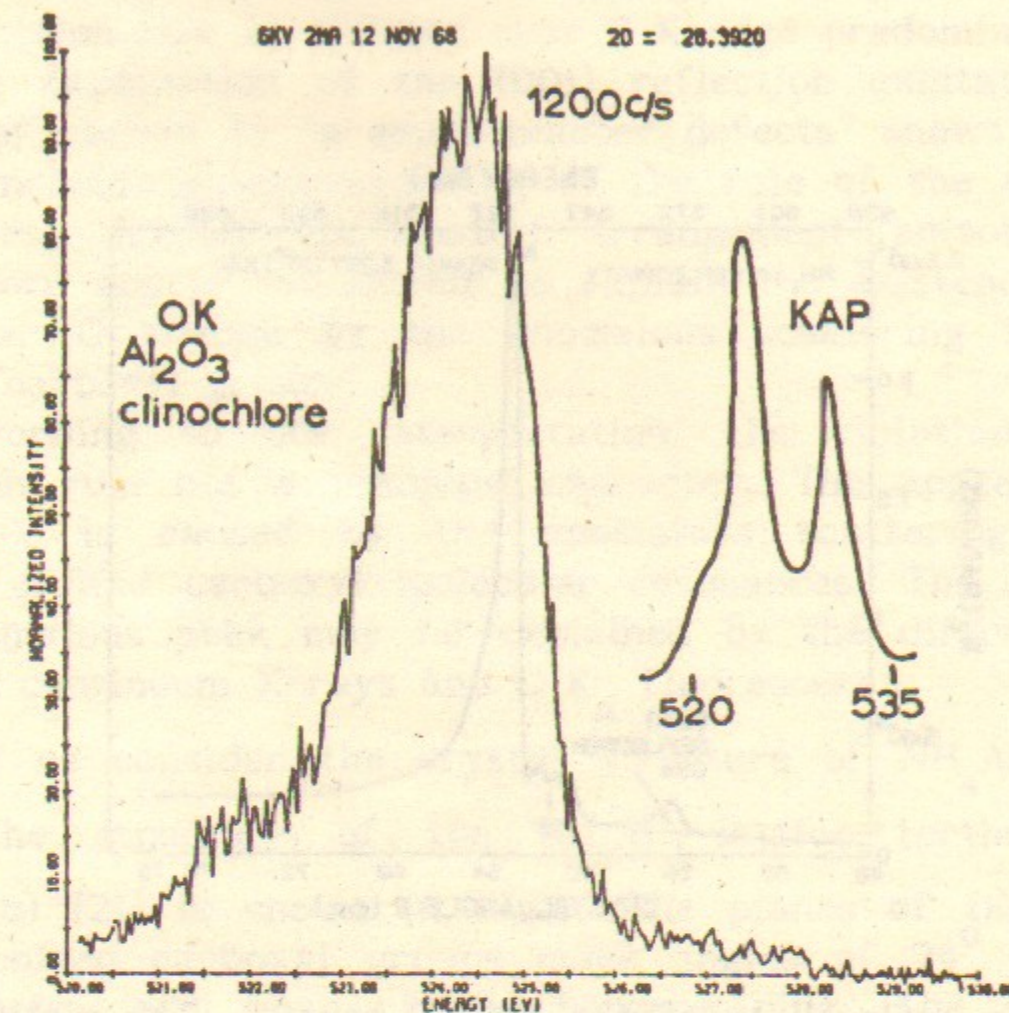

Fig.3. The oxygen K emission spectra from α-Al_2O_3 using the clinochlore [18] and KAP [19] crystals. The anomalous second peak in the KAP curve is typical for the phthalate crystals and is caused by resonant diffraction. The picture is reproduced from Ref.[18].

the sheet silicate is free from any functional group with π^*-resonance.

About a decade ago systematic experimental studies of the X-ray diffraction reflectivity of few commonly used acid phthalate (AP) crystals was carried out over the energy range 500-650 eV by a team from Los Alamos Scientific Laboratory (R.L.Blake et al. [20]). Their excellent measurements show a strong resonant peak near the K-edge of oxygen (Fig.4). This peak was correctly interpreted to be connected with the transition to the unoccupied molecular-orbital state.
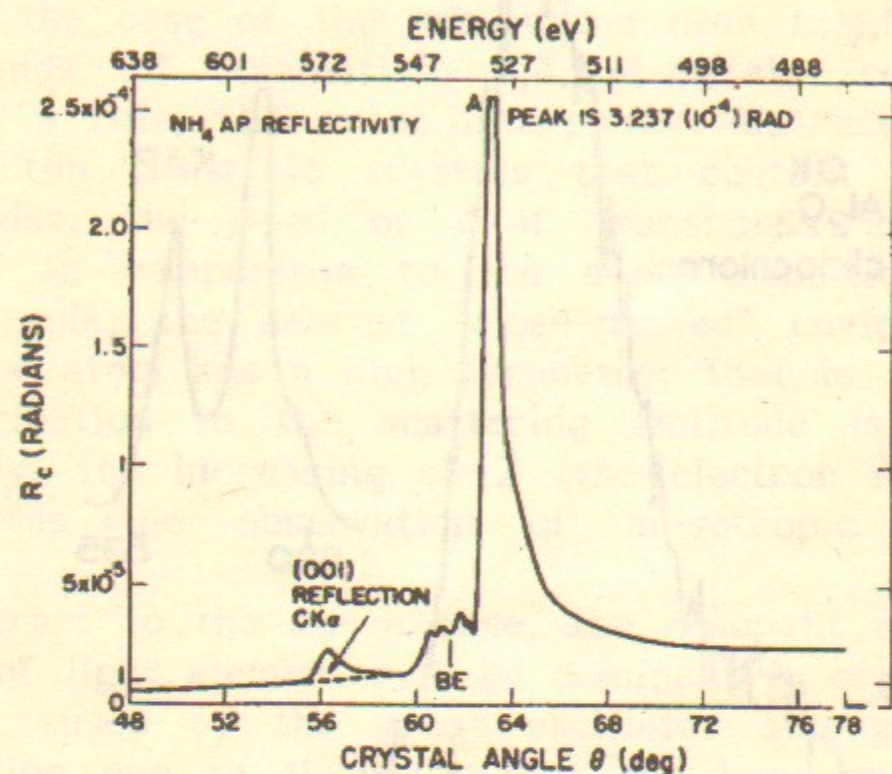
Fig.4. The reflectivity of the NH$_4$AP crystal. The picture is

taken from Ref.[20].

It is interesting to note that the experiments were performed using the continuum spectrum of the gold anode tube without primary monochromatization. Thus, it is obvious that the molecular resonance effect was dispersed and depressed. Nevertheless, the resonant peak was large.

In the case of NH$_4$AP, the additional peak on the high energy side was revealed (see Fig.4). This peak was interpreted by R.L.Blake et al. as the forbidden (001) Bragg reflection of C K$_\alpha$-radiation of the contaminated tube. They explained the violation of the extinction rule by "a small number of defects" of the crystal.

Their interpretation not explains adequately the absence of Au N$_{5,4}$ emission lines (250 eV) of the anode and the presence of C K$_\alpha$ emission band (280 eV) of the contami-

nated anode that is seem to be strange. The question is why the extinction rule is violated near C K-edge predominantly.

The explanation of the (001) reflection excitation near K-edge of carbon by "a small number defects" shows evidence of the incomplete understanding of the role of the molecular resonances, notably its spatial arrangement anisotropy. It would more appear reasonable to explain the existence of the peak near C K-edge by the anomalous scattering from the benzene/carboxyl groups.

According to our interpretation, the violation of the extinction rule has a resonant character. The appearance of this peak is caused by the anomalous scattering at the benzene or/and carboxyl molecular resonances. The origin of this anomalous peak may be explained by the diffraction of both the continuum X-rays and C K$_\alpha$ fluorescence.

Let us consider the crystal structure of NH$_4$AP in details. The structure of the NH$_4$AP lattice (orthorhombic, s.g. Pcab) [21] is shown in Fig.5. The planes of the ionized and unionized carboxyl groups make angles of 74° and 26°, respectively, with that of the benzene ring. The resonance directions of the ionized, unionized carboxyl and benzene groups are not parallel to the (001) plane. The extinction of the (001) reflection for the non-resonant diffraction is caused by the 2$_1$ screw-axis along z-direction. In the anomalous scattering conditions, due to the polarization factor (9), the σ-π and π-σ diffraction on the (001) planes is possible [9]. If x$_i$, y$_i$ and z$_i$ are the components of the unit vector along the resonance direction, the contribution of this resonance to the structure amplitude of the (001) reflection is determined by the space group symmetry operations and, for the s.g. Pcab, can be written as

$$F_{i \ \sigma\pi/\pi\sigma} \sim \cos\theta_B f_i z_i (x_i \cos(2\pi Z_i)\sin\Omega + iy_i \sin(2\pi Z_i)\cos\Omega) , \quad (10)$$
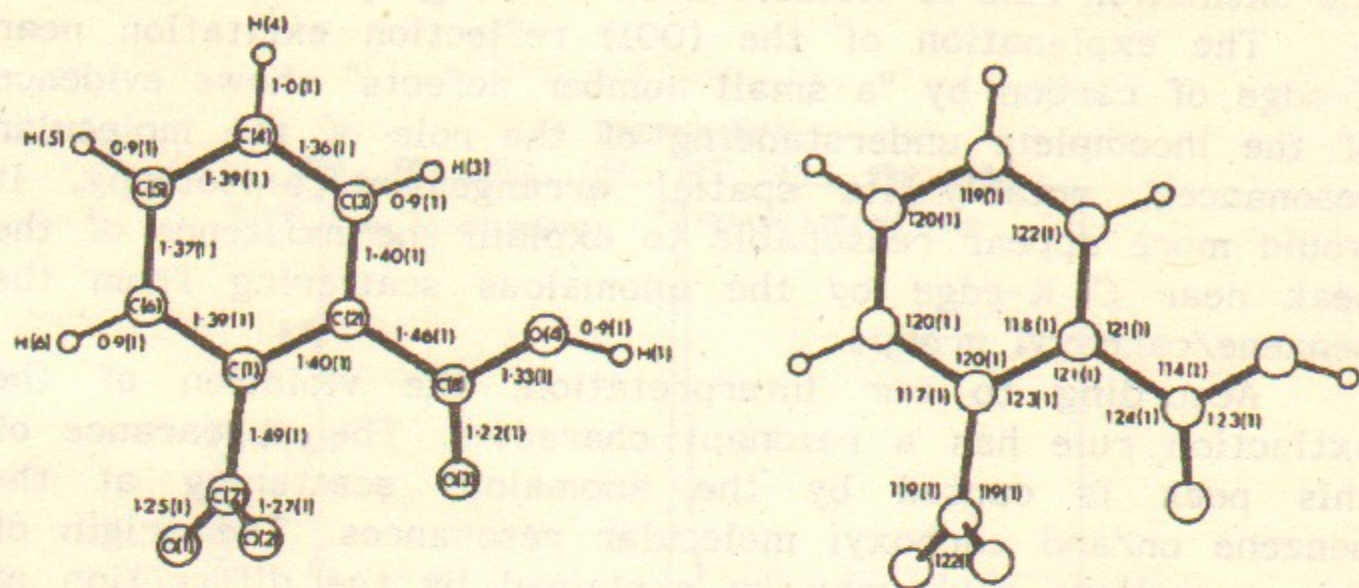
Fig.5. a) The structural unit of the NH$_4$AP lattice. The planes of the ionized and unionized carboxyl groups make angles of 74° and 26°, respectively, with that of the benzene ring. b) The structure of the NH$_4$AP lattice. The pictures is taken from Ref.[21].

where f_i is the scattering amplitude of the i-th resonance, Z_i is the coordinate of a resonant atom and Ω is an azimuthal angle. In Fig.6 the results of our calculations for carboxyl and benzene groups are shown. In these calculations it was supposed that the interference of the carboxyl and benzene resonances is negligible, and the mixing of $\sin\Omega$ and $\cos\Omega$ terms was, therefore, omitted.

The number of intensity oscillations (Fig.6) is determined by the crystal symmetry. It is necessary to note that the azimuthal dependence of the intensity of the usual (not forbidden) reflection in the resonant conditions should have similar behaviour.

The experimental conditions of the investigation [20] not allow to obtain the comprehensive data on the diffraction in resonant fluorescence conditions. The integrated
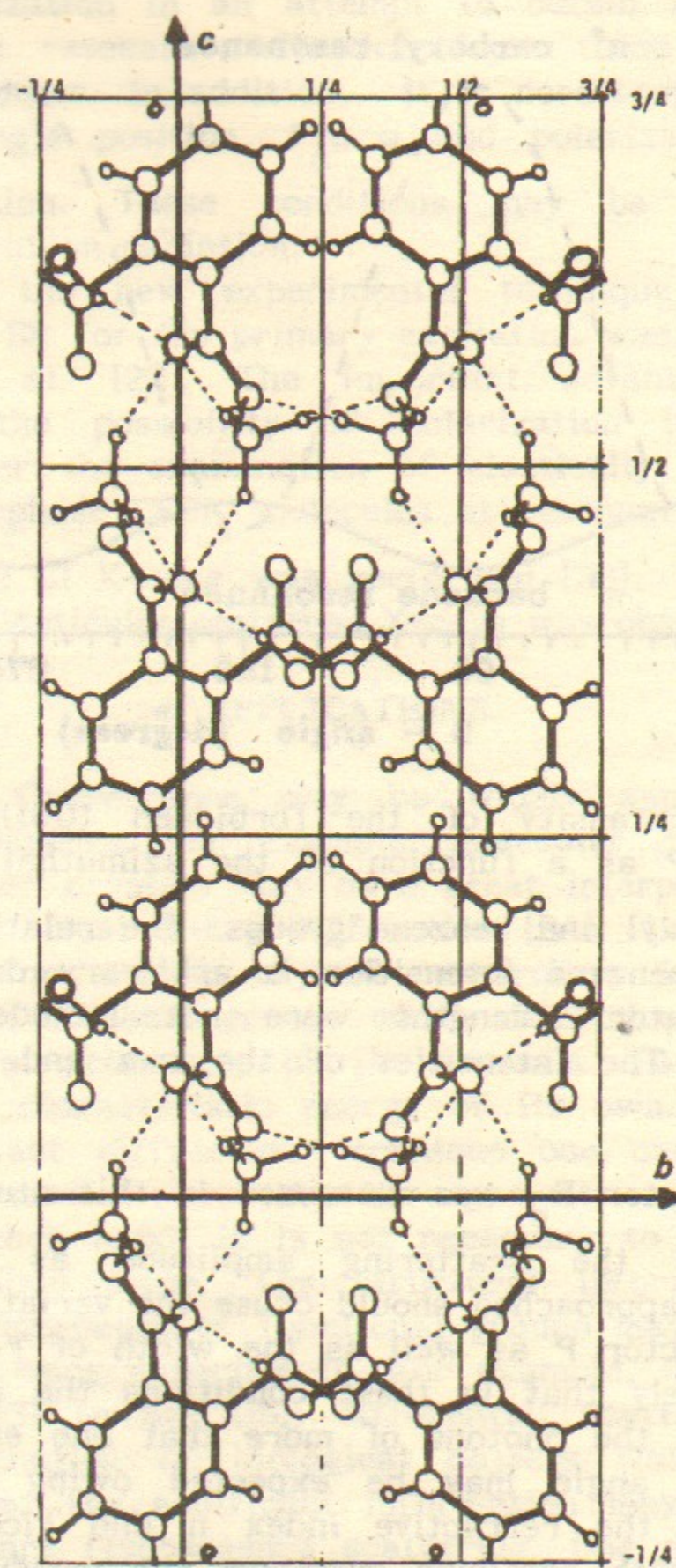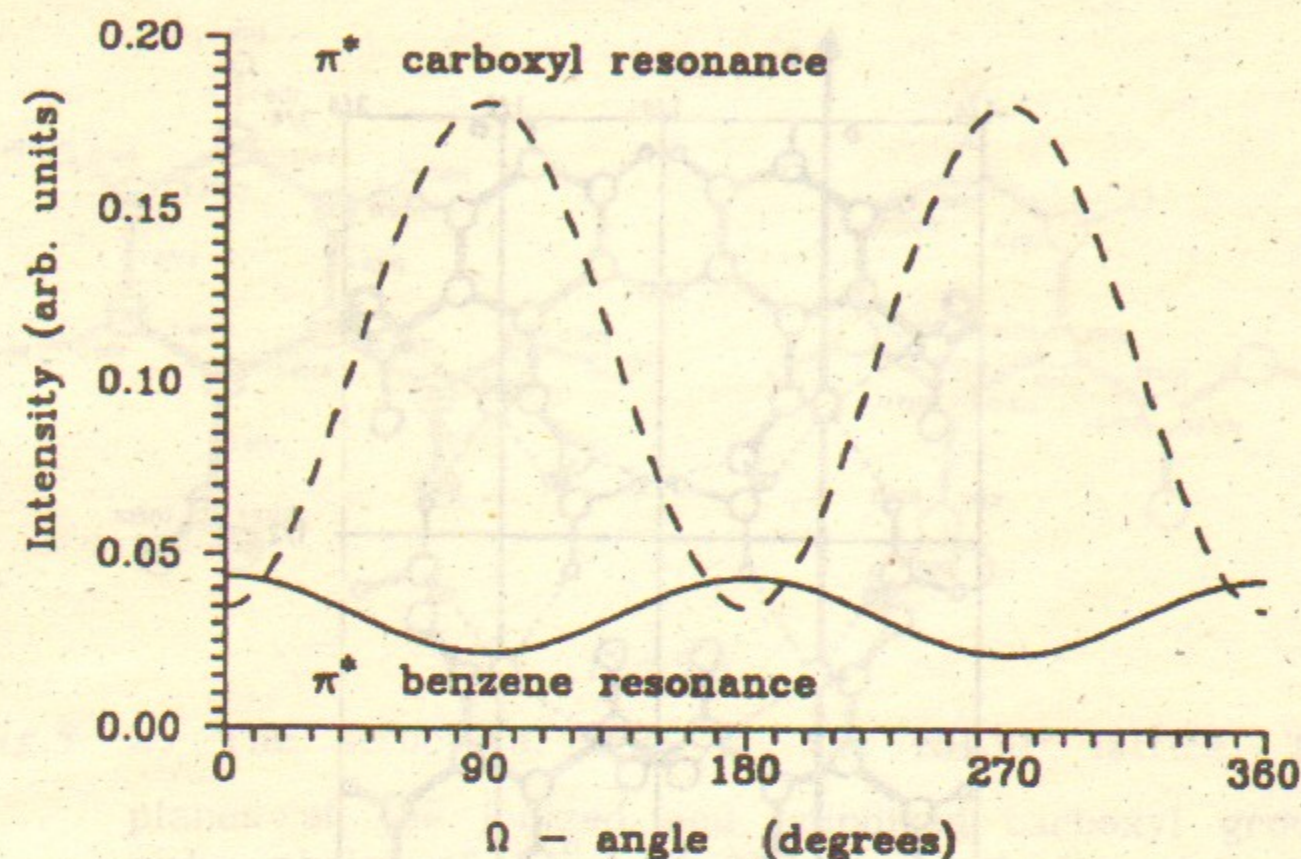
Fig.5,b.

Fig.6. The intensity of the forbidden (001) reflection of NH$_4$AP as a function of the azimuthal angle for the carboxyl and benzene groups. The relation of carboxyl and benzene intensities is arbitrary due to that the oscillator strengths were not included in calculation. The intensities of the σ-π and π-σ cases are equal.

reflection factor R$_c$ was measured in this study. The strong variation of the scattering amplitude as the resonance maximum is approached should cause the variation of the peak reflection factor P as well as the width of rocking curve ω. It seems likely that in these conditions the case where the reflection of the photons of more that one energies for the fixed Bragg angle may be expected owing to the strong variation of the refractive index n and vice versa. Using the source with continuum spectrum the measurements of R$_c$ contain a possibility for the ambiguous interpretation. Obviously, it is necessary to use the tuneable monochromatic

($\Delta E \cong 0.1 \div 0.01$ eV) and collimated incident beam with a required polarization in an attempt to obtain futher information on the resonant reflection from these crystals as well as from other. In addition, it is necessary to measure exactly the angle position, P$_c$, ω and polarization of diffracted radiation. These conditions may be fulfilled by using of synchrotron radiation.

Recently, the new experimental technique which uses monochromatic SR for the primary excitation was developed by C.C.Perera et al. [22]. The important advantage of this technique is the possibility of polarization investigations. Some time later the examination of elastically scattered X-rays from gas-phase CFCl$_3$ molecules at resonant intermediate states near the Cl K-edge was performed [23]. The depolarization of the elastically scattered X-rays was observed.

4. APPLICATIONS

Resonant fluorescence may be widely applied in USX structural researches. For example, molecular crystals, protein and polymer crystals may have great interplanar distances enough for usual X-ray diffraction [24]. As a rule, the main interest for organic crystal researchers is the arrangement of the functional groups which determines the chemical and physical properties of the crystals. Each functional group has the characteristic energy of its own. Thus, using the USX resonant diffraction technique one can obtain the structural information about this arrangement.

On the other hand, it is not necessary to use the diffraction technique alone. The structural information about the spatial arrangement of functional groups may be obtained from USX scattering experiments. For example, it was proposed in Ref. [25] to use USX differential scattering technique for examination of biological objects which have the chiral structure. The additional information may be obtained by using resonant fluorescence scattering. One more application is the use of the full external reflection.

The large absorption in the USX region complicates the

use of the small angle scattering. Perhaps, this technique may be used in some cases.

Research activities in the field of resonant magnetic X-ray scattering may have been intensified in the recent period [26]. Resonant fluorescence can be also used in these experiments.

At last, it is possible to use USX resonant diffraction for the creation of new USX optics. For example, using the diffraction on the liquid crystal, one can generate the USX beam with any desired polarization.

5. CONCLUSION

The scattering amplitude of resonant fluorescence in USX region should be considerably larger than the non-resonant scattering amplitude and should provide the main contribution to the scattering and diffraction.

The dynamical theory with strong absorption must be applied to the description of the crystal diffraction. The rocking curve of the crystal must be large.

The diffraction and scattering in resonant fluorescence conditions are essentially anisotropic and have unusual polarization properties. The glide-plane and screw-axis extinction rules may be no longer true. A σ-polarized incident beam can give a π-polarized diffracted one and vice versa.

The resonant-like increase in the reflectivity of the USX crystal-analyzers was observed and reported in the literature repeatedly. The interpretation of this effect, as a rule, was incorrect. We suppose that this resonant reflectivity is caused by the σ-π and π-σ diffraction in the resonant fluorescence conditions should have a oscillation dependence as a function of the azimuthal angle.

The resonant fluorescence effects may be used widely in crystallographic research. Because of experimental difficulties, the present state of USX diffraction and scattering experiments is characterized by very weak activity. However, we hope that this situation will change in the not distant future. Moreover, USX diffraction experiments are believed to stimulate the creation of new USX optics whith unique polarization properties.

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