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NITROPRUSSIDE SINGLE CRYSTALS

by

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MÖSSBAUER HYPERFINE INTERACTIONS IN SODIUM
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SUMMARY

The Mössbauer absorption spectrum of ^{57}Fe in single crystals of $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ has been studied. The angular variation of the ratio of intensities of the quadrupole splitted lines with the incident radiation has been measured at different crystal orientations. The results may be satisfactorily interpreted by considering the detailed symmetry of the crystal and the effects of the anisotropy of the recoilless absorption probability. It was found that an axially symmetric field gradient with its principal axis oriented along the Fe-NO directions couples with the nuclear quadrupole moment of ^{57}Fe giving a positive interaction with the value $e q = + 0.585 \times 10^{18} \text{ V/cm}^2$. This field gradient is assumed to originate from unbalanced d electron density and the electronic population calculated for the molecule agrees with that obtained by molecular orbital methods. The large total s-electron density at the ^{57}Fe nucleus measured by the isomer shift is quantitatively related to the effective 3d electron population and to the 4s partial occupation. Estimates of the 4s density also agree with that reported from molecular orbital calculations.

The Mössbauer spectrum of sodium nitroprusside (sodium pentacyanonitrosyl (II), $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) is in many respects a remarkable one ^{1, 2, 3}. It presents a relatively large quadrupole splitting, $\Delta E = 0.1726 \pm 0.0002$ cm/sec, and the nuclear isomer shift ($- 0.0075$ cm/sec relative to ^{57}Co in Cr) indicates an unusually large s-electron density at the iron nucleus. The spectrum shows the narrowest linewidth observed with iron compounds $\Gamma = 0.0202$ cm/sec. These hyperfine interactions change very little on going from room to liquid nitrogen temperature.

The peculiarities and stability of this spectrum under different external conditions makes attractive the use of sodium nitroprusside as a standard for nuclear isomer shift measurements with iron ⁴.

The Mössbauer spectrum of sodium nitroprusside has been discussed in connection with other iron nitrosyl complexes ⁵. In this paper we report angular variation measurements of the Mössbauer hyperfine interactions in sodium nitroprusside single crystals and its relations with the molecular structure of the complex.

Experimental

Sodium nitroprusside grows in large orthorhombic single crystals, with space group symmetry $D_{2h}^{12} - \text{Pnmm}$. The usual habit and the orientation relative to the cell constants ⁶ $a = 6.17 \pm 0.03\text{A}$, $b = 11.84 \pm 0.06\text{A}$ and $c = 15.43 \pm 0.08\text{A}$ are shown in fig. 1.

Large single crystals, carefully grown from saturated aqueous

solution of the complex, were cut in a fixed orientation and platelets about 1 cm^2 were polished to the desired thickness.

The platelets were used as absorbers and could be mounted at any particular orientation relative to the incident gamma radiation emitted by the Mössbauer source. A 5 mc ^{57}Co in Cu was used as source, attached to a loudspeaker device driven with a triangular velocity waveform. The spectrometer is operated in the pulse-height mode, with pulses from a single channel analyser modulated with the velocity waveform. Pulse height sorting is performed with a 512 Nuclear Data multichannel analyser, the half of the memory being used for register of the spectrum and the other half stores a standard pulse which is used for normalization of the Mössbauer spectrum.

Typical results are illustrated in fig. 2 which reproduce the Mössbauer spectra obtained with single crystal platelets cut along the planes (bc) $|100|$ and (ab) $|010|$, with the gamma radiation incident perpendicular to the plane of the platelet.

All measurements were obtained at $23 \pm 2^\circ\text{C}$.

Theoretical Considerations

The 14.4 keV Mössbauer gamma radiation of ^{57}Fe is emitted in a transition from the first excited state with spin $3/2$ to the ground state with spin $1/2$. The Hamiltonian for coupling between the quadrupole moment Q of the $3/2$ state (the ground state with $I = 1/2$ has no quadrupole moment) with an electric field gradient

(EPG) produced at the nucleus is given by:

$$H = \frac{1}{4} e^2 q Q \left[I_z^2 - \frac{5}{4} + \frac{1}{6} \eta (I_+^2 + I_-^2) \right] \quad (1)$$

where $e q$ is the EFG in the \hat{z} (major axis) direction, η the asymmetry about \hat{z} ($0 < \eta < 1$) and I_+ and I_- raising and lowering operators.

The eigenvalues:

$$E_Q = \pm \frac{1}{4} e^2 q Q \left(1 + \frac{1}{3} \eta^2 \right)^{\frac{1}{2}} \quad (2)$$

define two hyperfine components of the Mössbauer transition, $I_3(\pm 3/2 \rightarrow \pm 1/2)$ and $I_1(\pm 1/2 \rightarrow \pm 1/2)$, characterizing the two absorption peaks of the observed spectra.

The experimental variable used for the determination of the electric field gradient parameters (EFG) are the absorption peak areas ⁷. As has been shown by Zory ⁸, the ratio of the areas of the two peaks as a function of the polar and azimuthal angles θ and φ that the incident gamma radiation makes with perturbing field causing the splitting, is given by:

$$\frac{a_n}{a_m} = \frac{\sum_i^{\text{sites}} p_n(\theta_i, \varphi_i) f'(\theta_i, \varphi_i)}{\sum_i^{\text{sites}} p_m(\theta_i, \varphi_i) f'(\theta_i, \varphi_i)} \quad (3)$$

$P_n(\theta_i, \varphi_i)$ is the relative angular dependent absorption probability for the transition n and $f'(\theta_i, \varphi_i)$ is the recoilless absorption probability (Debye-Waller or Mössbauer factor) whose angular dependence derives from the anisotropy in the mean square displacement of the vibrating nucleus. The sum extends to the

total number of equivalent sites per unit cell being equivalent those sites in which the surroundings of the absorbing nuclei are the same but differ in orientation.

The derivation of the explicit form of $P_n(\theta_i, \varphi_i)$ is given by Zory⁸, using first order perturbation methods for the quadrupole splitting of the 14.4/ev transition of Fe⁵⁷. The results for the hyperfine, transitions $p_3(\pm 3/2 \rightarrow \pm 1/2)$ and $p_1(\pm 1/2 \rightarrow \pm 1/2)$ are respectively:

$$p_3(\theta_i, \varphi_i) = 4 \left[\frac{(3 + \eta^2)}{3} \right]^{\frac{1}{2}} + (3 \cos^2 \theta_i - 1 + \eta \sin^2 \theta_i \cos 2 \varphi_i) \quad (4)$$

$$p_1(\theta_i, \varphi_i) = 4 \left[\frac{(3 + \eta^2)}{3} \right]^{\frac{1}{2}} - (3 \cos^2 \theta_i - 1 + \eta \sin^2 \theta_i \cos 2 \varphi_i)$$

On the form of $f^3(\theta_i, \varphi_i)$ we have no a priori information.

We consider now the specific problem of sodium nitroprusside. The basic structural unit of the crystal⁶ is shown in fig. 3. The nitroprusside ion in the crystal has, within the experimental error, the C_{4v} symmetry. The Fe = N = O portion of the ion is strictly linear as are the Fe - C N groups. The unit cell of the crystal is composed of four of these distorted octahedra. These four ions form two equivalent sites. A view down the c-axis is shown in fig. 4. We neglect translation from one site to the other, which has no interference in the angular dependence.

Let us now express the relations (4) passing from the coordinates θ_i and φ_i to the coordinates θ and ϕ which define the crystalline axis as is illustrated in fig. 5. Since \vec{a} , \vec{b} and \vec{c} directions are orthogonal, the following expressions relate θ_i ,

φ_i to θ_i and Φ and the unknown Euler angles relating site 1 to the axes (\vec{a} , \vec{b} , \vec{c}):

$$\sin \theta_i \cos \varphi_i = \cos(\gamma, \hat{x}_i) = (\hat{a} \cdot \hat{x}_i) \sin \theta_i \cos \Phi + (\hat{b} \cdot \hat{x}_i) \cos \theta_i + (\hat{c} \cdot \hat{x}_i) \sin \theta_i \sin \Phi$$

$$\sin \theta_i \sin \varphi_i = \cos(\gamma, \hat{y}_i) = (\hat{a} \cdot \hat{y}_i) \sin \theta_i \cos \Phi + (\hat{b} \cdot \hat{y}_i) \cos \theta_i + (\hat{c} \cdot \hat{y}_i) \sin \theta_i \sin \Phi$$

$$\cos \theta_i = \cos(\gamma, \hat{z}_i) = (\hat{a} \cdot \hat{z}_i) \sin \theta_i \cos \Phi + (\hat{b} \cdot \hat{z}_i) \cos \theta_i + (\hat{c} \cdot \hat{z}_i) \sin \theta_i \sin \Phi \quad (5)$$

Each of the direction cosines, (\hat{a}, \hat{x}_i) , (\hat{b}, \hat{y}_i) etc can be expressed as a function of the same Euler angles α_i , β_i , γ_i .

The symmetry relation between the two sites of the unit cell is a 180° rotation about the a axis and can be written as

$$\begin{aligned} \hat{a} \cdot \hat{x}_1 &= \hat{a} \cdot \hat{x}_2 \\ \hat{b} \cdot \hat{x}_1 &= -\hat{b} \cdot \hat{x}_2 \\ \hat{c} \cdot \hat{x}_1 &= -\hat{c} \cdot \hat{x}_2 \end{aligned} \quad (6)$$

with analogous relations for \hat{y}_1 and \hat{z}_1 .

Assuming that f^i is isotropic and taking into account (4), (5) and (6) one finds by substitution in (3) the following relation:

$$\frac{a_3}{a_1} = \frac{4[(3+\eta^2)/3]^{\frac{1}{2}} + [3K-1+\eta K^i]}{4[(3+\eta^2)/3]^{\frac{1}{2}} - [3K-1+\eta K^i]} \quad (7)$$

where

$$K = \left\{ (Z_a^2 \cos^2 \Phi + Z_c \sin^2 \Phi) \sin^2 \theta_i + Z_b Z_c \sin 2 \theta_i \sin \Phi + Z_b^2 \cos^2 \theta_i \right\} \quad (8)$$

$$K^i = \left\{ \left[(X_a^2 - Y_a^2) \cos^2 \Phi + (X_c^2 - Y_c^2) \sin^2 \Phi \right] \sin^2 \theta_i + \left[X_b X_c - Y_b Y_c \right] \sin 2 \theta_i \sin \Phi + \left[X_b^2 - Y_b^2 \right] \cos^2 \theta_i \right\}$$

The quantities $Z_a, Y_a, \text{etc.}$, are the direction cosines $\hat{Z} \cdot \hat{a}, \hat{y} \cdot \hat{c}, \text{etc.}$

Eq. 8 is similar to that derived by Zory for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ but the parameters K are different due the different symmetry of the $\text{Na}_2|\text{Fe}(\text{CN})_5\text{NO}|2\text{H}_2\text{O}$.

Results

The general equation (7) is rather complicated. The following observation directions were investigated:

$$\begin{aligned}
 \text{a) } |\theta| &= \frac{\pi}{2} & 0 \leq \Phi \leq \frac{\pi}{2} \\
 \text{b) } \Phi &= \frac{\pi}{2} & 0 \leq \theta \leq \frac{\pi}{2} \\
 \text{c) } \Phi &= 0 & 0 \leq \theta \leq \frac{\pi}{2}
 \end{aligned} \tag{9}$$

These directions were obtained with single crystal platelets cut along (ac), (bc) and (ab) planes.

For cases (a) and (b) it can be seen that the relations (4), (5) and (6) give for the angular dependence of the absorption probabilities $p_3(\theta_1, \varphi_1) = p_3(\theta_2, \varphi_2)$ and $p_1(\theta_1, \varphi_1) = p_1(\theta_2, \varphi_2)$.

For these cases the problem became equivalent to that of a crystal with a single site in the unit cell. It is important to observe that in such conditions eq. (7) remain valid even if the factor f' is anisotropic.

Further simplification can be made by observing that a rotation of $\pi/2$ around the Fe - NO direction does not introduce any modification in the molecule. We may thus assume that the z axis

of the EFG tensor is parallel to the ab plan of the crystal and coincides with the Fe - NO direction. The EFG is thus axially symmetric ($\eta = 0$) and entirely determined by its z component.

As a consequence of the axial symmetry of the EFG the general relation (5) for the cases (a) and (b) reduces to:

$$(a) \quad \frac{a_3}{a_1} = \frac{1 + k \cos^2 \phi}{\frac{5}{3} - k \cos^2 \phi} \quad (|\theta| = \frac{\pi}{2}, 0 \leq \phi \leq \frac{\pi}{2}) \quad (10)$$

$$(b) \quad \frac{a_3}{a_1} = \frac{1 + k' \cos^2 |\theta|}{\frac{5}{3} - k' \cos^2 |\theta|} \quad (\phi = \frac{\pi}{2}, 0 \leq \theta \leq \frac{\pi}{2})$$

with $k = \cos^2 33^\circ 55'$ and $k' = \cos^2 56^\circ 05'$.

Fig. 6 illustrates the results obtained for different absorber thickness in the (a,c) plane. On decreasing the thickness of the absorbers the results tend to the theoretical values of the area ratios. These values are obtained with absorbers of thickness ≤ 0.02 cm as is shown below:

ϕ	$ \theta $	Exp ± 0.05	calc
$\frac{\pi}{2}$	$\frac{\pi}{2}$	0.62	0.60
$\frac{\pi}{2}$	45°	0.78	0.77
$\frac{\pi}{2}$	10°	1.02	0.96

The agreement between experimental and theoretical results means that the ratio of the high energy experimental absorption area to the low energy one is equal to $\frac{a_3}{a_1}$ and not to $\frac{a_1}{a_3}$. This means

that the ($\pm 3/2 \rightarrow \pm 1/2$) sub-level is higher than the ($\pm 1/2 \rightarrow \pm 1/2$) sub-level, which is equivalent to saying that the quadrupole interaction ΔE with ^{57}Fe in sodium nitroprusside is positive.

The area ratio for the experimental situation (c) is given by:

$$\frac{a_3}{a_1} = \frac{1 + [k + (k' - k) \cos^2 |\theta|]}{\frac{5}{3} - [k + (k' - k) \cos^2 |\theta|]} \quad (\Phi = 0, 0 \leq |\theta| \leq \frac{\pi}{2}) \quad (11)$$

Fig. 7 compares the results obtained with an effectively thin absorber (0.02 cm) with those calculated from (11).

The lack of agreement between experimental and calculated values which becomes greatest near $|\theta| = 45^\circ$ may be attributed to the fact that f' is not isotropic, as was assumed in the derivation of eq.(11). Evidence for the anisotropy of the factor f' is given by the Mossbauer spectra of polycrystalline sodium nitroprusside ² which exhibits a marked Goldanski effect ⁹, the peak area ratio being 0.97.

If we consider that the probability of the recoilless factor is anisotropic, $f'(\theta_1, \varphi_1)$, eq. (11) may be written for two sites as:

$$\frac{a_3}{a_1} = \frac{f''(p_3(\theta_1, \varphi_1) + p_3(\theta_2, \varphi_2))}{f''(p_1(\theta_1, \varphi_1) + p_1(\theta_2, \varphi_2))} \quad (12)$$

where f'' is the ratio of the anisotropy factor for the two directions corresponding to the sites.

The usual harmonic approximation for the anisotropy factor gives ¹⁰

$$f' = \exp \left[-k^2 r^2 (\theta_1, \varphi_1) \right] \quad (13)$$

where k is the photon wave vector and $\overline{r^2(\theta_1, \varphi_1)}$ the expectation value of the square of the nuclear displacement projected in the (θ_1, φ_1) direction.

Assuming that the principal axis of the nuclear vibration tensor coincides with those of the EFG, it is possible to show⁸ that in the experimental conditions (c) one has:

$$f'' = \exp - k^2 2 \alpha \sin 2 \theta \quad (14)$$

where α does not depend on $|\theta|$ and Φ .

Introducing (14) in (12) and taking into account the simplifications for the experimental situation (c) it is easy to show that the difference between the area ratios calculated by (12) from those calculated by (11) goes through a maximum at $|\theta| = 45^\circ$, in agreement with the results illustrated in fig. 7.

Discussion

The Mossbauer quadrupole interaction in sodium nitroprusside single crystals show that an axially symmetric field gradient with its principal axis oriented along the Fe \leftrightarrow NO direction couples with the nuclear moment of ^{57}Fe ($Q = + 0.29$ barns) giving a positive interaction of $+ 0.1726$ cm/sec. From eq. (2) one calculates $eq = + 0.585 \times 10^{18}$ V/cm² or 0.627 a.u.

A qualitative description has been given of the Mossbauer hyperfine interactions of the nitroprusside molecule⁵ on the basis of a M.O. bonding scheme proposed for nitrosyl-transition metal complexes¹¹. Recently detailed M.O. calculations have been reported¹²

and a quantitative interpretation of these hyperfine interactions in terms of the electronic densities of the molecule can be compared with the results from the M.O. method.

The ground state configuration for iron in the nitroprusside molecule is $(d_{xz}, d_{yz})^4 (d_{xy})^2$, with the electrons in the lower (d_{xz}, d_{yz}) doublet strongly delocalized by back-donation to the $2p\pi$ orbitals of the nitrosyl ligand whereas the d_{xy} electrons can be slightly delocalized to the equatorial cyanides¹².

We assume that the major contribution to the EFG comes from this asymmetric expansion of the d electrons towards the ligands.¹³ Since the EFG due to a single d electron¹⁴ is $4/7 \langle r^{-3} \rangle$ we have, according to the ground state proposed for $\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}^{2-}$:

$$q = + \frac{4}{7} \langle r^{-3} \rangle n_{xy} - \frac{2}{7} \langle r^3 \rangle (n_{xz} + n_{yz}) \quad (15)$$

where the n's denote the effective number of d electrons in each sub-shell.

The equatorial cyanides can interact directly with the d_{xy} orbital. However n_{xy} is expected to be close to the ionic value since the d_{xy} shell remains essentially non-bonding in MX_5NO complexes. An estimate of the n_{zy} population can be made by using the covalency factor for bonding with the cyanides ligand in a paramagnetic complex¹⁵ such as $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$. The orbital reduction factor for this complex is $k = 0.87$ which gives a population

$$n_{xy} = 1.74 \quad (16)$$

Substituting (16) in (15) and taking into account the values

$q = + 0.627$ a.u. and $\langle r^{-3} \rangle_{3d} = 4.4$ a.u.¹⁶ one finds:*

$$(n_{xz} + n_{yz}) = 2.98 \quad (17)$$

The delocalization of a d_{xz} or d_{yz} orbital involves p_z orbitals on two equatorial cyanides and $p_x(p_y)$ orbitals on the axial cyanide and on the nitrosyl. If one neglects the delocalization to the equatorial cyanides it is possible to write from (17) the molecular orbital:

$$\psi_{xz(yz)} = 0.869 \phi_{xz(yz)} + 0.496 \pi_{x(y)}^* (\text{NO}) \quad (18)$$

This M.O. indicates a population of 24.5% π^* NO which is in good agreement with the value of 24.8% given in reference (12).

The quadrupole coupling has also been investigated in $\text{Mn}^{\text{II}}(\text{CN})_5\text{NO}^{2-}$, which has the same crystal structure¹⁷ as $\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}^{2-}$. The electron spin resonance spectrum of this paramagnetic complex shows satellite lines of low intensity between the $\Delta m = 0$ transitions. These $\Delta m = \pm 1$ transition were assigned¹⁸ as arising from the quadrupole coupling with ^{55}Mn . From the quadrupole coupling constant obtained - 62.4 Mc and the quadrupole moment of $^{55}\text{Mn} = 0.35$ b one calculates $eq = - 0.754$ a.u.

The ground state configuration for $\text{Mn}^{\text{II}}(\text{CN})_5\text{NO}^{2-}$ is $(d_{xz}, d_{yz})^4(d_{xy})^1$. A lower limit to the extent of delocalization of (d_{xz}, d_{yz}) has been calculated from (15) with $\langle r^{-3} \rangle_{3d} = 3.1$ a.u., and n_{xy} equal to one:

$$n_{xz} + n_{yz} = 2.858 \quad (19)$$

This gives a 28.5% π^* NO population which compares well with the result for $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ and confirms the strong delocalization of the d_{xz}, d_{yz} orbitals in the pentacyanitrosyls.

The high s-electron density indicated by the unusual value of the isomer shift of $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ complex has been assumed to be a consequence of the delocalization of the 3d electrons of the iron ion¹⁹.

The total s-electron density at the ^{57}Fe nucleus in the complex can be written as the sum of inner shells contribution and a fraction $\psi_{4s}^2(0)$ of 4s density arising from the partial occupation of this shell by electrons from the ligands²⁰.

$$\psi_s^2(0) = \sum_1^3 \psi_{is}^2(0) + x \psi_{4s}^2(0) \quad (20)$$

The total s-electron density $\psi_s^2(0)$ can be evaluated from the proportionality with the measured isomer shift:

$$\text{I.S.} = \alpha \psi_s^2(0) + \text{cte} \quad (21)$$

On the basis of effective charge calculations for ionic iron complexes we have derived the value²¹.

$$\alpha = -0.021 \text{ cm/sec} \quad (22)$$

From (21) it is possible to write:

$$\psi_s^2(0)_{\text{Fe-NO}} = \psi_s^2(0)_{\text{Fe}^{++}} + \frac{(\text{IS})_{\text{Fe-NO}} - (\text{IS})_{\text{Fe}^{++}}}{\alpha} \quad (23)$$

$\psi_s^2(0)_{\text{Fe}^{++}} = 11.879,8$ is the total s-electron density for the free ion $3d^6$ configuration²¹ and the corresponding $(\text{IS})_{\text{Fe}^{++}}$ has been taken as $+0.145 \text{ cm/sec}$ which is the value of the more ionic bivalent salts referred to a Cr source. With $(\text{IS})_{\text{Fe-NO}} = -0.0075 \text{ cm/sec}$ referred to the same source one finds from (23):

$$\psi_s^2(0)_{\text{Fe-NO}} = 11.887,0 \text{ a.u.} \quad (24)$$

In order to evaluate the contribution of the inner s-shells it is necessary to take into account that the s-electron density at the iron nucleus changes with the d^n configuration. This is due to the decrease in shielding of the s-electrons when the 3d electrons are removed ²⁰. From (16) and (17), which take into account the delocalization of the d_e electron of the metal, one has ²³:

$$n_{\text{eff}} = n_{xy} + n_{xz} + n_{yz} = 4.72 \quad (25)$$

Interpolating from the free ion wave functions calculated by Watson one finds for the contribution of the inner s-shells corresponding to the $3d^{4.7}$ configuration:

$$\sum_1^3 \psi_{1s}^2(0)_{3d^{4.7}} = 11.883 \text{ a.u.} \quad (26)$$

Substituting (24) and (26) in (20) gives:

$$x \psi_{4s}^2(0) = 4 \text{ a.u.} \quad (27)$$

The density at the ^{57}Fe nucleus due to a single 4s electron on the $3d^{4.7}$ configuration can be estimated using the Fermi-Segré-Goudsmith formula ²⁰. This gives 8 a.u. Comparing with (27) one finds ~ 0.5 which is to be compared with a 4s population of 44.9% calculated by M.O. methods ¹².

* * *

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Figure Captions

- Fig. 1 - The usual habit and orientation relative to the crystal axes of a single crystal of $\text{Na}_2|\text{Fe}(\text{CN})_5\text{NO}|2\text{H}_2\text{O}$.
- Fig. 2 -- Mossbauer spectra of single crystal of sodium nitropruside obtained with incident radiation: a) parallel to axes c and b) parallel to axes a.
- Fig. 3 - Basic structural unit of $\text{Na}_2|\text{Fe}(\text{CN})_5\text{NO}|2\text{H}_2\text{O}$.
- Fig. 4 - A view down the c - axes of the crystal showing the relative position of the Fe-NO directions in the unit cell.
- Fig. 5 - Orientation of the incident photon relative to the crystal axes (a, b, c) and to the EFG principal axes ($\hat{x}_1, \hat{y}_1, \hat{z}_1$).
- Fig. 6 - Angular variation of the ratio a_3/a_1 of the axes of the quadrupole peaks for several thickness of an absorber cut along the (a, c) plane: (⊙) 0.09 cm; (●) 0.05 cm; (+) 0.04 cm; (Δ) 0.03 cm.
- Fig. 7 - Comparison between theoretical area ratios assuming an isotropic Mossbauer factor and results obtained with a 0.02 cm thickness absorber cut along the (a,b) plane.

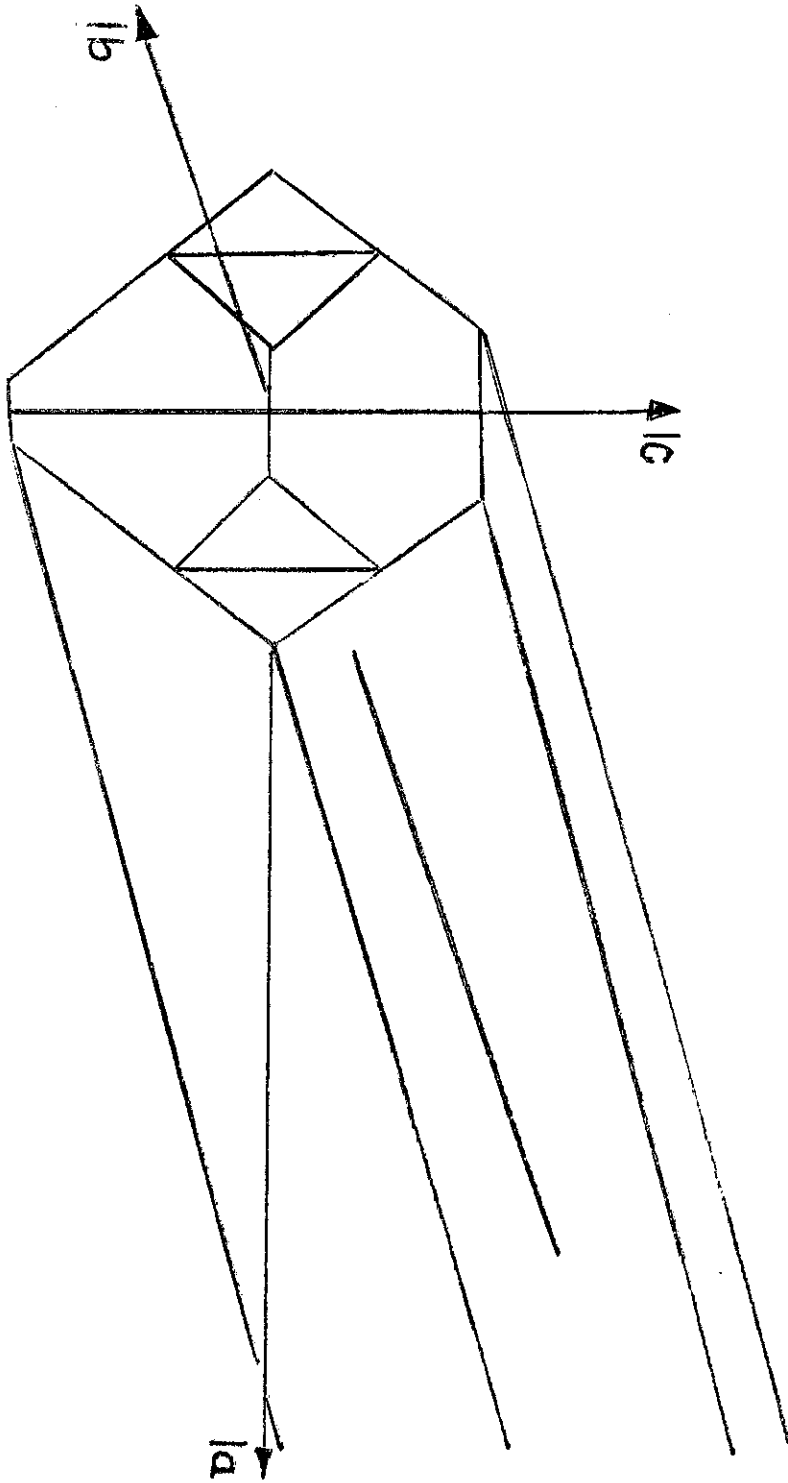


Fig. 1

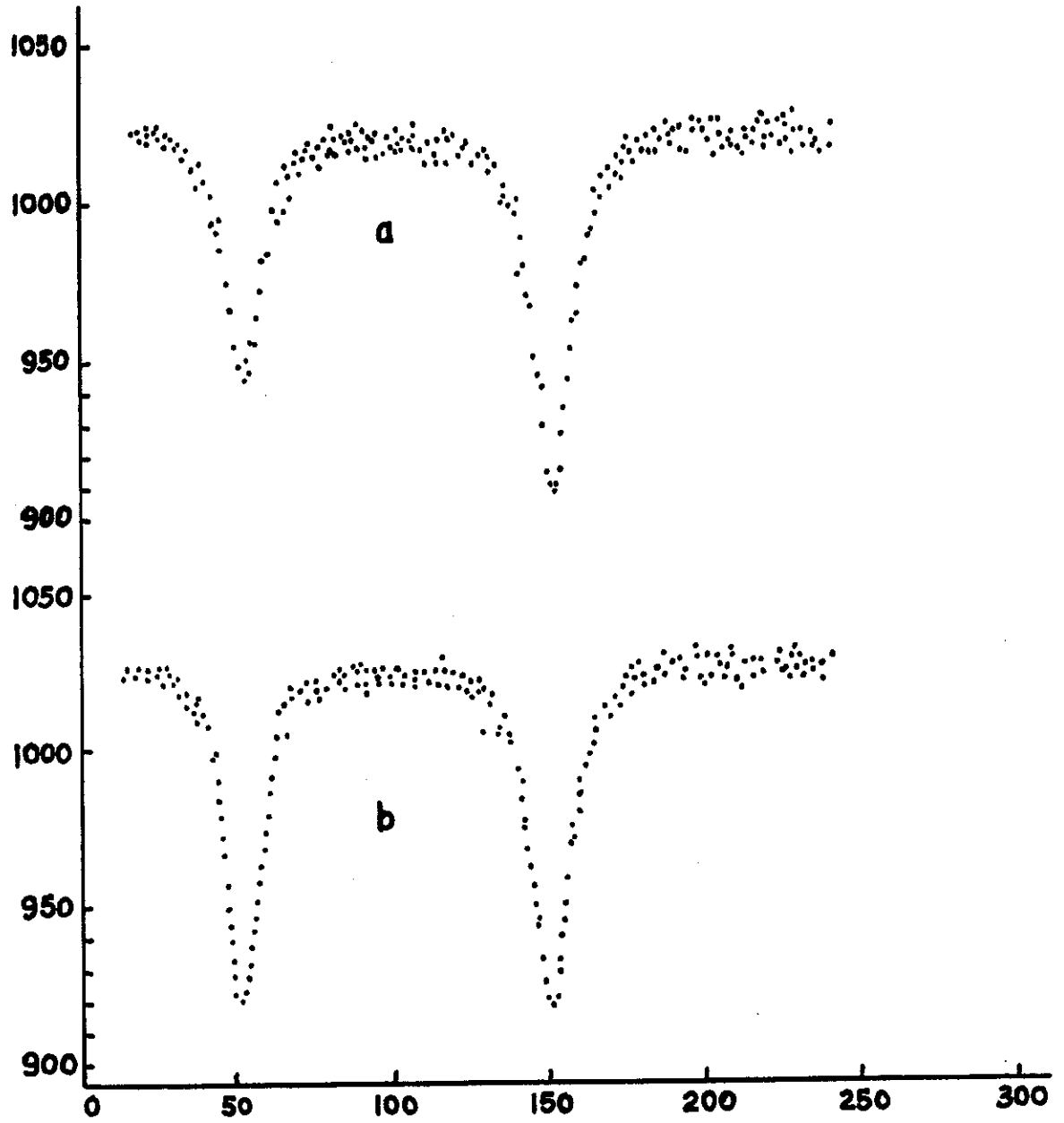


Fig. 2

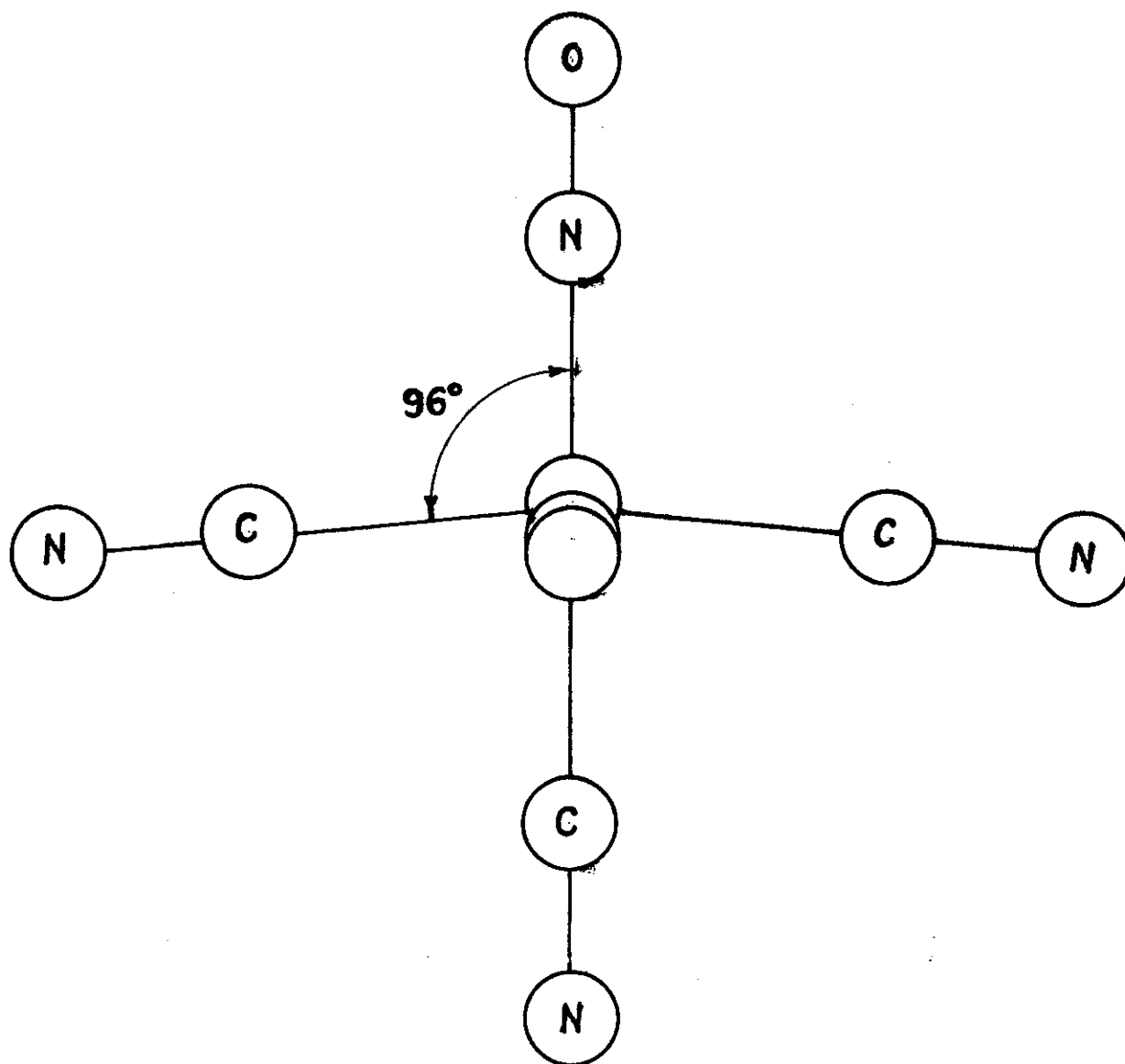


Fig. 3

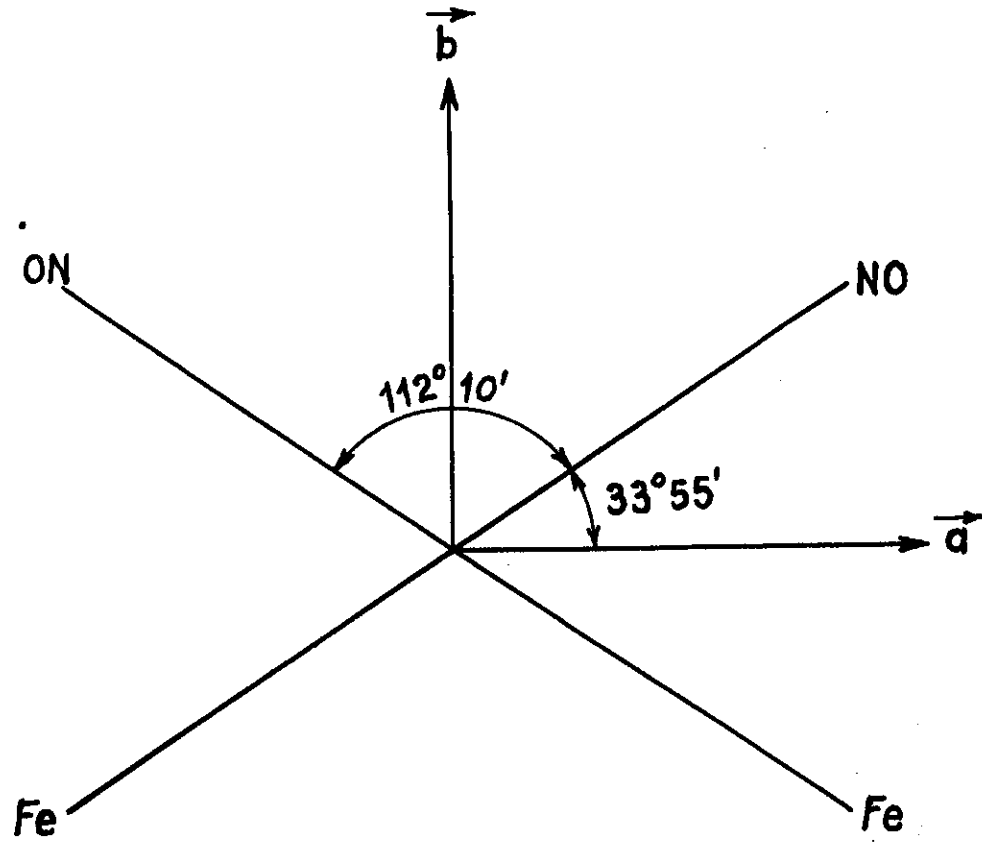


Fig. 4

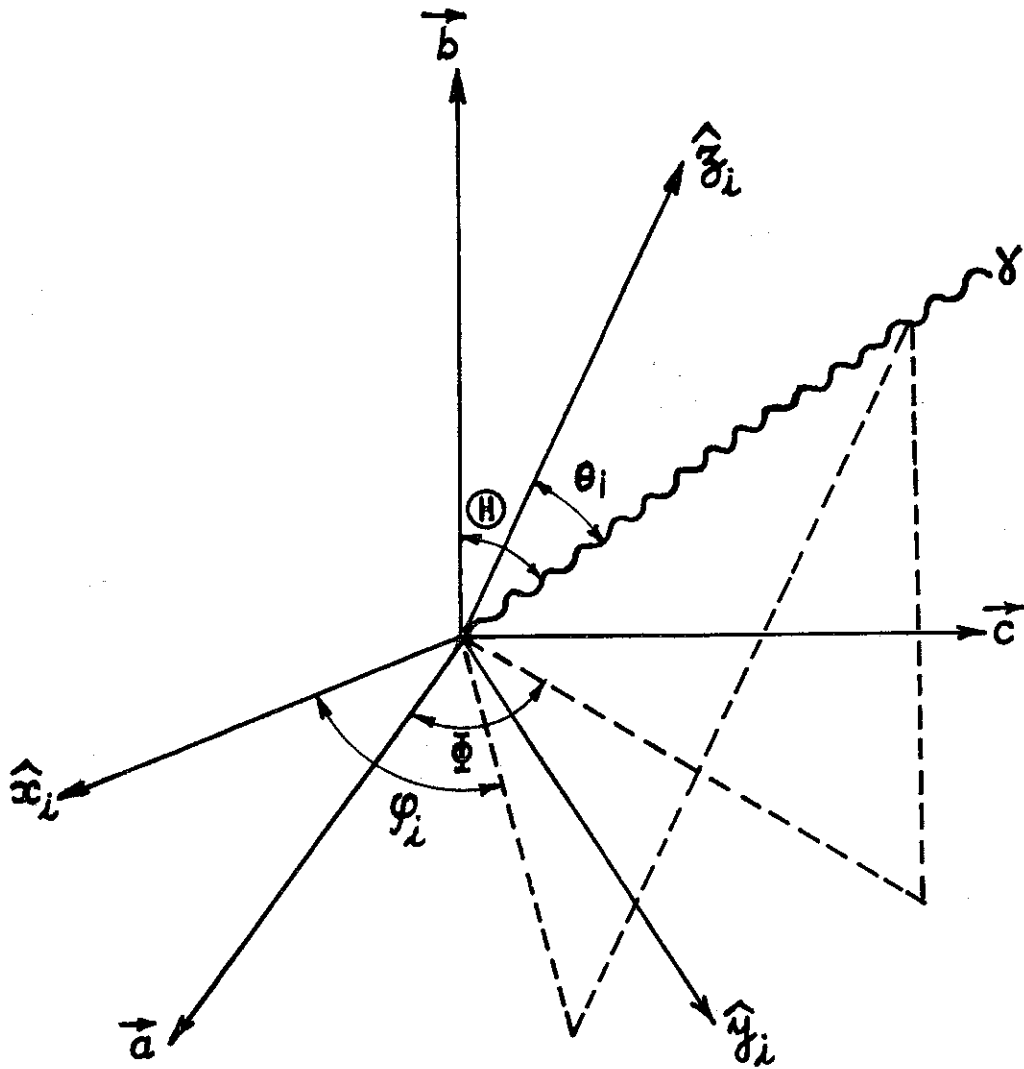


Fig. 5

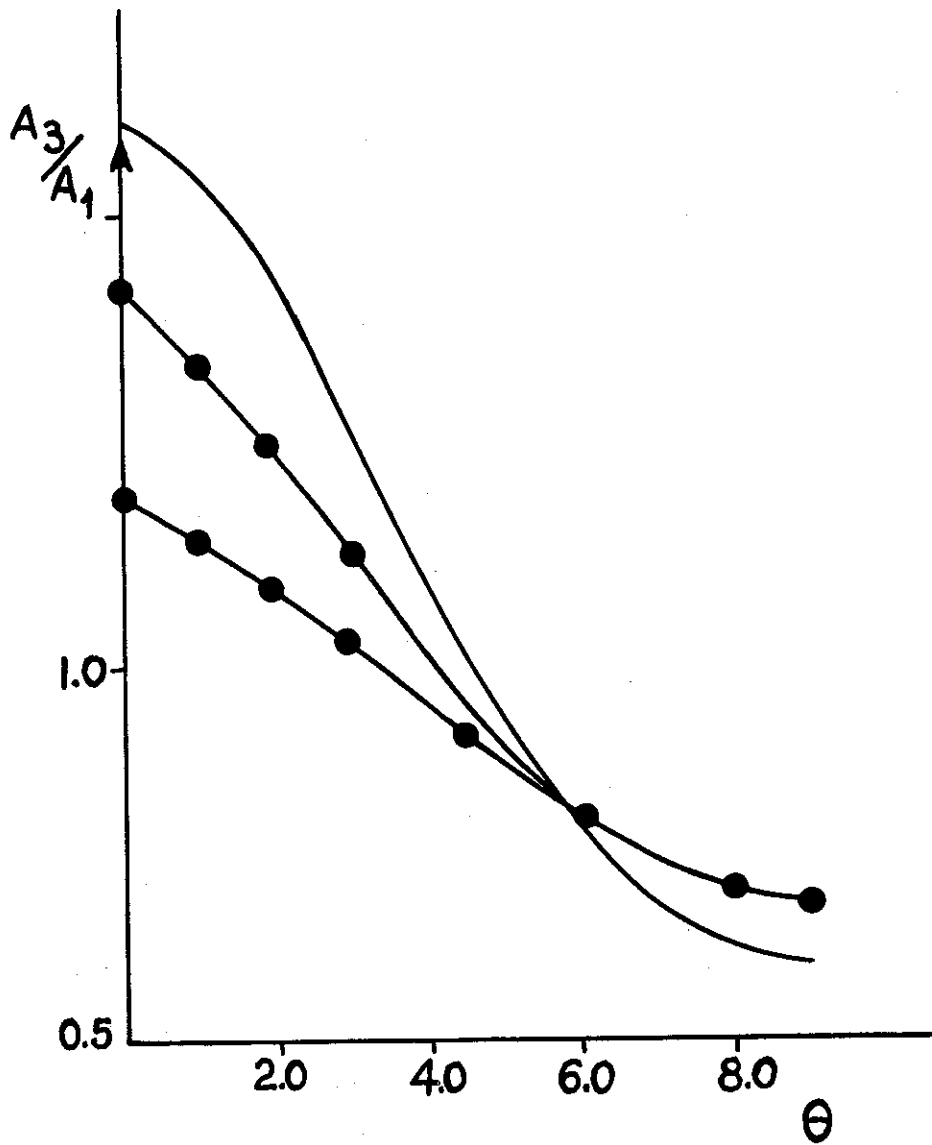
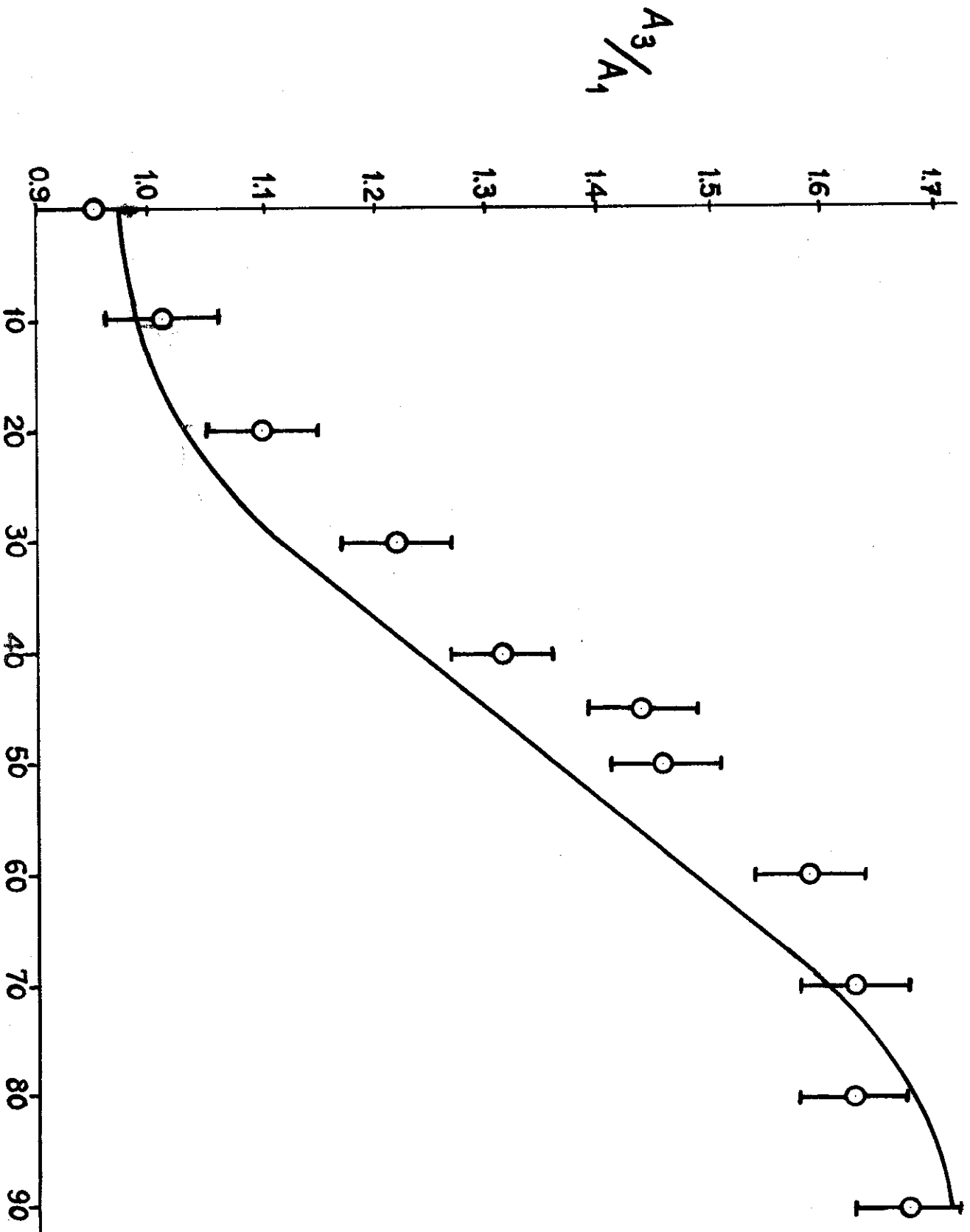


Fig. 6



θ
Fig. 7

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* We are indebted to Dr. Gilbert J. Perlow who suggested that we should evaluate covalency parameters by comparing the value of the quadrupole splitting in sodium nitroprusside to a standard splitting such as that of FeSiF_6 ($E = 0.37 \text{ cm/sec.}$). This approximation has they merit to avoid any assumption on the value of the quadrupole moment of $\text{Fe}^{57\text{m}}$ about which there are still some discussion. Using relations (15), (16) and a covalency coefficient $\alpha = 0.8$ for FeSiF_6 one calculates from the ratio of quadrupole splittings in the two compounds $n_{xz} + n_{yz} = 2.8$, which is close to the value given in (17)."