

Isomer shift determination in Eu compounds using stroboscopic detection of synchrotron radiation

I. Serdons,^{1,*} S. Nasu,² R. Callens,¹ R. Coussement,¹ T. Kawakami,² J. Ladrière,³ S. Morimoto,² T. Ono,² K. Vyvey,¹ T. Yamada,⁴ Y. Yoda,⁴ and J. Odeurs¹

¹*Instituut voor Kern- en Stralingsfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium*

²*Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

³*Laboratory of Nuclear Chemistry, Université Catholique de Louvain, Chemin du Cyclotron, 1348 Louvain-la-Neuve, Belgium*

⁴*Japan Synchrotron Radiation Research Institute, Kouto 1-1-1, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan*

(Received 9 February 2004; revised manuscript received 27 April 2004; published 27 July 2004)

The first application of stroboscopic detection of nuclear resonant scattering with synchrotron radiation on ¹⁵¹Eu is reported. It is shown that stroboscopic detection is a useful technique for the determination of isomer shifts and this is confirmed by a measurement of the isomer shift of ¹⁵¹Eu in EuPd₂Si₂ at pressures ranging from ambient pressure to 5 GPa. The results are compared with previous measurements.

DOI: 10.1103/PhysRevB.70.014109

PACS number(s): 76.80.+y, 42.50.Ct, 42.25.Hz, 42.25.Kb

I. INTRODUCTION

Since its discovery, the Mössbauer effect has proven many times to be a valuable technique to investigate the nuclear hyperfine levels in a variety of specific isomers. An important step was taken when this principle found a place at the synchrotron facilities via the nuclear resonant scattering technique.¹⁻⁴ The most important advantages were the wide energy range that became accessible, together with the high intensity of the well-collimated radiation. This wide energy range, with the help of suitable monochromators, opened the door to a range of isomers⁵ for which the preparation of a Mössbauer source was difficult or sometimes even impossible.

To measure isomer shifts with the nuclear resonant scattering technique, it is crucial to add a reference sample with a known isomer shift to the standard nuclear-resonant scattering setup. The isomer shift of the sample with respect to the reference sample can then be deduced from a beat pattern in time domain. With the recently developed stroboscopic detection scheme,⁶ the relative isomer shift between the sample and the reference sample is measured directly in energy domain, similar to Mössbauer spectroscopy with a radioactive source. The main characteristic of this technique is the use of a moving reference sample to construct velocity or energy-dependent spectra.

This paper reports the first application of the stroboscopic detection technique on an isotope different from ⁵⁷Fe and confirms the validity of this scheme for isomer shift measurements. ¹⁵¹Eu⁷⁻⁹ is a good choice for this purpose because the energy ($E_{res}=21.5$ keV) and the short lifetime ($\tau=14$ ns) of the first excited level make it very different from ⁵⁷Fe ($E_{res}=14.4$ keV and $\tau=144$ ns). It also has the advantage that Mössbauer data are available for comparison.

A measurement of the change in isomer shift of ¹⁵¹Eu in EuPd₂Si₂ as a function of varying pressure is presented. EuPd₂Si₂ has a tetragonal ThCr₂Si₂ structure.¹⁰ It is a mixed valence system¹¹ with Eu ions that undergo fast fluctuations ($\approx 10^{13}$ /s) between divalent and trivalent states.¹² An appreciable mean valence change in a narrow temperature band

(± 50 K) around 150 K^{12,13} is the main reason why this compound has attracted a lot of attention. Measurements of the electrical transport properties indicated that this compound also exhibited a pressure-induced valence change.¹⁴ This was examined by Mössbauer spectroscopy with a radioactive source, by measuring its isomer shift as a function of pressure.¹⁵ These results will be compared with the results presented here.

In Sec. II, the stroboscopic detection scheme will be briefly described, followed by an overview of the experimental conditions that can be optimized for isomer shift measurements. The experimental setup will also be discussed here. Section III contains the discussion of the measured spectra and the obtained results. The relationship between the isomer shift and the mean valence is also briefly discussed here. In the last section, conclusions will be drawn.

II. EXPERIMENTAL DETAILS

A. Stroboscopic detection of synchrotron radiation

The aim of the stroboscopic detection scheme is to determine the nuclear resonance energies of a sample by comparing them with those of a, preferably single-line, reference sample. This reference sample contains the same resonant isotopes as the sample under investigation does. Both samples are placed in the beam simultaneously. The reference sample is given a variable velocity, and the measurement is performed as a function of this velocity. Resonances will occur when the Doppler-shifted resonance energy of the reference sample is equal to one of the resonance energies of the sample under investigation. This is similar to Mössbauer spectroscopy with a radioactive source.

In the stroboscopic detection scheme, the data are collected during selected time intervals. The time function that describes these intervals is called the time window function. An example of such a function is depicted in Fig. 1. This function must be zero at the moments when the prompt radiation arrives at the detector. Hence, its frequency must be equal to or a multiple of the bunch frequency. The reason for

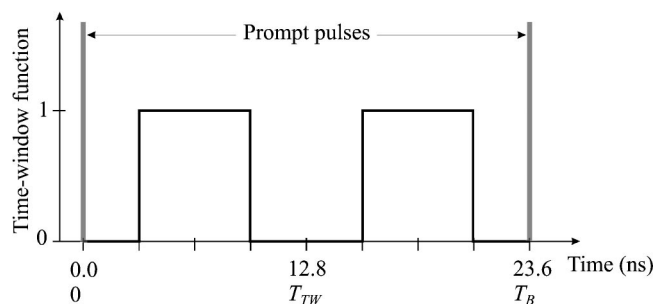


FIG. 1. Time structure of this experiment. The prompt pulse arrives at the detector at $T=0$, T_B represents the bunch period and T_{TW} represents the period of the time windows.

this is that the bandwidth of the monochromatized radiation is of the order of meV, while the width of the nuclear resonance is only of the order of 10 neV. Therefore the intensity of the nonresonant (prompt) photons is an order of 10^5 larger than that of the resonant photons. By putting well-chosen time windows, it is possible to distinguish the resonant from the nonresonant photons. In velocity domain, these time windows will generate several extra resonances. The shape of these stroboscopic resonances depends on the position of the time windows. Their shifts in velocity domain with respect to the central resonances are:

$$v_n = n \frac{c \omega_{TW}}{\omega_{res}}, \quad (1)$$

where v_n is the velocity shift of the n th order stroboscopic resonances, c is the velocity of light, ω_{TW} is the frequency of the time windows, and ω_{res} is the resonance frequency of the nuclear-excited level. All of these n th order resonances can be interpreted similarly to the central resonances and are easier to model since the quantum-mechanical path where a photon is resonantly scattered by both samples, i.e., the radiative coupling path, is suppressed for sufficiently high velocities.

B. General experimental considerations

When using the stroboscopic method to determine isomer shifts, there are several experimental parameters that can be optimized, such as the time windows, the velocity range, and the properties of the reference sample. These parameters will be discussed in this section.

First, the position, duration, and frequency of the *time windows* are important parameters that influence the shapes of the resonances in the stroboscopic spectrum. As mentioned above, the frequency of the time windows must be equal to or a multiple of the bunch frequency. Thereby the filling mode of the storage ring and the dead time of the detector after the prompt pulse are the limiting factors. Note that it may be useful to select a detector with a very short dead time over a more efficient one. Paying attention to these limitations, usually one still has a large freedom in choosing the position, duration, and frequency of the time windows. The position plays a role in the shape of the resonances. If one wants to produce positive and negative Lorentzian-like

resonances, then the time windows should be symmetric around half of the time-window period. An example of such a time window is visualized in Fig. 1. If the position of the time window is shifted, the shapes of the resonances become dispersionlike. The ideal duration for a specific experiment depends on which specific stroboscopic resonance one wants to concentrate on, keeping in mind that choosing a narrow time window is obviously statistically not preferable. Generally, a narrow time window produces a better signal-to-baseline ratio. A usually acceptable value for the width of the time window is 30% of the total period.⁶ The ideal frequency depends on the preferred shift of the stroboscopic resonances. The relation between this shift and the frequency of the time windows is given in Eq. (1). An ideal way to measure a stroboscopic spectrum is to use a two dimensional data-acquisition system, which allows one to determine for each detected photon two coordinates: one is the time delay of the photon and the other is the velocity of the Mössbauer drive. In this way, the time windows can be chosen during the off-line analysis, which gives the experimentalist great liberty in optimizing the time windows.⁶

Second, to choose the optimal *velocity range*, several aspects should be taken into account. On the one hand, this range should be chosen large enough to be able to deduce the isomer shift. On the other hand, a range that is too large is statistically not favorable. If only a small part of the stroboscopic spectrum is measured, the condition is that it must be possible to determine which stroboscopic order resonances are present. If this condition is fulfilled, the total stroboscopic spectrum can be reconstructed and thus the isomer shift of the sample with respect to the reference sample can be deduced. If a 2D data-acquisition system is available, the minimum required information is contained within the resonances of one stroboscopic order. By changing the time-window function off-line, the shape of the stroboscopic resonances can be altered. In this manner, it is possible to determine which specific order is present in the obtained spectrum. If such a system is not available, the required information is contained within the resonances of two successive stroboscopic orders. The distance between two successive orders can be calculated with Eq. (1). By comparing the shapes and the signal-to-baseline ratios, it is possible to determine the order of the resonances. Thus, considering also the expected width of the resonances, a least and sufficient velocity range can always be determined. Fortunately, the analysis can be made much more straightforward if the central resonances lie within the chosen velocity range. In this case, the isomer shift with respect to the reference sample can be determined in the same way as with a Mössbauer spectrum taken with a radioactive source.

Finally, the properties of the *reference sample* should be known exactly, especially its isomer shift with respect to the standard isomer shift reference material of the specific isotope. To simplify the spectra as much as possible, a single-line reference sample with a narrow linewidth is ideal. To determine the optimal effective thickness of the reference sample, two aspects should be taken into account. These are the resolution and the statistical quality of the obtained spectra. The resolution can be optimized by choosing a thin reference sample. To optimize the statistical quality, both the

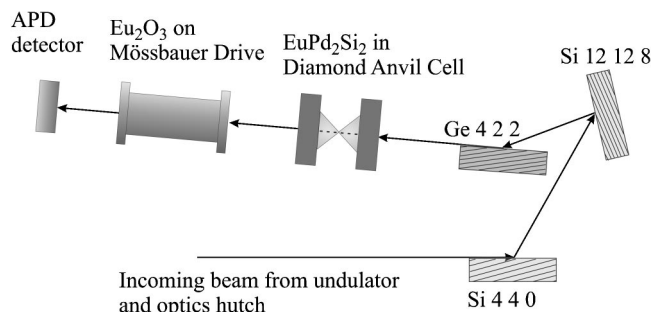


FIG. 2. Setup of the experiment.

nuclear and the electronic scattering should be considered. For high energies, like the 21.5 keV resonance in ^{151}Eu , especially the nuclear scattering plays an important role. Therefore thick samples will produce a larger count rate, keeping in mind that when the samples get too thick, electronic absorption can reduce the count rate. For single-line samples, the signal-to-baseline ratio is largest when the effective thicknesses of both samples are identical. Therefore, the effective thickness of the reference sample should be close to the effective thickness of the sample under investigation.

C. Experimental setup

The experiments were performed at the nuclear resonant scattering beamline, BL09XU,¹⁶ at the third generation synchrotron radiation facility SPring-8 in Japan. The typical setup for high-pressure nuclear forward-scattering studies was used, to which a Eu_2O_3 reference sample on a Mössbauer drive was added. This is illustrated in Fig. 2.

In order to reduce the energy width of the 21.5 keV radiation, a three-bounce-type high-resolution monochromator was set up. It consisted of three crystals, a first asymmetric Si 4 4 0 reflection, a second high-angle Si 12 12 8 reflection, and finally a third asymmetric Ge 4 2 2 reflection. The obtained resolution was 1.8 meV.

The EuPd_2Si_2 sample was prepared by arc-melting under a purified argon atmosphere. Constituent elements with purities better than 99.9% were used for the melting. The ingots were subsequently annealed in an evacuated quartz tube at 800 °C for one week.¹⁷ After this process, the powder was inserted into a Bassett-type diamond anvil cell (DAC)¹⁸ with a rhenium gasket ($\varnothing=350\ \mu\text{m}$). The Ruby fluorescence method^{19,20} was utilized for the pressure calibration during the decompression process.

A pellet of Eu_2O_3 was used as a reference sample. To prepare this pellet, 34.13 mg of Eu_2O_3 was carefully grinded with 100 mg of benzoic acid in order to obtain a homogeneous distribution of the Mössbauer isotope in the absorber. The resulting powder was then pressed in a cylindrical ($\varnothing=13\ \text{mm}$) hydraulic press at 10 tons/cm² for 5 min.

The radiation was detected by an avalanche photodiode (APD) detector. This detector was inclined to have an effective thickness of 20 μm , a diameter of 3 mm, and an efficiency of $\sim 5\%$. The time resolution of this detector is typically of the order of 0.16 ns.²¹

The bunch period was 23.6 ns and the time-window period was chosen to be half of this (Fig. 1). As a consequence, the stroboscopic-order resonances of order n are shifted by $v_n = n \times 4.82\ \text{mm/s}$ with respect to the central resonances.

To calibrate the velocity, the Eu_2O_3 reference sample was kept on the Mössbauer-drive while the DAC with the EuPd_2Si_2 was replaced by an identical sample of Eu_2O_3 . The velocity calibration could then be deduced from the position of the single-line resonances.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Interpretation of the stroboscopic spectra

Figure 3 shows several stroboscopic spectra that were taken at room temperature with pressures ranging from 5 GPa down to ambient pressure. The spectra are symmetric around a central resonance. This resonance is situated at a velocity that corresponds to the isomer shift of ^{151}Eu in EuPd_2Si_2 with respect to ^{151}Eu in the Eu_2O_3 reference sample. Several other resonances are very pronounced, these correspond to the higher-order stroboscopic resonances. In order to determine the isomer shift with respect to the EuF_3 standard,²² a conventional Mössbauer experiment using a Sm_2O_3 source was performed on both the Eu_2O_3 reference sample and a EuF_3 sample. An isomer shift of Eu_2O_3 with respect to EuF_3 of 0.92(3) mm/s was found.

During the analysis of these spectra, it became clear that the velocity drive, which was in triangular mode, showed some nonlinearities. Since these did not change the values of the isomer shift beyond the intrinsic error, no extra corrections were taken into account. To model the broadening of the lines, the effective thickness and an electric-field gradient were included as fit parameters.

B. Results

Figure 4 shows the pressure dependence of the isomer shift of ^{151}Eu in EuPd_2Si_2 with respect to ^{151}Eu in EuF_3 . Note that the pressure distribution on the sample was fairly large as is indicated on the graph. It is depicted as the standard deviation with respect to the average pressure. The results of this work can be compared to the results of Schmiester *et al.*,¹⁵ obtained by Mössbauer spectroscopy with a radioactive source, which are also shown. The pressure calibration of this measurement was performed using the isomer shift of the ^{119}Sn gamma-resonance in $\beta\text{-Sn}$.^{23–25} This pressure calibration has been corrected using a more recent investigation of the pressure dependence of this isomer shift by Chow *et al.*²⁶ In this investigation, the ruby fluorescence method was used for the pressure calibration.

Qualitatively, the isomer shift grows nonlinearly with pressure. This corresponds to the results of Schmiester *et al.*¹⁵ Quantitatively, the values of the isomer shift obtained in our measurement differ somewhat from theirs. This is most probably caused by the different sample preparations, combined with a weak, hidden satellite-line, which was taken into account in the analysis of Schmiester *et al.* This satellite line could not be resolved from the stroboscopic spectra. The main reason was the large line broadening in our spectra.

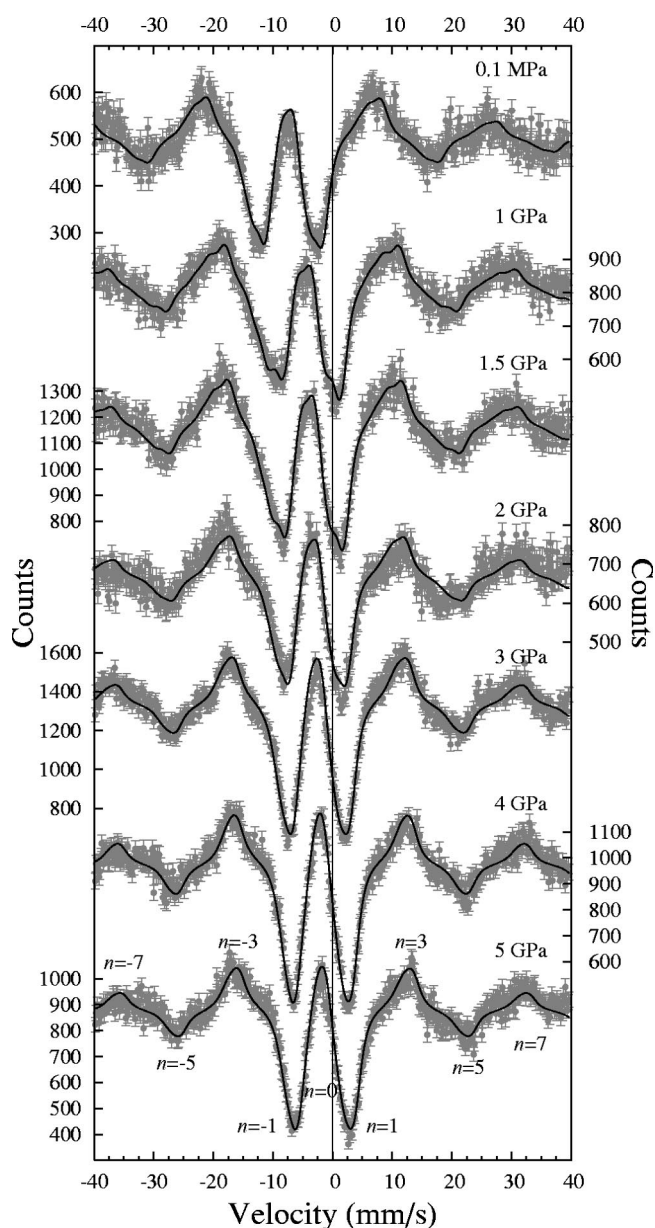


FIG. 3. Stroboscopic spectra of EuPd_2Si_2 for pressures ranging from ambient pressure to 5 GPa with Eu_2O_3 as reference. The dots represent the data points while the lines are fits. n indicates the stroboscopic order of the specific resonance.

These lines can be narrowed by either decreasing the pressure distribution or changing the reference sample. This can either be a thinner reference sample or one where the ^{151}Eu isotope is located in a cubically symmetric environment, e.g., the Eu-chalcogenides.²⁷ A second improvement would be to better resolve the several stroboscopic orders by increasing the frequency of the time windows, which were put on-line during this experiment.

C. Discussion

Since the timescale of the nuclear resonant scattering process (~ 14 ns) is much longer than the period of the valence fluctuations ($\sim 10^{-4}$ ns),¹² the measured isomer shift is the

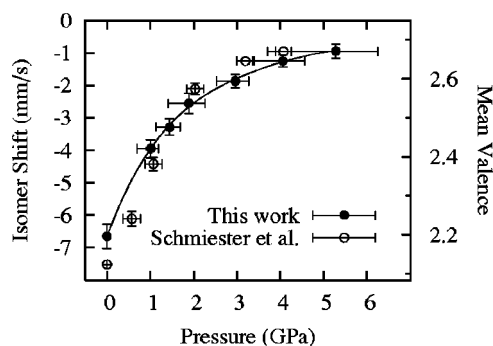


FIG. 4. Relationship between the isomer shift of ^{151}Eu in the EuPd_2Si_2 sample with respect to EuF_3 as a function of the applied pressure at room temperature. The filled circles represent our results, while the blank circles represent previous results obtained by Mössbauer spectroscopy using a radioactive source.¹⁵ The line is a guide to the eye.

time-averaged isomer shift. The relationship between the isomer shift and the valence of ^{151}Eu in EuPd_2Si_2 is given by¹⁵

$$\delta(P) = \delta_2 + (\delta_3 - \delta_2)\nu(P). \quad (2)$$

$\nu(P)$ represents the fractional occupation of the Eu^{3+} state at pressure P and at room temperature. The mean valence of ^{151}Eu in EuPd_2Si_2 at pressure P and at room temperature is thus $2 + \nu(P)$. $\delta(P)$ represents the pressure-dependent isomer shift of ^{151}Eu in EuPd_2Si_2 at room temperature. δ_2 and δ_3 are the isomer shifts for integral-valent $^{151}\text{Eu}^{2+}$ and $^{151}\text{Eu}^{3+}$, respectively, in similar environments as EuPd_2Si_2 . Following a previous analysis,¹⁵ δ_2 was set equal to $-9.0(7)$ mm/s, which corresponds to the average of the established values for the metallic systems EuNi_2Si_2 and EuSi_2 ($\delta = -9.6$ mm/s) and EuPd_2 ($\delta = -8.5$ mm/s).^{13,28} For $\delta_3 - \delta_2$ a value of 12 mm/s was assumed. It is deduced from Fig. 4 that, as the pressure increases, the mean valence of the ^{151}Eu ion in EuPd_2Si_2 increases from ~ 2.2 to ~ 2.7 . A detailed analysis of the physical consequences of these results is beyond the scope of this article and can be found elsewhere.¹⁵

IV. CONCLUSION

The stroboscopic detection scheme can easily be extended to isotopes with properties that differ from those of ^{57}Fe . This opens the possibility of creating energy-resolved spectra for isotopes that do not have a suitable Mössbauer source. It has also been shown that the stroboscopic detection technique is useful for isomer shift determination. Thanks to the energy-resolved spectra, no complicated analysis is required and the isomer shift of the sample with respect to the reference sample can be determined easily from the spectra. To demonstrate this, the isomer shift of EuPd_2Si_2 with respect to a Eu_2O_3 reference sample has been measured as a function of pressure. The results qualitatively confirm previous results and show a nonlinear dependence of the isomer shift of ^{151}Eu in EuPd_2Si_2 upon pressure.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Baron for providing us with an excellent detector. Our gratitude also goes to Prof.

Mitsuda who lent us his EuPd₂Si₂ samples. Dr. Cottenier is thanked for the helpful discussions. This work was supported by a research program of the FWO-Vlaanderen. R.Ca. and K.V. are particularly grateful to FWO-Vlaanderen for finan-

cial support. J.L. would like to thank the Interuniversity Institute for Nuclear Science (Belgium) for financial support. The experiments were performed at SPring-8 (Experiment No. 2001B0461-NMD-np).

*Electronic address: inge.sermons@fys.kuleuven.ac.be

- ¹E. Gerdau, R. Ruffer, H. Winkler, W. Tolksdorf, C. P. Klages, and J. P. Hannon, *Phys. Rev. Lett.* **54**, 835 (1985).
- ²J. B. Hastings, D. P. Siddons, U. van Büurck, R. Hollatz, and U. Bergmann, *Phys. Rev. Lett.* **66**, 770 (1991).
- ³U. van Büurck, D. P. Siddons, J. B. Hastings, U. Bergmann, and R. Hollatz, *Phys. Rev. B* **46**, 6207 (1992).
- ⁴E. Gerdau and H. de Waard, *Nuclear Resonant Scattering of Synchrotron Radiation*, *Hyperfine Interact.* **123/124** and **125** (Baltzer Science Publishers, 1999–2000) and references therein for an overview.
- ⁵O. Leupold, A. I. Chumakov, E. E. Alp, W. Sturhahn, and A. Q. R. Baron, *Hyperfine Interact.* **123/124**, 611 (1999) for an overview.
- ⁶R. Callens, R. Coussement, C. L'abbé, S. Nasu, K. Vyvey, T. Yamada, Y. Yoda, and J. Odeurs, *Phys. Rev. B* **65**, 180404(R) (2002); R. Callens, R. Coussement, T. Kawakami, J. Ladrière, S. Nasu, T. Ono, I. Sermons, K. Vyvey, T. Yamada, Y. Yoda, and J. Odeurs, *ibid.* **67**, 104423 (2003).
- ⁷I. Koyama, Y. Yoda, X. W. Zhang, M. Ando, and S. Kikuta, *Jpn. J. Appl. Phys., Part 1* **35**, 6297 (1996).
- ⁸O. Leupold, J. Pollmann, E. Gerdau, H. D. Röter, G. Faigel, M. Tegze, G. Bortel, R. Ruffer, A. I. Chumakov, and A. Q. R. Baron, *Europhys. Lett.* **35**, 671 (1996).
- ⁹O. Leupold, K. Rupperecht, and G. Wortmann, *Struct. Chem.* **14**, 97 (2003).
- ¹⁰E. V. Sampathkumaran, R. Vijayaraghavan, K. V. Gopalakrishnan, R. G. Pillay, and H. G. Devare, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 193.
- ¹¹I. Nowik, *Hyperfine Interact.* **13**, 89 (1983).
- ¹²R. Nagarajan, E. V. Sampathkumaran, L. C. Gupta, R. Vijayaraghavan, Bhaktdarshan, and B. D. Padalia, *Phys. Lett.* **81A**, 397 (1981).
- ¹³E. V. Sampathkumaran, L. C. Gupta, R. Vijayaraghavan, K. V. Gopalakrishnan, R. G. Pillay, and H. G. Devare, *J. Phys. C* **14**, L237 (1981).
- ¹⁴V. Vijayakumar, S. N. Vaidya, E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, *Phys. Lett.* **83A**, 469 (1981).
- ¹⁵G. Schmiester, B. Perscheid, G. Kaindl, and J. Zukrowsky, in *Valence Instabilities*, edited by P. Wachter and H. Boppert (North-Holland, Amsterdam, 1982), p. 219.
- ¹⁶Y. Yoda, M. Yabashi, K. Izumi, X. W. Zhang, S. Kishimoto, S. Kitao, M. Seto, T. Mitsui, T. Harami, Y. Imai, and S. Kikuta, *Nucl. Instrum. Methods Phys. Res. B* **467**, 715 (2001).
- ¹⁷A. Mitsuda, H. Wada, M. Shiga, H. A. Katori, and T. Goto, *Phys. Rev. B* **55**, 12 474 (1997).
- ¹⁸W. A. Bassett, T. Takahashi, and P. W. Stook, *Rev. Sci. Instrum.* **38**, 37 (1967).
- ¹⁹K. Kurimoto, S. Nasu, S. Nagatomo, S. Endo, and F. E. Fujita, *Physica B* **139-140**, 495 (1986).
- ²⁰P. M. Bell and H. K. Mao, *Year Book - Carnegie Inst. Washington* **74**, 399 (1975).
- ²¹A. Q. R. Baron, M. Yabashi, T. Kudo, and T. Ishiwaka, *SPring-8 Annual Report* (1999), p. 149.
- ²²J. G. Stevens and W. L. Gettys, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 901.
- ²³V. Panyushkin and F.F. Voronov, *Sov. Phys. JETP* **2**, 97 (1965).
- ²⁴H. S. Möller, *Z. Phys.* **212**, 107 (1968).
- ²⁵V. N. Panyushkin, *Sov. Phys. Solid State* **10**, 1515 (1968).
- ²⁶L. Chow, P. A. Deane, J. N. Farrell, P. A. Magill, and L. D. Roberts, *Phys. Rev. B* **33**, 3039 (1986).
- ²⁷P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. Eyring (North Holland, Amsterdam, 1979), p. 507.
- ²⁸E. R. Bauminger, G. M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 561.