Examples of the Fourier Transform Technique in Sharpening ^{121}Sb Mössbauer Spectra

A. KJEKSHUS and D. G. NICHOLSON

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

The Fourier transform technique has become increasingly more common in the analysis of poorly resolved experimental data. It has also entered the field of Mössbauer spectroscopy where Stone [1] and Ure and Flinn [2] have shown that significant sharpening is obtainable on deconvoluting the source line-shape from ^{57}Fe and ^{125}Te spectra. A major problem associated with ^{121}Sb Mössbauer spectroscopy is the poorly resolved eight or twelve line quadrupole split spectra. For this reason it is considered to be of interest to explore the advantages of the Fourier transform process to this Mössbauer nuclide. In choosing actual data for this trial we conveniently have at hand those recently communicated for $CoSb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RhSb_3$, and $IrSb_3$, which were presented with reservations concerning the values derived for the quadrupole interaction parameters.

The Fourier transform computations were based on the programme of Ure and Flinn [2] and the experimental data least squares fitted to twelve superimposed Lorentzian peaks employing the resonance line coefficients and transition probabilities of Shenoy and Dunlap.[4]

The Fourier transformed reduced spectra for $CoSb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ under consideration are shown in Fig. 1. The features revealed include possible evidence for contamination of the $CoSb_3$ sample with antimony.[5,6] The presence of this impurity, which thus must be amorphous because it does not appear on the Guinier photographs, would have gone unnoticed but for the Fourier transform reduction. For the remaining compounds of which the $Fe_{0.5}Ni_{0.5}Sb_3$ transform is a typical example, the sharpening of the absorption envelope permits preliminary estimates as to the input parameters for the least squares procedure. The new values for the quadrupole splittings (Table 1) confirm the validity of the reservations expressed in the previous paper.[3] The small deviations between the present values for the coupling constants would accord with the virtually constant average deviation of the bond angles about Sb from the tetrahedral value of 109.47°. On the other hand the revised quadrupole coupling constants no longer show a significant correlation with the difference (d_1-d_2) in Sb−Sb bond lengths in these compounds.[7] This inadequacy of the

Table 1. ^{121}Sb Mössbauer parameters (at 4.2 K) for $CoSb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RhSb_3$, and $IrSb_3$. Chemical shifts with respect to $Ba^{121}SnO_3$. Asymmetry parameters (η) lie between 0.9 and 1.0. Probable errors are ± 0.1 mm/s in δ and ± 1 mm/s in $|eQV_{zz}|$.

Compound	δ (mm/s)	$\|eQV_{zz}\|$ (mm/s)	Γ (mm/s)
$CoSb_3$	−9.9		
$Fe_{0.5}Ni_{0.5}Sb_3$	−10.2	10.0	3.9
$RhSb_3$	−9.5	10.4	3.3
$IrSb_3$	−9.0	10.6	3.1

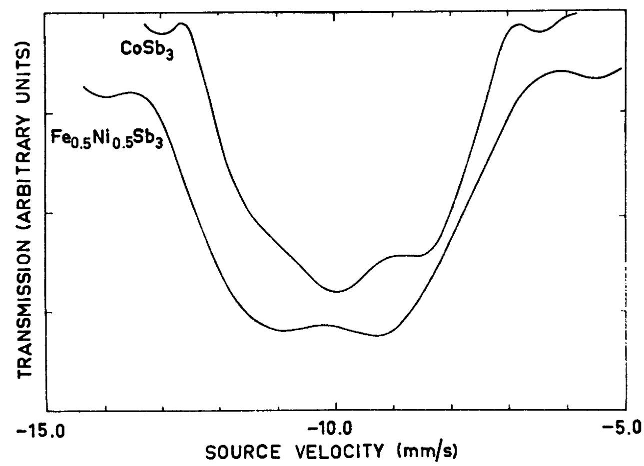

Fig. 1. Fourier transformed reduced spectra of $CoSb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$.

previous treatment results to some extent from the neglect to take more than eight lines into account (which is particularly inappropriate when $\eta > 0.5$) and the presumably consequent terminations of the least squares procedures at false minima.

In the present instance the Fourier transform technique has proved useful in detecting impurities and providing input parameters for the least squares refinements. However, the advantages of this procedure are even more promising in cases where the spectral envelope consists of more than one profile.

1. Stone, A. J. *Chem. Phys. Lett. 6* (1970) 331.
2. Ure, M. C. D. and Flinn, P. A. *Mössbauer Eff. Methodol. 7* (1969) 245.
3. Kjekshus, A., Nicholson, D. G. and Rakke, T. *Acta Chem. Scand. 27* (1973) 1315.
4. Shenoy, G. K. and Dunlap, B. D. *Nucl. Instrum. Methods 71* (1969) 285.
5. Dokuzoguz, H. Z., Bowen, L. H. and Stadelmaier, H. H. *J. Phys. Chem. Solids 31* (1970) 1565.
6. Avenarius, I. A., Kuz'min, R. N. and Opalenko, A. A. *Soviet Phys. JETP Lett. 14* (1971) 331.
7. Kjekshus, A. and Rakke, T. *Acta Chem. Scand. A 28* (1974) 99.

Received March 14, 1974.