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Nuclear Electric Field Gradient and Mean Square Displacement of the Iron Sites in Sodium Nitroprusside

R. W. GRANT, R. M. HOUSLEY, AND U. GONSER
Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360

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Both the electric-field-gradient (EFG) and mean square displacement (MSD) tensor parameters at the Fe sites in sodium nitroprusside at 23°C have been determined with a high precision by the Mössbauer technique. The EFG asymmetry parameter is $\eta=0.01\pm0.01$. The principal axes of the two tensors do not coincide. Taking proper account of saturation effects was essential, even though the absorbers were only ~0.2 mm thick. For the MSD, proper consideration of polarization effects was also important. A total of 34 runs on an absolutely calibrated mechanical drive gave for the quadrupole splitting $\Delta E_Q=1.7048\pm0.0025$ mm/sec.

I. INTRODUCTION

As discussed in the preceding paper[1] (hereafter referred to as I), Mössbauer absorption with single-crystal samples can be used to determine the electric-field-gradient (EFG) and mean-square displacement (MSD) tensors at the sites of the resonant nuclei. Zory[2] and Hien[3] have recently discussed the analysis of the EFG in single-crystal absorbers containing Fe^{57}, while Karyagin[4,5] has discussed the more general case of a nuclear transition of arbitrary multipolarity, all in the thin absorber limit. Zory[2] applied his analysis to ferrous chloride tetrahydrate and evaluated all the EFG parameters while Danon and Iannarella[6] used the same analysis to confirm their expectations concerning the field-gradient parameters in sodium nitroprusside. More recently, Ingalls, Ono and Chandler,[7] and Chandra and Puri[8] have applied a similar analysis to the determination of the EFG as a function of temperature in ferrous ammonium sulfate. Unfortunately, in all these cases it has been necessary to use samples of sufficient thickness that the thin absorber analysis cannot be completely justified.

In this paper, we present data on sodium nitroprusside $Na_2Fe(CN)_5NO\cdot 2H_2O$, which is considerably more precise than any previously published. We derive the room-temperature EFG from this data using the finite thickness absorber analysis described in the preceding paper. We also discuss the measurement of the MSD from Mössbauer data and determine the vibrational dynamics at room temperature of the Fe atoms in sodium nitroprusside.

Sodium nitroprusside is a material of considerable interest in Mössbauer spectroscopy with Fe^{57}. The National Bureau of Standards recently issued a document[9] suggesting the use of sodium nitroprusside as a standard reference material for calibrating Mössbauer drives and relating isomer shifts in iron-containing compounds. As noted previously by several authors,[10–12] the fairly large and relatively temperature-insensitive quadrupole splitting and the weak-temperature dependence of the isomer shift (at room temperature and below)[13] observed in sodium nitroprusside coupled with the easily available high chemical purity and stability of the material in addition to the near natural resonance linewidths are favorable factors for using this material as a standard. Several other investigators[14–18] have obtained spectra of sodium nitroprusside and the room-temperature values of the quadrupole splitting quoted in the literature vary from 1.65–1.85 mm/sec. In the present study, we have obtained an accurate determination of this splitting.

Throughout Refs. 6, 9, and 12, the labeling of crystal axes is incorrect. Thus the single-crystal Fe^{57} standard reference material supplied by the National Bureau of Standards is actually the *ac* plane and not the *bc* plane. While our conclusions regarding the EFG are similar to Ref. 6 after appropriate relabeling of axes, the data, analysis, and subsequent EFG parameters presented in this paper are of much higher accuracy.

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II. EXPERIMENTAL

An automated programmable mechanical cam-driven constant velocity spectrometer in the normal transmission mode was used for the Mössbauer measurements. The source was Co^{57} in Cu at 23°C. The resonant radiation was the 14.4-keV transition in Fe^{57}. The γ rays were detected with a NaI crystal ~ 1 mm thick. The spectrometer employs photoelectric gating circuits. To determine the Doppler velocity, a mechanical gate length is measured with an inherent accuracy of ≈ 0.002 mm and in conjunction with the photoelectric gates is used to store scaled down pulses from a 100-kc quartz crystal oscillator.

All absorbers used for the measurements were cut from one very large single crystal kindly provided to us by Dr. J. J. Spijkerman of the National Bureau of Standards. The crystals were cut with a wire saw and thinned down to approximately 0.2 mm by mechanical polishing techniques. A microscopic examination of the crystals so obtained indicated that they were uniform in thickness to within 10%. The surface density of the crystal was determined by accurately weighing and measuring areas. The areas were measured by overlaying the crystals on a fine grid. The crystals were then oriented to within $\approx 0.1°$ by x-ray diffraction techniques. The actual uncertainty in crystal alignment after mounting the sample in the Mössbauer spectrometer was estimated to be $\approx 0.25°$. All data were obtained at room temperature (23 ± 1°C).

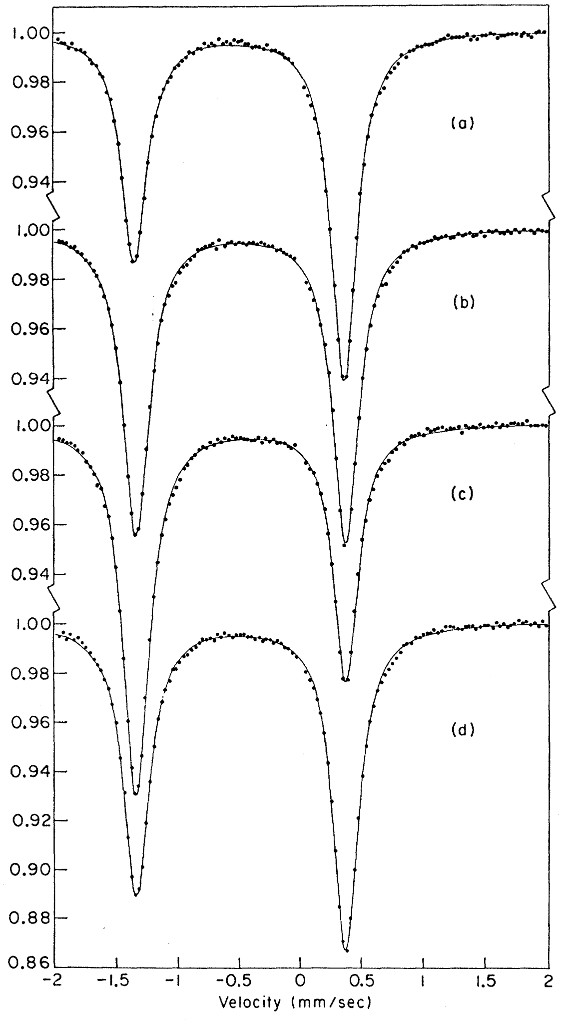

FIG. 1. Mössbauer absorption spectra obtained with a Co^{57} in Cu source at 23°C and single-crystal absorbers of sodium nitroprusside also at 23°C. The orientation of the γ-ray propagation direction relative to the crystal axes is (a) $\mathbf{k} \| a$, (b) $\mathbf{k} \| b$, (c) $\mathbf{k} \| c$, and (d) $\mathbf{k} \perp c$ and 54° from a.

To avoid possible corrections to data due to geometrical effects, fairly small specimens and fairly large source to absorber distances (typically ≈ 4 in.) were used. This geometry made the maximum spread in velocity $\approx 0.05\%$ and its effect on the experimental spectrum was ignored. All spectra were analyzed by least-square computer fitting to two Lorentz line shapes with no restrictions on line positions, widths, or intensities.

The Mössbauer spectra obtained for the γ-ray propagation direction $\mathbf{k}$ parallel to a, b, c, and at an angle of 54° from a within the ab plane are shown in Fig. 1 together with the least-squares fitted curves. As will become apparent from the discussion in Sec. IV, these directions all satisfy one of the symmetry conditions described in I so that only pure absorption effects will have to be considered in the analysis of the data. Experimental linewidths ranged from 0.24 to 0.27 mm/sec. In Table I, lines 2 and 3, we give the dimensionless areas A equal to $2/\pi f \Gamma$ times the measured areas after background corrections have been made, derived from these spectra. The quantity f is the Debye-Waller factor of the source[19] ($f=0.71$ for Fe in Cu at 23°C), and $\Gamma = 0.097135$ mm/sec is the natural linewidth of the 14.4-keV state.[20] Background corrections were $\lesssim 20\%$ and were made by standard filter techniques,[21] the single-channel analyzer window having been set so that background from Fe and Cu x rays could be neglected. It is thought that systematic errors introduced by the background correction are less than 0.25%. All limits of error, unless otherwise stated, represent one standard deviation. The standard deviation quoted on experimental data represent the statistical uncertainties based on at least five independent measurements. The standard deviations quoted on parameters derived from complex functions were computed in the usual way.[22]

During the course of the measurements, the quadrupole splitting ΔE_Q and isomer shift δ observed at the

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TABLE I. Experimental and derived parameters for sodium nitroprusside.[a]

Line		γ-ray propagation direction			k 54° from a and $\perp c$	
		$\mathbf{k}\Vert a$	$\mathbf{k}\Vert b$	$\mathbf{k}\Vert c$	1st sample	2nd sample
1	Sample thickness (mg/cm^2)	30.07 ±0.11	39.25 ±0.30	31.52 ±0.29	34.26 ±0.37	29.26 ±0.32
2	A_3	0.6486±0.0025	0.6147±0.0054	0.4474±0.0017	0.6150±0.0054	0.5332±0.0101
3	A_1	0.4212±0.0047	0.5983±0.0058	0.6941±0.0021	0.5174±0.0028	0.4561±0.0060
4	A_3/A_1	1.540 ±0.018	1.027 ±0.013	0.6446±0.0031	···	···
5	p_3^0	0.7732±0.0035	0.7256±0.0074	0.5035±0.0022	0.7260±0.0074	0.6148±0.0134
6	p_1^0	0.4707±0.0057	0.7029±0.0079	0.8384±0.0032	0.5939±0.0038	0.5145±0.0077
7	p_3^0/p_1^0	1.643 ±0.021	1.032 ±0.016	0.6005±0.0035	···	···
8	$p_1^0+p_3^0$	1.244 ±0.007	1.429 ±0.011	1.342 ±0.004	···	···
9	p_1+p_3	1.256 ±0.007	1.482 ±0.014	1.352 ±0.004	···	···
10a	$f'(\alpha=9.00)$	0.4006±0.0026	0.3620±0.0038	0.4114±0.0040	0.3788±0.0061[b] 0.3770±0.0061[b]	
10b	$f'(\alpha=8.17)$	0.3674±0.0024	0.3320±0.0035	0.3773±0.0037	0.3474±0.0056[b] 0.3457±0.0056[b]	
11a	$\langle r^2\rangle\times10^{+18}$ cm^{-2} ($\alpha=9.00$)	1.715 ±0.012	1.905 ±0.020	1.665 ±0.014	1.819 ±0.030[b] 1.828 ±0.030[b]	
11b	$\langle r^2\rangle\times10^{+18}$ cm^{-2} ($\alpha=8.17$)	1.877 ±0.013	2.067 ±0.022	1.827 ±0.015	1.982 ±0.033[b] 1.991 ±0.033[b]	

[a] All uncertainties represent one standard deviation.
[b] Weighted average. Twice as much data were collected with the 29.26-mg/cm^2 crystal as with the 34.26-mg/cm^2 crystal.

Fe sites in sodium nitroprusside were determined 34 times. The average values and standard deviations obtained for these parameters at 23°C are

$$\Delta E_Q = 1.7048\pm0.0025 \text{ mm/sec},$$
$$\delta = -0.4844\pm0.0010 \text{ mm/sec}.$$

The value for ΔE_Q is not in good agreement with the latest reported measurement[9] of $\Delta E_Q=1.726\pm0.002$ mm/sec and the cause of this discrepancy is as yet unresolved. Our value is in considerably better agreement with an earlier reported value[12] of 1.712 ± 0.004 mm/sec. We have checked for the possible influence of geometrical effects by increasing the source to absorber distance but find no change in ΔE_Q to well within the quoted error limits. We also note that geometrical effects tend to increase rather than decrease the experimental value of ΔE_Q. We have also checked our frequency standard and the linearity of our spectrometer for possible sources of systematic error; we find these errors to be well within our quoted standard deviations.

III. ELECTRIC-FIELD-GRADIENT AND MEAN SQUARE DISPLACEMENT TENSORS

Both the EFG and MSD are determined by symmetric (3×3) tensors which can be diagonalized in a principal axes system and completely specified by the diagonal components and three orientation parameters relating the principal axes to the crystal axes. For the MSD this is strictly true only for harmonic forces.[23] However, for simple cases which have been studied,[24,25] it is a very good approximation even when third- and fourth-order anharmonic forces are considered. Therefore, we will assume that it adequately represents the motion of the relatively heavy Mössbauer atoms in most cases and in particular for these measurements of Fe in sodium nitroprusside. Because only s electrons whose wave functions are spherically symmetric have a finite charge density at the nucleus, Laplace's equation requires the EFG to be a traceless tensor so that only two of the three diagonal components are independent variables. Since no fundamental expression relates the diagonal elements of the MSD, in general, more measurements will be required to uniquely determine the MSD than are required to determine the EFG.

If the Mössbauer atom is located at a site of sufficiently low symmetry, the orientation of the principal axes of both the EFG and MSD relative to the crystal axes must be determined experimentally. Although both of these tensors must satisfy the point symmetry of the site, their principal axes will not, in general, be colinear at a site of low symmetry (i.e., at sites with point symmetry 1, $\bar{1}$, 2, m, and $2/m$). The possibility of having an anisotropic MSD which is noncolinear with the EFG principal axis system can complicate the determination of EFG parameters from single-crystal data when there is more than one equivalent molecular unit which differs in orientation with respect to the crystal axes.

In describing the EFG, it is conventional to define two independent variables q and η where $q=V_{zz}/|e|$ and the asymmetry parameter η is $\eta=(V_{xx}-V_{yy})V_{zz}^{-1}$. The electronic charge is $|e|$. The three diagonal elements of the EFG (V_{xx}, V_{yy}, and V_{zz}) are chosen so that $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$ implying $0\leq\eta\leq1$.

For Fe^{57} where the excited and ground states have nuclear spins $\frac{3}{2}$ and $\frac{1}{2}$, respectively, the presence of an EFG produces an absorption spectrum of two lines separated in energy by $\Delta E_Q=e^2qQ(1+\eta^2/3)^{1/2}/2$, where Q is the nuclear quadrupole moment of the 14.4-keV excited state in Fe^{57}.

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[23] D. W. J. Cruickshank, Acta Cryst. **9**, 747 (1956).
[24] A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).
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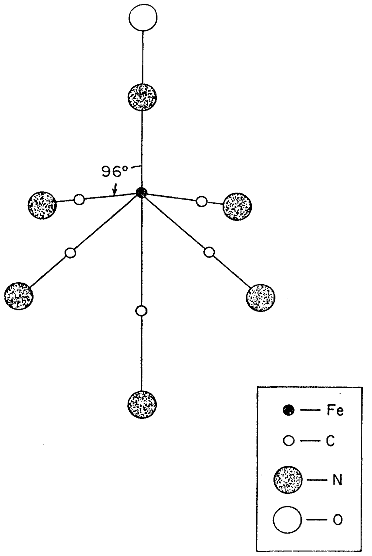

FIG. 2. Idealized C_{4v} structure of the nitroprusside ion.

There is no convention for labeling the principal axes of the MSD tensor so we will arbitrarily choose them to correspond as closely as possible to those of the EFG.

IV. SYMMETRY CONSIDERATIONS

Sodium nitroprusside crystallizes in the orthorhombic space group *Pnnm* (D_{2h}^{12}) with four molecules per unit cell.[26] The detailed crystal structure has been determined by Manoharan and Hamilton.[27] The Fe sites are all equivalent and are in the 4*g* positions $\pm(x,y,\frac{1}{2})$ and $\pm(\frac{1}{2}+x,\ \frac{1}{2}-y,\ 0)$ with point symmetry *m*. The lattice constants are $a=6.17\pm0.03$, $b=11.84\pm0.06$, and $c=15.43\pm0.08$ Å. The nitroprusside ion lies on the mirror plane and has approximate C_{4v} symmetry. In Fig. 2, we show the idealized C_{4v} structure of the nitroprusside ion as determined by Manoharan and Hamilton.[27] The Fe atom is displaced about 0.2 Å above the plane (toward the NO group) of the 4 C atoms in the CN groups located cis to the NO group. Since it will be of interest to relate the EFG to the structure of this ion, we will for convenience refer to the N of the NO group as N_1 and the C of the CN group in the trans position to the NO group as C_1. The mirror planes in this crystal lie parallel to the *ab* plane and are equally spaced at the separation distance of 0.5*c* along *c*. The mirror planes contain the atoms N-C_1-Fe-N_1-O of each nitroprusside ion. In Fig. 3, we show the projection onto the crystallographic *ab* plane of the four N-C_1-Fe-N_1-O groups associated with the four nitroprusside ions in a unit cell. The actual positions of atoms along *c* are indicated in decimal units of *c*. It is obvious that all four nitroprusside ions have different orientations relative to the crystallographic axes. However, these four sites are related by 2-fold screw axes parallel to either the *a* or the *b* axes (at 0.25*c*) as shown in Fig. 3. Manoharan and Hamilton[27] find that the vectors connecting Fe to N_1 make angles of 33°54′, 146°6′, 213°54′, and 326°6′ relative to the crystallographic *a* axis. The corresponding vectors connecting C_1 to Fe make angles of 37°16′, and 142°44′, 217°16′, and 322°44′ relative to the *a* axis. Since the EFG and MSD are symmetric with respect to inversion, the four Fe sites with different orientations can be grouped into two sets of two sites having different orientations of EFG and MSD relative to the crystal axes. The two sites $\pm(x,y,\frac{1}{2})$ have identical orientations of EFG and MSD as do the two sites $\pm(\frac{1}{2}+x,\ \frac{1}{2}-y,\ 0)$.

Since the Fe atoms are located at special positions, a considerable simplification of our problem is obtained by making use of the point symmetry of the atom sites. The mirror planes which contain all Fe sites in sodium nitroprusside requires one of the principal axes of both the EFG and MSD tensors to lie parallel to the crystallographic *c* axis; the other remaining axes are thus located in the *ab* plane. Because all Fe sites are related by the 2-fold screw axes, the MSD along the crystal *a* and *b* axes is the same for all sites as is also true along the *c* axis. Along both the *a* and *b* axes the absorption cross sections and polarizations for the two sets of sites are the same.

The point symmetry of the iron sites itself sets no restrictions on η. However, since the nearest-neighbor atoms are expected to have the strongest influence on the EFG, the approximate local symmetry C_{4v} suggests that η will be small and that the V_{zz} direction will most likely be along the Fe—N_1 bond direction.

V. DETERMINATION OF EFG PARAMETERS

The samples used in the measurements were thin enough that polarization effects are expected to be moderate and analysis through successive approximations is expected to be feasible (sample thicknesses are given in line 1 of Table I). Therefore, the dimensionless areas listed in lines 2 and 3 of Table I were first converted into preliminary p (notation defined in I) values, p^0, taking the fractional polarization (also defined in I) $a=0$ in all cases. For this purpose Eq. (21) of I with $a=0$ is very convenient. These and the ratios $p_3{}^0/p_1{}^0$ are listed in lines 5–7 of Table I. The sign of q in sodium nitroprusside has previously been determined[28] to be positive so the higher energy line denoted by the subscript 3 is associated with the excited nuclear state having $m_I=\pm\frac{3}{2}$, while that denoted by 1 comes from $m_I=\pm\frac{1}{2}$, assuming for the moment that $\eta=0$ so that m_I is a good quantum number.

There are two experimental difficulties that might influence the p^0 values obtained above. The sample

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[27] P. T. Manoharan and W. C. Hamilton, Inorg. Chem. **2**, 1043 (1963).

[28] See R. W. Grant, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum Press, Inc., New York, 1966), Vol. 2, p. 23.

thicknesses might not have been entirely uniform and the resonance might be slightly broader than the natural width. Estimates of these effects may easily be made. Allowing for a possible 10% variation in thickness across the samples which seems a reasonable limit from a microscopic examination, we have found by taking into account both the distribution in nuclear attenuation and the corresponding variation in electronic attenuation the p^0 values will not be changed by more than about 0.2%. This is considerably smaller than the statistical uncertainties, and hence we will not consider it further.

As is known, experimentally determined areas are insensitive to instrumental broadening in the thin absorber approximation. However, if we assume that all the width in the experimental spectra not directly accounted for by thickness broadening is due to broadening of the absorber resonance lines, then all the p^0's would be increased 2–3%. The main effect of this would be to slightly increase the absolute values of the MSD parameters with smaller changes in the relative values and the EFG parameters. Because of this and our feeling that most of the broadening is instrumental, we take the p^0 values listed in Table I, lines 5–7, as the correct starting values for further refinement. The ~1% uncertainty in areas due to uncertainty in the source Debye-Waller factor will for similar reasons be disregarded.

To obtain initial estimates of the EFG and MSD parameters, we used Zory's[2] expression for the relative absorption intensities, which is valid in the thin absorber limit. For convenience we have included this expression in the Appendix along with the general expression for the MSD in the harmonic approximation. For the symmetry under consideration in sodium nitroprusside, simultaneous equations were obtained and solved algebraically for the initial estimates of the EFG and MSD parameters.

In refining the EFG parameters, we used the six p^0 values measured along the a, b, and c crystallographic directions. In addition to the sample thicknesses, these depend on η, the three parameters describing the orientation of an EFG with respect to the crystallographic axes, and the absorber Debye-Waller factor values f' in the three directions f_a', f_b' and f_c'.

Fortunately, the crystal symmetry restricts the z principal axis of the EFG [29] to be either parallel to c or in the ab plane. The ratio $p_3^0/p_1^0=0.60$ along c is inconsistent[30] with $V_{zz}\|c$ for any value of η. Therefore, V_{zz} must lie in the ab plane. If p_1^0 and p_3^0 were interchanged, no value of η would fit the ratio. Therefore, this is an independent determination of the sign of q.

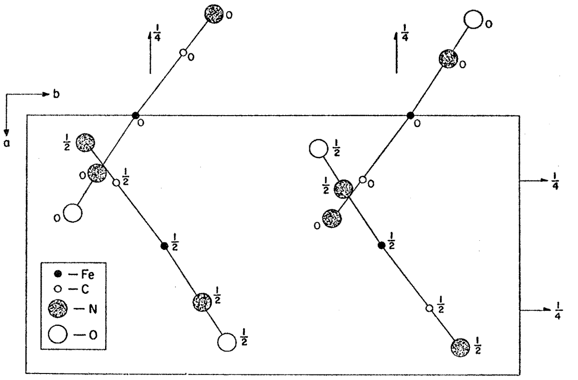

FIG. 3. Projection of the four N-C_1-Fe-N_1-O groups per unit cell in sodium nitroprusside onto the ab plane.

Knowing that V_{zz} is in the ab plane, it is possible to write down the elements of the effective thickness matrices at resonance ($x=x_{ij}$) describing the absorption along the three crystal axes in terms of η and the angle β between V_{zz} and the a axis. The effective thickness matrix is defined in I, Eq. (14) and x is related to the energy E by $x=2E/\Gamma$. We will arbitrarily assume $V_{xx}\|c$. If, in fact, $V_{yy}\|c$, then η from our analysis will come out negative, but will have the right magnitude. The basis systems have been chosen according to the prescription given in Sec. III of I and the letters in front of the expressions for the σ's indicate the crystallographic axis along which the corresponding basis vectors lie. The + and − signs correspond, respectively, to the E_3 and E_1 transitions. The quantities n and σ_0 are the number of resonant nuclei per unit area and the fixed nucleus cross section, respectively.

$$\begin{aligned}
&\mathbf{k}\|a\\
b:\;& \sigma_{11}{}^a(x_{ij})/nf_a'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}(1-\eta)\,,\\
c:\;& \sigma_{22}{}^a(x_{ij})/nf_a'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\
&\qquad\times(1-3\sin^2\beta+\eta\cos^2\beta)\,,\\
&\sigma_{12}=\sigma_{21}=0\,,
\end{aligned}\tag{1}$$

$$\begin{aligned}
&\mathbf{k}\|b\\
a:\;& \sigma_{11}{}^b(x_{ij})/nf_b'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}(1-\eta)\,,\\
c:\;& \sigma_{22}{}^b(x_{ij})/nf_b'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\
&\qquad\times(1-3\cos^2\beta+\eta\sin^2\beta)\,,\\
&\sigma_{12}=\sigma_{21}=0\,,
\end{aligned}\tag{2}$$

and

$$\begin{aligned}
&\mathbf{k}\|c\\
a:\;& \sigma_{11}{}^c(x_{ij})/nf_c'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\
&\qquad\times[(1+\eta)\cos^2\beta-2\sin^2\beta]\,,\\
b:\;& \sigma_{22}{}^c(x_{ij})/nf_c'\sigma_0=\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\
&\qquad\times[(1+\eta)\sin^2\beta-2\cos^2\beta]\,,\\
&\sigma_{12}=\sigma_{21}=0\,.
\end{aligned}\tag{3}$$

For $\mathbf{k}$ along a and b, these effective thickness matrix elements could be obtained from Eq. (36) of I by in-

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[29] Throughout the remainder of this paper, we will use the convenient and descriptive, although inexact, notation that V_{zz} is collinear with the z principal axis of the EFG, etc.

[30] See Fig. 4 of U. Gonser and R. W. Grant, Phys. Status Solidi **21**, 331 (1967).

spection since for these directions the $\hat{\theta}$ and $\hat{\varphi}$ basis vectors for the two pairs of sites are the same. For **k** along *c* this is not the case, and it was necessary to rotate the basis for one pair of sites by β and that for the other pair of sites by $-\beta$ before adding effective thickness matrix elements. This was done by the standard prescription for expressing a matrix in a rotated coordinate system.

To solve for η, β, f_a', f_b', and f_c' by successive iterations, we set the six $p=[\sigma_{11}(x_{ij})+\sigma_{22}(x_{ij})]/2$ expressions obtained from Eqs. (1), (2), and (3) equal to the six preliminary experimental p^0 values calculated assuming $a=0$ and found the best solution for the parameters consistent with the statistical uncertainties in the data. This gives $\eta\leq 0.013$ and $\beta=36°4'\pm 25'$. Using these values, polarization fractions a could be obtained. It appears that one more step in this procedure would yield a self-consistent solution.

We actually obtained our final solution in a slightly different way. We found a set of linear equations in the unknown parameters by expanding Eq. (17) of I in a Taylor series about the values obtained above and eliminated f_a', f_b', and f_c' from the pairs of equations along the same directions. This left three equations in $d\eta$ and $d\cos\beta$. The best solution consistent with the statistical uncertainties was found graphically. It gives $\eta=0.01\pm 0.01$ and $\beta=+36°15'\pm 38'$ where the quoted uncertainties approximate one standard deviation. Using the values of η and β just determined, new values of p_1+p_3 in the three directions were also obtained and are compared with the values from the previous iteration in lines 8 and 9 of Table I.

As discussed in I, there is an inherent uncertainty in the sign of β, i.e., $\beta=\pm 36°15'$. This is evident since the relative absorption areas only depend on the square of trigometric functions. Thus two solutions exist which are consistent with the present experimental results, namely, that V_{zz} is either almost $\|$ to the Fe-N$_1$ direction as expected or is at an angle of $\approx 72°$ from the Fe-N$_1$ direction. Because of the approximate C_{4v} symmetry of the nitroprusside ion as previously discussed, we will not consider the solution with $V_{zz}\approx 72°$ from Fe-N$_1$ further.

VI. DETERMINATION OF MSD PARAMETERS

Along the three crystal axes f' values were obtained using the p_1+p_3 values in line 9 and the sample thicknesses in line 1 of Table I. In determining f' values, it is necessary to know the value of σ_0 since $p_1+p_3=nf'\sigma_0$. In turn, σ_0 depends on the internal conversion coefficient α. The value $\alpha=9.00$ is in current use,[20] but recent careful measurements[31] give $\alpha=8.17$. The results in line 10a were computed using $\alpha=9.00$, while those in 10b are for $\alpha=8.17$. The MSD's derived from the two f' values are listed, respectively, in lines 11a and 11b. We have used the relationship[24,25] $f'=\exp(-k^2\langle r^2\rangle)$, where $\langle r^2\rangle$ is the MSD parallel to **k**, and have taken[20] $k^2=5.334\times 10^{17}$ cm^{-2}.

The data for **k** along *a* and *b* are not sufficient to determine the orientation of the principal axes of the MSD in the *ab* plane since there is no condition on the MSD similar to the condition that the trace of the EFG=0. In fact, if we assume that the *z* principal axis of the MSD for one site lies in the *ab* plane at an angle ω to the *a* axis and that the *x* principal axis lies along the *c* axis, we can describe the MSD for that site along an arbitrary direction in the *ab* plane making an angle Ω with the *a* axis by[4,32,33] (also see Appendix)

$$\langle r^2\rangle=\langle z^2\rangle\cos^2(\Omega-\omega)+\langle y^2\rangle\sin^2(\Omega-\omega). \tag{4}$$

We see that we must have measurements along three directions in the *ab* plane to solve for the three unknowns $\langle z^2\rangle$, $\langle y^2\rangle$, and ω. Therefore, the measurements at $\Omega=54°$ listed in the last two columns of Table I were made.

Along this direction the f' values for the two pairs of sites cannot be assumed to be equal. Also the angles with respect to V_{zz} for the two pairs of sites will be different. However, the effective thickness matrix must be diagonal in the $\hat{\theta}$, $\hat{\varphi}$ basis, as discussed in I, Sec. III, since these vectors are, respectively, perpendicular and parallel to the *ab* mirror plane. The effective thickness matrix elements for **k** at an angle Ω from a (**k** in the *ab* plane) are

$$\begin{aligned}\sigma_{11}(x_{ij})&=\tfrac{1}{2}[n(f_1'+f_2')\sigma_0]\{\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}(1-\eta)\}\,,\\ \sigma_{22}(x_{ij})&=\tfrac{1}{2}nf_1'\sigma_0\{\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\ &\qquad\times[1-3\sin^2(\Omega-\beta)+\eta\cos^2(\Omega-\beta)]\}\\ &\qquad+\tfrac{1}{2}nf_2'\sigma_0\{\tfrac{1}{2}\pm\tfrac{1}{4}[3/(3+\eta^2)]^{1/2}\\ &\qquad\quad\times[1-3\sin^2(\Omega+\beta)+\eta\cos^2(\Omega+\beta)]\}\,,\\ \sigma_{12}&=\sigma_{21}=0\,.\end{aligned}\tag{5}$$

We found f_1' and f_2' by an iteration procedure similar to that described in the section on the EFG parameters. We set the p^0's equal to the p's obtained from Eqs. (5) and solved for f_1' and f_2' making use of the values of η and β previously determined. Having preliminary f_1' and f_2' values, we calculated the polarizations and carried through another iteration. A further iteration using these values did not lead to significant changes in f_1' and f_2'. The final values and the corresponding MSD's are listed in Table I.

Arbitrarily choosing ω to be in the same quadrant as β, we can now use the two groups of four MSD values $\langle a^2\rangle$, $\langle b^2\rangle$, $\langle r_1^2\rangle$, and $\langle r_2^2\rangle$ and Eq. (4) to find a consistent set of values for $\langle z^2\rangle$, $\langle y^2\rangle$, and ω. With either group, the result is $\omega=+1\pm 7°$ and hence $\langle z^2\rangle\approx\langle a^2\rangle$ and $\langle y^2\rangle\approx\langle b^2\rangle$. As previously mentioned, $\langle x^2\rangle=\langle c^2\rangle$ from symmetry

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[31] W. Rubinson and K. P. Gopinathan, Phys. Rev. **170**, 969 (1968).

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considerations. The angle ω is rather insensitive to the choice of α. The existence of a consistent solution supports our assumption that f' in sodium nitroprusside can be described in the quasiharmonic approximation. As with the principal axes of the EFG, there is an inherent uncertainty in the sign of ω. However, the simultaneous analysis of both the EFG and MSD as indicated above establishes that only the $\omega=+1°$ solution is consistent with the data when we choose $\beta=+36°15'$.

VII. CONCLUSIONS

A complete determination of both the EFG and MSD tensors and their orientation parameters relative to the crystal axes has been presented for the Fe sites in sodium nitroprusside. We find that the principal axes of the two tensors are not colinear. From physical arguments, this seems reasonable since the EFG will reflect electron charges located mainly on nearest-neighbor atoms. The MSD on the other hand will be strongly influenced by long-wavelength vibrations in the crystal which reflect the basic symmetry of the lattice rather than the approximate local symmetry of the Fe atoms. The coincidence of the MSD tensor axes and the crystal axes (within the experimental uncertainty) support this view. The nitroprusside ion is a rather stable ion and probably, in part, vibrates as a molecular unit in the crystal.

The EFG determined in the present study is consistent with the suggestion of Manoharan and Hamilton that the departure of the nitroprusside ion in sodium nitroprusside from ideal C_{4v} symmetry is not significant at room temperature. This is suggested by both the fact that $\eta=0$ to within experimental error and that V_{zz} is located at $36°15'\pm38'$ from the a axis in the ab plane. The x-ray results show that the Fe-N_1 direction is $33°54'$ from the a axis, while the C_1-Fe direction is $37°16'$ from the a axis. Thus, V_{zz} falls almost exactly in between these two directions and may, in fact, represent a more accurate measure of the C_1-Fe-N_1 direction (assuming linearity) than the x-ray determination.

Danon and Iannarella[6] concluded that their measurements were consistent with $\beta=33°55'$ and felt they found evidence for a large anisotropy in the MSD. These differences from our conclusions appears to arise mainly from the fact that the data they present in their Fig. 7 is in disagreement with our measurements. This may be due to the extrapolation procedure they illustrate in their Fig. 6, although this is certainly not clear. A linear extrapolation procedure is only valid in general for very thin absorbers, as can be seen from Eq. (17) of I or Fig. 1 of Ref. 34.

The MSD determined in the present work could be compared with thermal factors determined in an x-ray or neutron crystal structure determination. In the structural determination of Manoharan and Hamilton,[27] photographic data was used and absorption corrections were not applied. In the refinement the thermal factors were considered to be isotropic. From their value of $B=0.62\pm0.04$ Å^2, for the Fe atom we find an average $\langle r^2\rangle=0.78\pm0.05\times10^{-18}$ cm^2. This is about a factor of 2 smaller than an average value obtained from our measurements. We do not believe our value can be in error by more than about 10% primarily due to the present uncertainty in the internal conversion coefficient. A more interesting comparison would be with x-ray or neutron data obtained by counter techniques and refined without the restriction of isotropy.

Finally, this paper has shown the importance of considering both saturation and polarization effects in calculating EFG and MSD parameters from even relatively thin absorbers.

Calculation of the parameters from the measured areas without taking into account saturation effects at all gave $\eta=0.12$ and correspondingly large errors in all the other parameters. On the other hand, the preliminary analysis taking into account saturation, but neglecting polarization, gave results fairly close to the final values. This is so because the samples were quite thin and because the polarization was small in all observation directions, $a\leq0.5$. Nonetheless, the change in p_1+p_3 along the b axis, the direction for which the polarization is largest, is considerably larger than the statistical uncertainty. Calculation of MSD parameters from the preliminary $p_1^0+p_3^0$ values gave, for example, $\omega=+6°\pm5°$ which differs considerably from our final result of $+1°\pm7°$.

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APPENDIX

Zory[2] has shown that in the thin absorber limit anisotropy in the MSD modifies the relative absorption intensities of a quadrupole split doublet ($I=\frac{3}{2}\rightleftarrows I=\frac{1}{2}$ transition) associated with a single set of crystallographically equivalent sites in the following way:

$$\frac{p_3}{p_1}=\frac{\sum_i f_i\{4[(3+\eta^2)/3]^{1/2}+(3\cos^2\theta_i-1+\eta\sin^2\theta_i\cos2\varphi_i)\}}{\sum_i f_i\{4[(3+\eta^2)/3]^{1/2}-(3\cos^2\theta_i-1+\eta\sin^2\theta_i\cos2\varphi_i)\}}, \tag{6}$$

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where the angles θ and φ are the polar and azimuthal angles which describe the orientation of $\mathbf{k}$ relative to the principal axes of the EFG. The sums $\sum_i$ are to be performed over the i equivalent sites per unit cell and f_i is the recoil-free fraction of the ith site along $\mathbf{k}$.

In the harmonic limit, the general expression for f_i can be found in the following simple way. If $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ represent displacement vectors along the principal axes of the MSD, then a displacement vector in an arbitrary direction $\mathbf{r}$ is just

$$\mathbf{r}=\mathbf{z}\cos\delta+\mathbf{x}\cos\epsilon\sin\delta+\mathbf{y}\sin\epsilon\sin\delta\,,$$

where the angles δ and ϵ are the polar and azimuthal angles which describe the orientation of $\mathbf{k}$ relative to the principal axes of the MSD. The mean square displacement in some arbitrary direction for the ith nucleus is just

$$\langle r^2\rangle_i=\int_{-\infty}^{+\infty} r^2P(x,y,z)dxdydz$$
$$=\langle z^2\rangle\cos^2\delta_i+\langle x^2\rangle\cos^2\epsilon_i\sin^2\delta_i+\langle y^2\rangle\sin^2\epsilon_i\sin^2\delta_i\,,\quad(7)$$

where $P(x,y,z)$ describes the probability of finding the resonant nucleus at point (x,y,z) and $\langle x^2\rangle$, $\langle y^2\rangle$, $\langle z^2\rangle$ are the three components of the diagonalized MSD tensor. Substitution of $f_i=\exp[-k^2\langle r^2\rangle_i]$ into Eq. (6) therefore gives a completely general expression for the relative absorption intensities in terms of only tensor components and orientational parameters (in the thin absorber limit).

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Possibility of Observing Effects of the Superconducting Transition on Positron Thermalization in Metals*

A. Perkins and E. J. Woll, Jr.
McMaster University, Hamilton, Ontario, Canada

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An investigation is made of the possibility of observing effects of superconductivity on positron thermalization in metals. Energy is calculated as a function of time for a positron which loses energy by exciting quasiparticles out of the BCS ground state of the superconductor. The minimum positron energy observable in annihilation experiments at low temperature is predicted to change sharply if the metal goes from the superconducting state to the normal state (preferably by applying a magnetic field greater than the critical field). The possible magnitude of the change is estimated to be 6% of the minimum positron energy in the most favorable cases.

I. INTRODUCTION

The use of positron-annihilation experimental techniques in investigating properties of superconductors has not been expected to yield significant results. The basis for this expectation is that positrons annihilate with all valence electrons of a metal, whereas only a very small fraction of these electrons participate in the building up of the superconducting state. The experiments of Briscoe, Beardsley, and Stewart[1] measuring two-quantum angular correlation in lead through the superconducting transition temperature confirm this expectation, showing no effect of the transition.

However, the situation is different with respect to the process of positron thermalization. At low energy, a positron can lose further energy only by exciting electrons near the Fermi surface. When the positron energy approaches the size of the superconducting energy gap, its further energy loss must proceed using electrons whose properties are strongly affected by their participation in the superconducting state. The question of positron thermalization through interaction with the electron gas at zero temperature has been recently investigated theoretically by Carbotte and Arora,[2] whose treatment is based on earlier work of Lee-Whiting.[3] They found that the rate of energy loss decreases sharply as the positron energy lowers. The result is that, at low temperatures, the positron annihilates before it has completely thermalized. Kim, Stewart, and Carbotte[4] reported experimental observation of the failure to thermalize, using the technique developed by Stewart and his group[5,6] for measurement of positron effective mass. They unfolded the positron contribution to the angular-correlation curves

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