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Quadrupole Interaction in Sb^{121} by Mössbauer Techniques*

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Mössbauer techniques have been used to study the quadrupole resonance of Sb^{121} in cubic Sb_2O_3 (senarmontite). The interaction constant was measured to be $e^2qQ=+557\pm20$ MHz; except for the sign, this had earlier been determined more accurately by electric-quadrupole-resonance measurements. The sign, which implies a negative electric field gradient, is consistent with a partially covalent bonding of the $5p$ electrons to the three nearly coplanar oxygen atoms surrounding each antimony atom. The previously unknown quadrupole moment of the first excited $\frac{7}{2}^+$ state is found by measuring $R=Q(\frac{7}{2}^+)/Q(\frac{5}{2}^+)$; its value is found to be 1.38 ± 0.02. Then, using $Q(\frac{5}{2}^+)=-(0.54\pm0.07)$ b from optical spectroscopy, $Q(\frac{7}{2}^+)=-(0.75\pm0.09)$ b.

INTRODUCTION

A PREVIOUS work[1] has shown that the long-lived metastable state in Sn^{121m} decays by beta emission to the $\frac{7}{2}^+$ first excited state at 37.2 keV in Sb^{121}, and that the γ ray from this level is suitable for study by Mössbauer techniques. This paper reports a study of the hyperfine splitting of this γ ray as a result of an electric field gradient acting on the nucleus.

One reason for this study is to allow the future use of Mössbauer techniques on chemical and solid-state problems involving antimony. Once the unknown ratio R between the quadrupole moment of the first excited state and that of the ground state is known, then future measurements on γ rays from antimony nuclei in electric fields can be readily interpreted as measurements of that particular field-gradient tensor (EFG). Although the same measurement can frequently be made more accurately by electric-quadrupole-resonance (EQR) techniques, there are times (notably inside conductors) when this method cannot be used and then Mössbauer measurements are the only alternative. Additional important information is usually available from the isomer shift, and, although its value for a given spectrum is in principle independent of the nuclear quadrupole moments, in most cases the precise value of R is needed for an accurate evaluation of the isomer shift.

A second reason for this study is to increase our knowledge of the systematics of nuclear quadrupole moments in this region. For example, EQR measurements,[2] on the ground states of the two stable antimony isotopes have established that $Q^{123}(\frac{7}{2}^+)/Q^{121}(\frac{5}{2}^+)=1.275$. The first excited state of Sb^{121} differs from the $\frac{7}{2}$ ground state in Sb^{123} only by the subtraction of a pair of neutrons. Therefore, one anticipates that the ratio $R=Q^{121}(\frac{7}{2}^+)/Q^{121}(\frac{5}{2}^+)$ to be measured here should give a similar number. It will be pertinent to compare the forthcoming result with nuclear models such as that due to Kisslinger and Sorensen.[3]

The resolution in Mössbauer measurements on Sb^{121} is poor because of the rather short half-life of the first excited state. A large EFG at the nucleus is essential if a resolved hyperfine pattern is to be observed. Examination of the EQR literature[4] indicated that Sb_2O_3 has one of the largest EFG yet measured in antimony compounds and in addition the asymmetry parameter η is zero in this crystal. Since the cubic form of this material (senarmonitite) is readily available as a powder, it was anticipated that examination of this compound alone would suffice for our problem.

Unfortunately, an ambiguity developed in the interpretation of our data (as is discussed further below). This resulted in a search for an antimony compound with a larger EFG. Potassium antimono-tartrate (PAT) was investigated despite the fact that no EQR data existed for e^2qQ or η in this compound.

The field gradients in antimony compounds are not large enough to give fully resolved hyperfine spectra. For the interpretation of the spectra an exact knowledge of the linewidth obtained under the present experimental conditions is essential. For this purpose, we included measurements on cubic InSb. In this compound, the electron cloud surrounding the antimony nucleus is highly symmetric. It was therefore expected that absorbers having the "natural" linewidth could readily be prepared from the unusually pure single-crystal samples of this material which were available.

APPARATUS

As described in Ref. 1, the source was produced by irradiating a sample of SnO_2 enriched to 98.4% in Sn^{120} for a period of one month in a thermal neutron flux of

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[2] R. G. Barnes and P. J. Bray, J. Chem. Phys. **23**, 1177 (1955); S. Ogawa, J. Phys. Soc. Japan **12**, 1105 (1957).

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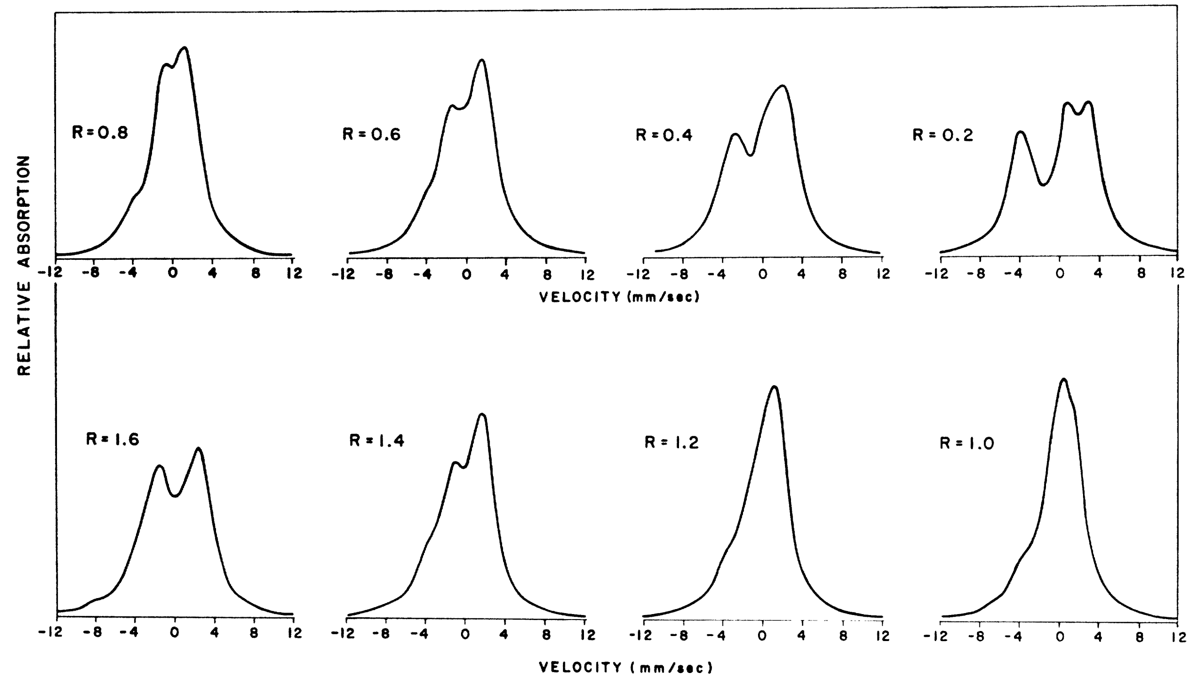

FIG. 1. Calculated Mössbauer spectra for Sb^{121} in an electric field gradient appropriate to senarmontite (cubic Sb_2O_3), for various ratios R of the excited state quadrupole moment to the ground-state moment.

5×10^{14} n cm^{-2} sec^{-1} in the Oak Ridge National Laboratory reactor. Following the removal of unwanted impurities, the material was converted to tin metal and 100 mg was electroplated onto a piece of copper foil 0.06 cm thick×2.5 cm diam.

Absorbers of InSb, Sb_2O_3, and $KSbC_4H_4O_7\cdot\frac{1}{2}H_2O$ (potassium antimono-tartrate, PAT) were made by mixing appropriate amounts of the absorbing materials with powdered Lucite and compressing the mixtures with a heated press into disks 0.4 cm thick×31. cm diam. Absorber thicknesses varied from 24 down to 1.5 mg/cm² of natural antimony; each compound was measured at several thicknesses.

The source and absorber were mounted in the exchange-gas chamber of a helium cryostat, and the absorber was moved via a stainless-steel tube driven by a double loudspeaker similar to a system previously described.[5] A Hewlett-Packard sine-wave generator in connection with a negative-feedback system drove the speaker and synchronized it to a RIDL 400-channel analyzer which was used in multiscalar mode. A standard transmission geometry was used. The proportional counter used to detect the γ-ray spectrum was filled with a mixture of CH_4 and Xe, had a 2×2-in. window of 10-mil Be, and was 3 in. in diameter by 7 in. long. The 37-keV pulses are barely resolved from the strong x-ray line. However, the signal-to-background ratio was enhanced when the window of the single-channel analyzer was placed on the escape peak of the 37-keV γ rays. Furthermore, approximately twice as many counts were found in the escape peak compared to the full-energy line. The spectrometer was calibrated with sources of Co^{57} in iron and copper and an enriched Fe^{57} absorber. The rather low specific activity of Sn^{121m} limits the counting rate in the single-channel window to about 50 cps even under optimal geometric conditions so that rather long counting times are involved in the experiments.

METHODS OF ANALYSIS

In our samples, for which magnetic hyperfine splitting can be excluded and where there is only a single lattice site for Sb in a given absorber, it should be possible to fit the data to a spectrum derived from a pure quadrupole interaction. If the asymmetry parameter η of the EFG tensor is zero the hyperfine line positions are given by

$$v_{m^*,m}=A[RC(I^*,m^*)-C(I,m)]+S\,, \qquad (1)$$

where $C(I,m)=[3m^2-I(I+1)]/I(2I-1)$, $A=(c/E_\gamma)\times(\frac{1}{4}e^2qQ)$, R is the ratio of the quadrupole moments $Q(\frac{7}{2}^+)/Q(\frac{5}{2}^+)$, and S is the isomer shift.

Since $C(I^*,m^*)$ takes on four values and $C(I,m)$ has three, one anticipates 12 lines. However, the intensities of four are zero. There are then eight velocities at which nuclear resonance absorption should be seen for each triplet of values A, R, and S.

For any value of R, there are many possible spectra

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[5] M. Kalvius, in *Mössbauer Effect Methodology*, edited by I. Gruverman (Plenum Press, New York, 1965), p. 176.

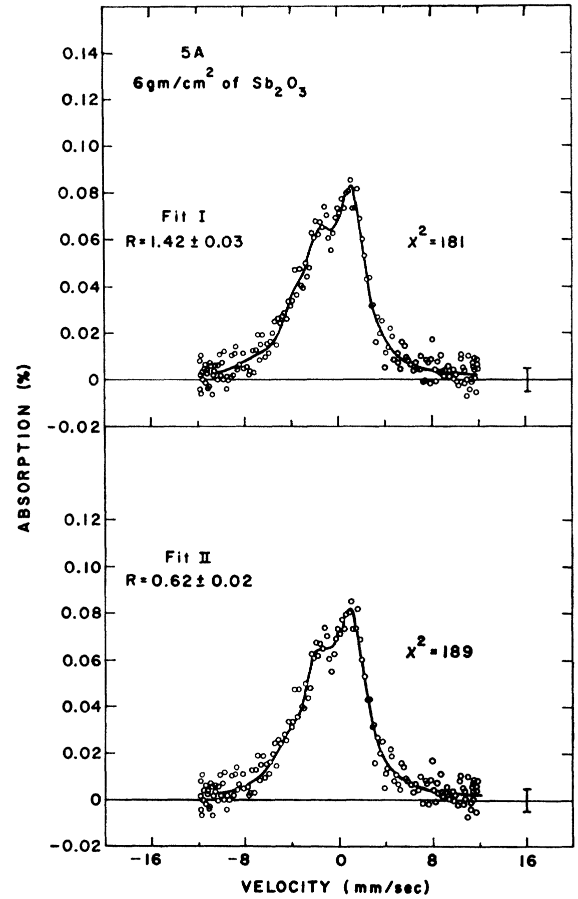

FIG. 2. Experimental data on Sb_2O_3. The curves drawn are results of a curve-fitting procedure. The two fits are done on the same data and differ only in the initial guess for R (1.4 and 0.7). The six free parameters in these fittings are the base line rate, the linewidth, the vertical scale, A, R, and S.

since A and S can be varied. Given an experimental spectrum, our problem is to find a triplet of A, R, and S that gives the best fit. Figure 1 shows the hyperfine spectra to be expected for various R, while keeping $S=0$ and e^2qQ appropriate for Sb_2O_3 .They were calculated with the use of a computer program described elsewhere.[6] The hyperfine structure is only partially resolved and the decision for R will have to be based on the shape rather than on clearly resolved line positions. Direct comparison with Eq. (1) will not be too helpful and more sophisticated techniques are called for.

The "metric minimization" program originally written by Davidon[7] has been modified for use in the least-squares fitting of up to 13 Lorentzian lines to the experimental data. Each line is described by three parameters (intensity, width, and position) and an additional parameter is used to adjust the base line or off-resonance rate. If desired, the computer can then vary up to 40 parameters to get the best fit.

Allowed that much freedom, the program frequently ends in a false minimum, for which some of the parameters are physically unreasonable. The use of linear constraints between some of the parameters largely overcomes this problem. For example, since it is (nearly) true physically, the linewidths of the eight lines in this problem are usually constrained to be equal to each other; the computer is still allowed the freedom to choose one single best width for all the eight. Similarly the relationships between peak positions given in Eq. (1) can be expressed as constraints. The eight line positions chosen by the computer would then always correspond to one (A,R,S) triplet. Further, the relative intensities of the lines as determined by the squares of the appropriate Clebsch-Gordan coefficients can be expressed as constraints. This forces the relative amplitude of the various lines to be consistent with a pure quadrupole interaction. In the present case, most work was done with 19 constraints, so arranged that the computer was in effect choosing only six parameters—the baseline, the linewidth, the vertical scale, A, R, and S.

It is important to realize that this procedure is quite subject to error. Such a fit can be described as profoundly biased in favor of one's own prejudices as told to the computer via the constraint equations. For example, an extra line in the experimental data, perhaps due to an error in the sample preparation, would have to be quite large before it would even be noticed.

Our program does not search the parameter space for optimal values but rather attempts to find the local gradient and follows it to the minimum variance. Thus if the computer has a partial fit to the data as represented by a local minimum, it is unlikely that it can climb "over the hill" to find some other smaller variance elsewhere. Therefore, it is necessary to begin with reasonable guesses for the parameters; the program then refines these.

In the program, the variance is normalized to unity per degree of freedom. Since each spectrum contains 200 points, and the data to be discussed were fitted with six free variables, one anticipates $\chi^2 \approx 194$; this quantity would have a standard deviation of ± 41. Experience with the program indicates that $\chi^2 > 210$ usually signals a false minimum or some incorrect physics.

It is worth noting that a normal χ^2 is no guarantee that the parameters are uniquely chosen. If two sets of parameters give rise to quite similar spectra (as in fact happens in the Sb_2O_3 data to be discussed below), then χ^2 for both can be normal. The incorrect fit could be exposed by running the experiment for a longer time because its χ^2 would then steadily increase as the data became more and more precise. The correct fit would

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[6] J. R. Gabriel and S. L. Ruby, Nucl. Instr. Methods **36**, 23 (1965).

[7] W. C. Davidon, Argonne National Laboratory Report No. ANL-5990 (revised) (unpublished). The version of the program used here is called PHY 103.

TABLE I. Curve-fitting results on Sb_2O_3. Each run is fitted twice—once for each of two initial guesses for the variable parameters. Fit I used $A=5.0$, $R=1.4$, $S=0$; and fit II used $A=5.0$, $R=0.7$, and $S=0$.

Run No. Temperature	$5A$[a] 4.2°K	$6A$[a] 4.2°K	21 78°K	22 4.2°K	Combined result
			Fit I		
A[b] (mm/sec)	4.34±0.19	4.84±0.11	4.95±0.24	4.55±0.10	4.68±0.10
R	1.42±0.026	1.36±0.013	1.37±0.04	1.38±0.014	1.38±0.02
S (mm/sec)	−0.50±0.037	−0.57±0.021	−0.60±0.07	−0.55±0.02	−0.56±0.021
FWHM[c] (mm/sec)	2.68±0.09	2.59±0.09	3.30±0.25	2.59±0.07	
χ^2	181	186	189	168	
			Fit II		
A	4.26±0.17	4.15±0.09	4.23±0.27	4.10±0.10	4.17±0.10
R	0.62±0.03	0.58±0.01	0.48±0.05	0.58±0.02	
S	−0.48±0.04	−0.47±0.02	−0.61±0.08	−0.48±0.03	
FWHM	2.58±0.10	2.22±0.09	3.22±0.27	2.43±0.08	
χ^2	189	207	202	211	

[a] The samples used in runs 5A and 6A had extra lines of moderate intensity in their x-ray spectra. These lines indicate a mixture of senarmontite and valentinite.
[b] EQR measurements give $A=|4.66|\pm0.01$ mm/sec.
[c] Separate runs on InSb indicate full width at half-maximum $\gtrsim 2.6$ mm/sec.

keep the value of χ^2 at the normal value no matter how long the experiment was continued.

RESULTS

Our first measurements were on InSb to establish the line-width of our white tin source. The electronically measured half-life[8] of this level is $(3.5\pm0.2)\times10^{-9}$ sec. From this the minimum linewidth of the source becomes 1.05±0.06 mm/sec and therefore the narrowest possible experimental line (for a perfect source with thin single-line absorber) is 2.1±0.12 mm/sec. By examining InSb at 12, 6, 3, and 1.5 mg/cm^2, we find the minimum linewidth with the present source to be 2.6±0.1 mm/sec.

The width in excess of the anticipated 2.1 mm/sec is not yet understood. Quite possibly it reflects the slightly noncubic nature of white tin. This is the same explanation used for the well-known unresolved doublet found in Sn^{119} Mössbauer spectra taken with white tin as source or absorber. On the other hand, the purity and metallurgy of our tin source are not well known and the extra linewidth may merely be due to some kind of imperfections in the source. In any case, the extra width is small and has only little effect on the interpretation of the hyperfine data.

Samples of Sb_2O_3 were run at 4.2°K with thicknesses of 24, 12, and 6 mg/cm^2 of natural antimony. Data on each sample were collected twice and thus runs could be checked for internal consistency. Also, the velocity spread was varied to give more detail in the center of the pattern. Figure 2 shows an example of the experimental data along with two 19-constraint least-mean-square fits to it; these fits differ only in their initial guesses.

The data were analyzed in several ways. At first, initial guesses were made over wide ranges of A and R; all but two of the eight minima so discovered had χ^2 of 250 or worse. However, two A, R, and S triplets consistently gave acceptable χ^2 and could fit all the runs. As shown in Fig. 2, here fit I gave $A=4.34\pm0.19$, $R=1.42\pm0.03$, $S=-0.50\pm0.04$ with $\chi^2=181$, and fit II yielded $A=4.26\pm0.17$, $R=0.62\pm0.03$, $S=-0.48\pm0.04$ with $\chi^2=189$. A comparison with Fig. 1 shows that indeed the spectra for $R=1.4$ and 0.6 do look quite alike. This ambiguity is further stressed in Fig. 3 in which the bar graphs show the spectra corresponding to $A=4.6$ and $S=0$, while $R=1.4$ and 0.6. It is easy to become convinced that with poor resolution these spectra will indeed be difficult to distinguish.

Sb_2O_3 has two crystallographic forms—senarmontite and valentinite. The first, stable at low temperatures, forms a cubic crystal. If the temperature is raised above 570°C, the Sb_2O_3 transforms into the orthorhombic valentinite. Our first samples of Sb_2O_3 proved upon x-ray analysis to be a mixture of the two phases. By sealing off Sb_2O_3 in a long evacuated quartz tube and placing the end with the sample in a hot furnace, cubic crystals were grown by sublimation onto the cool walls of the exterior part of the tube. After x-ray analysis had shown them to be senarmontite, these crystals were ground, and then made into absorbers as indicated above.

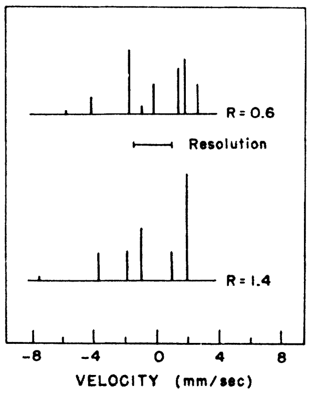

FIG. 3. Bar graph representation of the hyperfine transitions for the two fits shown in Fig. 2.

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[8] Y. Y. Chu, O. C. Kistner, A. C. Li, S. Monaro, and M. L. Perlman, Phys. Rev. 133, B6 (1964).

The cubic samples were run both at 78° and at 4.2°K. Each run lasted for several days; the data were collected daily and analyzed as several individual runs, as well as a single composite run. Table I shows the combined results of these runs and also for the 4.2°K runs on the first mixed-phase Sb_2O_3 sample. Note that the data were always analyzed twice—the second time with initial guesses that led to minimum II for χ^2. There are several reasons for preferring the first fit of A, R, and S to the second: (a) χ^2 is normal in all four cases for fit I and high (though only barely) for three of four cases for fit II; (b) in each of four cases, χ^2 is greater for fit II than for fit I; and (c) the values of e^2qQ from EQR measurements[4] for Sb_2O_3 give 551.38 and 554.83 MHz at 300 and 78°K, respectively. Using 555.5 MHz as an extrapolation for $T=4.2$°K, we calculate that A should be $|4.66|$ mm/sec, which agrees with the first but not the second fit.

In an attempt to find a compound with a larger value of e^2qQ, potassium antimonyl tartrate was examined despite the lack of EQR data. With $R=0.59$, no adequate fit could be made for any values of A, η, and S. Using $R=1.38$, a very nice fit ($\chi^2=168$) could be made with $e^2qQ=-592$ MHz, $\eta=0.55$, and $S=-0.91$ mm/sec. However, a recent publication[9] indicates the possibility of two Sb lattice sites and therefore the interpretation of our measurements on PAT should not be considered conclusive. However, if EQR measurements should confirm the above interaction constant and asymmetry parameter, then the PAT data would provide a conclusive argument for choosing fit I as the proper answer to the ambiguity.

CONCLUSIONS

Our main result is that $Q^{121}(\frac{7}{2}^+)/Q^{121}(\frac{5}{2}^+)=1.38\pm0.02$, as compared with the EQR result,[2] $Q^{123}(\frac{7}{2}^+)/Q^{121}(\frac{5}{2}^+)=1.275$. Dividing out the $\frac{5}{2}^+$ state, we find $Q^{121}(\frac{7}{2}^+)/Q^{123}(\frac{7}{2}^+)=1.09\pm0.02$. This is to be compared with the value 1.02 predicted by Kisslinger and Sorensen. It chould be noted, however, that these authors predict that same number again for the first two ratios and are here in moderate conflict with the experiments. Furthermore, Horie and Arima[10] predict $Q^{123}(\frac{7}{2}^+)/Q^{121}(\frac{5}{2}^+)=1.5$ also only in rough agreement with the measured ratio 1.275, but make no prediction for the ratio $Q^{121}(\frac{7}{2}^+)/Q^{123}(\frac{7}{2}^+)$.

It has to be noted that the numerical value for these moments is quite uncertain. The difficulty lies in accurately calculating the EFG for a given electronic configuration. Optical data[11,12] on Sb(I) and Sb(II) agree well with each other giving $Q^{123}=-0.54\pm0.08$ and $Q^{121}=-0.53\pm0.10$. A recent atomic-beam result[13] has been interpreted to give $Q^{121}=-0.20\pm0.03$. The EQR literature usually does not attempt this analysis. Using the optical value $Q^{121}(\frac{5}{2}^+)=-0.54\pm0.07$ b, we find $Q^{121}(\frac{7}{2}^+)=-0.75\pm0.09$ b.

Since A is measured as positive and Q is known to be negative, then $q=d^2V/dz^2$ is negative. Crudely put, the electron cloud is cigar shaped. The crystal structure of senarmontite[14] shows each Sb atom lying nearly in the plane and at the center of three oxygen atoms. This suggests sp^2 bonding. Starting from a s^2p^3 configuration for a free Sb atom, the sp^2 bonding would give rise to the observed negative EFG, if the remaining p electron stays largely in an orbit perpendicular to the oxygen plane. A purely ionic model for senarmontite would not be able to explain the large EFG and furthermore would predict the wrong sign. Numerically we find: $(1-\gamma)d^2V/dz^2=-4.26\times10^8$ V/cm^2, where γ is the Sternheimer shielding factor.

Finally, a general conclusion is that the 37-keV transition in Sb^{121} is rather well suited to supply chemical and solid-state information via Mössbauer measurements.

ACKNOWLEDGMENTS

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