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Mössbauer effect for ^{57}Fe and ^{57}Co in TiO_2 (rutile)*

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TiO_2 (rutile) powder has been doped with 1-at.% ^{57}Fe for Mössbauer absorber studies, and with Co (^{57}Co) in the percent and parts per million (ppm) ranges for Mössbauer source studies. The absorber and percent sources show simple trivalent iron spectra, with quadrupole splittings of 0.70 and as large as 0.15 mm/sec, respectively. The ppm ^{57}Co sources are more complex, exhibiting three different spectra, all showing quadrupole interactions and all probably divalent. Possible configurations corresponding to these spectra are discussed and the results compared to EPR data.

I. INTRODUCTION

The Mössbauer effect has often been used for the investigation of the charge states and lattice environments of impurity ions in various solids (see Ref. 1 for a review of much of this work). A considerable fraction of these investigations have focused on ^{57}Fe, with both stable iron and radioactive ^{57}Co as dopants. While some understanding now exists of the behavior of iron as a dilute impurity, there is still much uncertainty in the source work about the relationship between the parent cobalt ion and the iron daughter ion which results from the ^{57}Co electron-capture decay. The assumption is often made (see, e.g., Ref. 2) that when ^{57}Co is doped into a crystal composed of different elements, the resulting spectra will relate to the properties of the otherwise ideal crystal. Because of intrinsic crystal defects this is a questionable assumption. Very dilute dopants may well lead to results quite different from those for percent dopants.

Information is already available from Mössbauer[3-7] and EPR[8-10] experiments on Fe doped into the rutile modification of TiO_2 at the percent level, and from specific-heat and spectroscopic analyses[11] as well as EPR[12] for Fe in the ppm range. There is further information from EPR for Co in rutile at the high doping level.[13,14]

Unfortunately, Mössbauer spectroscopy cannot be done with absorbers containing iron in only the ppm range. Therefore, to obtain ppm spectra rutile has to be doped with ^{57}Co, with the ^{57}Co then decaying to ^{57}Fe. These samples can then be used as Mössbauer sources which give some information about ppm iron in rutile. There are, however, two complications introduced by this process; the iron enters the lattice not directly, but rather as a cobalt ion, and the electron-capture decay of ^{57}Co with its subsequent Auger processes produces, at least fleetingly, a number of different charge states[1] for the resulting ion. The daughter ion might then be in a state different from that of an equivalent-doped iron ion because of the different initial surroundings of the cobalt ion, because the aftereffects leave it in an excited charge state, or because these aftereffects lead to a different coupling with a defect complex.

This paper is a report on Mössbauer studies performed on ^{57}Fe and ^{57}Co doped into TiO_2 (rutile).[15] It was intended to study the aftereffects of the radioactive electron-capture decay of ^{57}Co, to investigate the differences between percent and ppm dopings as well as between sources and absorber, and to compare the results with previous data on Fe and Co in rutile.

II. EXPERIMENTAL DETAILS

The percent absorber was prepared by dissolving reagent-grade TiO_2 powder plus ^{57}Fe-enriched Fe_2O_3 in hot H_2SO_4 in a Pyrex beaker. The liquid was then evaporated off using a hot plate. The residue was placed in quartz thimbles and heated for 10 h at about 1300 K in a quartz tube under slowly flowing air. The sample was then cooled to room temperature in minutes. Powder x-ray diffraction patterns indicated rutile.

Two separate ppm sources were prepared in a similar manner, except that 1 mCi of carrier-free ^{57}Co in an HCl solution was added in place of the Fe_2O_3. Three other sources were additionally doped with nonradioactive Co from $Co(NO_3)_2 \cdot 6H_2O$. Two of these were doped with approximately 1-at. % Co and one with $\frac{1}{3}$ at. %. Nonradioactive controls were simultaneously prepared and their x-ray patterns checked to insure that only rutile was formed.

The absorber and sources were exposed to various heat treatments to test their stability as described below. However, except for the annealing of one lattice configuration in the ppm sources, the sources and absorber displayed longterm stability even on exposure to air, as shown by the constancy of their Mössbauer spectra.

The Mössbauer spectra were accumulated using a standard constant-acceleration electromechanical-drive system.[16] The variable temperatures were achieved in cryostats with heaters, with temperature stabilities of better than 3 K. The Mössbauer absorber spectra were taken using ^{57}Co-in-Cu single-line sources. The same sources were used with sodium nitroprusside and iron-foil absorbers for velocity calibrations. Source studies utilized a sodium-ferrocyanide single-line absorber. All isomer shifts are given with respect to iron metal with a positive velocity corresponding to an energy state above that of Fe metal. Thus, for absorber studies positive velocities mean that the source was approaching the absorber, while for source studies positive velocities mean that the source was receding from the absorber.

III. EXPERIMENTAL RESULTS

A. Absorber

The 1-at.-%-Fe-in-rutile absorber was examined at various temperatures and at various velocity ranges to find the previously undetermined Mössbauer Debye temperature and a further check on preparation procedures. All data showed the slightly assymetric doublet of Fig. 1. No evidence was seen of the relaxation phenomena observed by some using different preparation techniques.[4,6] The computer fits of two Lorentzians to these data yielded isomer shifts of 0.47 ± 0.02 mm/sec (88 K), 0.37 ± 0.02 mm/sec (295 K), and 0.23 ± 0.02 mm/sec (490 K), with a temperature-independent quadrupole splitting of 0.70 ± 0.03 mm/sec and a temperature-independent linewidth (full width at half-maximum) of 0.67 ± 0.04 mm/sec. Within the limits of experimental error, the temperature dependences of the isomer shifts for this absorber and all source spectra are consistent with the expected second-order Doppler shift. The temperature dependence of the magnitude of the Mössbauer effect yields a Mössbauer Debye temperature of 430 ± 30 K. No significant change was noted in the spectrum after rapid cooling from 1300 K to room temperature, annealing at 500 K, or bombardment overnight by a 2000-Ci source of 661-keV Cs^{137} γ rays (corresponding to 10^7 R).

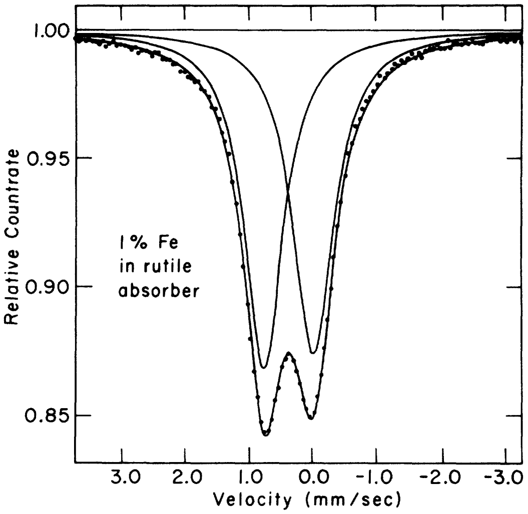

FIG. 1. Room-temperature Mössbauer spectrum of TiO_2 (rutile) doped with 1–at.% Fe enriched in ^{57}Fe. The velocity scale is with respect to α-Fe; positive velocity means the source is approaching the absorber.

B. Percent sources

The three sources prepared with $\frac{1}{3}$ to 1-at. % Co in rutile all gave spectra which could be fitted equally well at all temperatures with a single line of width 0.56 mm/sec or, as in Fig. 2, a doublet

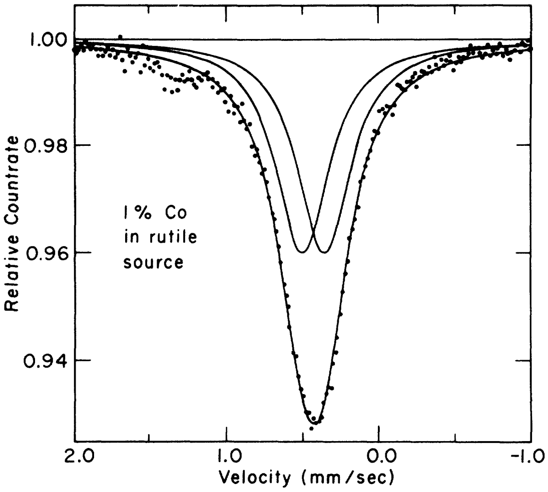

FIG. 2. Room-temperature Mössbauer spectrum of TiO_2 (rutile) doped with 1–at.% Co containing a mCi of ^{57}Co. The velocity scale is with respect to α-Fe; positive velocity means the source is receding from the absorber.

of linewidth 0.40 mm/sec and a quadrupole splitting of 0.15 mm/sec. The small extra peak in Fig. 2 is preparation dependent and may be associated with some of the weak spectra seen in the Co EPR work.[14] In mm/sec, the isomer shifts were 0.52± 0.03 (136 K), 0.46± 0.04 (190 K), 0.42± 0.02 (295 K), 0.33± 0.02 (400 K), and 0.26± 0.02 (480 K). A room-temperature spectrum taken with the 1-at. % Fe absorber and the 1-at. % Co source verified the finding that the isomer shift of the source is slightly above that of the absorber. The temperature dependence of the magnitude of the source effect also corresponded to a Mössbauer Debye temperature of 430± 30 K.

C. ppm sources

The two sources prepared with ppm of ^{57}Co in rutile could both be best and most simply fitted by three doublet spectra, identified as *a*, *b*, and *c*, shown in Figs. 3 and 4. (The spectra of both sources are shown in each figure to demonstrate the internal consistency of these fits.) Other fits were either redundant, did not fit the spectra as well, or led to inconsistencies among the many spectra taken with these sources. Thus, while the relative intensities of these doublets varied from source to source, with annealing, and with

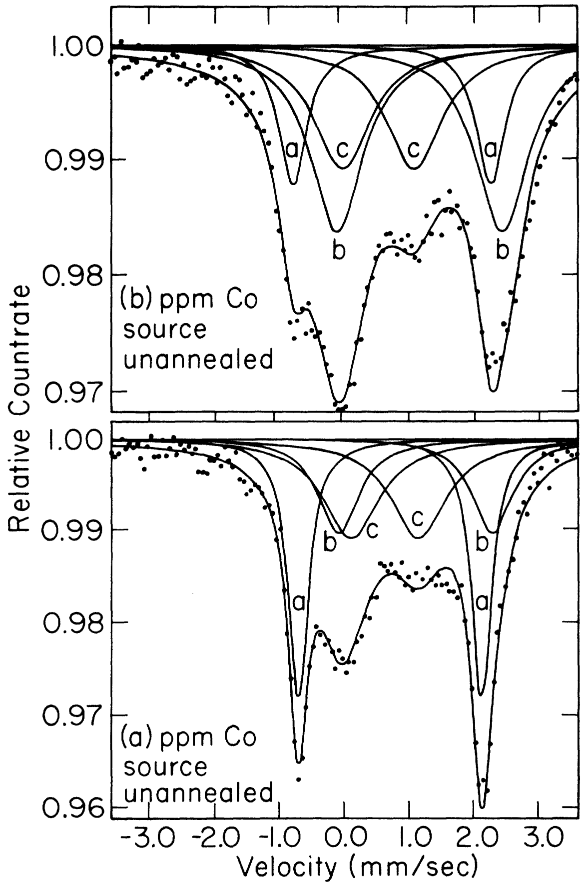

FIG. 3. Room-temperature Mössbauer spectra of two unannealed rutile samples doped with ppm of ^{57}Co. The velocity scale is with respect to α-Fe; positive velocity means the source is receding from the absorber. Doublets *a*, *b* and *c* refer to three different Fe configurations. (a) Sample 1. (b) Sample 2.

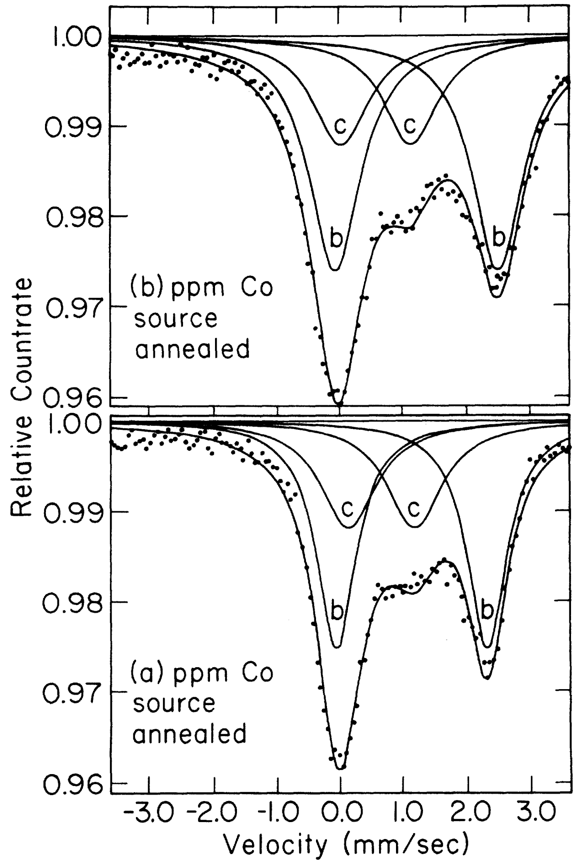

FIG. 4. Room-temperature Mössbauer spectra of the two samples of Fig. 3 after annealing at 500 K. The velocity convention is the same as Fig. 3. Doublets *b* and *c* correspond to two different Fe-defect configurations; doublet *a* of Fig. 3 has annealed out. (a) Sample 1. (b) Sample 2.

TABLE I. Mössbauer parameters in mm/sec of ppm ^{57}Co-in-rutile sources at room temperature.

Spectrum	Isomer shift	Quadrupole splitting	Linewidth
a	0.66 ± 0.04	2.88 ± 0.07	0.45 ± 0.07
b	1.08 ± 0.04	2.41 ± 0.07	0.89 ± 0.07
c	0.54 ± 0.10	1.04 ± 0.10	1.04 ± 0.06

temperature, their room-temperature Mössbauer parameters listed in Table I remained constant within experimental error.

1. Spectrum a

Spectrum *a* was found in the first room-temperature data taken for both ppm sources after quenching from 1300 K to room temperature in minutes. Between 295 and 500 K it irreversibly annealed out, primarily to spectrum *b*. The values in Table I were arrived at by fixing the isomer shift, quadrupole splitting, and linewidth of spectra *b* and *c* as obtained from the samples after annealing, as shown in Fig. 4, and allowing the computer to then best fit an additional doublet to the unannealed spectra as shown in Fig. 3. The fit thus involves six lines but only six adjustable parameters (the same number of parameters as would be used for two independent lines). The agreement of the resulting parameters of spectrum *a* from two independent samples confirms this analysis. Because of the annealing effect, no other temperature-dependent properties of spectrum *a* were studied.

2. Spectra b and c

Some parameters characterizing spectra *b* and *c* are presented in Table II. The room-temperature emission from spectrum *b* was greater than that of spectrum *c* after annealing for both ppm sources, but the ratio of the emissions were not the same.

Figure 5 shows the temperature dependence of the magnitudes of spectra *b* and *c* for source 727. For spectrum *b* this dependence can be fitted from 90 to 400 K with a Mössbauer Debye temperature at 260 K, but at 500 K either this characteristic temperature would have to be decreased to below 200 K or some of the spectrum *b* sites are converting to *c* sites. In contrast, Fig. 5 shows that the total emission from spectrum *c* is relatively constant with temperature, perhaps even increasing between 400 to 500 K. The Mössbauer Debye temperature to fit this data even poorly would have to be in excess of 2000 K. No change in either spectrum *b* or *c* was noticed after a ^{137}Cs γ-ray irradiation of over 10^7 R.

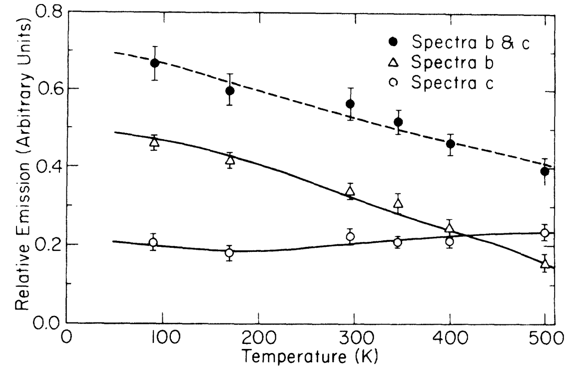

FIG. 5. The temperature dependence of the emissions from the configurations giving spectra *b* and *c* and their sum, in annealed TiO$_2$ doped with ppm of ^{57}Co. The dashed line is a fit to the total *b* plus *c* emission corresponding to a $\Theta_D = 330$ K. The solid lines in addition assume a thermal activation energy for *b* to *c* interconversion of 0.09 eV.

TABLE II. Temperature dependence of the isomer shift and the quadrupole splitting $\frac{1}{2}e^2qQ$ of an annealed ppm ^{57}Co-in-rutile source in units of mm/sec.

	Spectrum *b*		Spectrum *c*	
$T(K)$	Isomer shift	$\frac{1}{2}e^2qQ$	Isomer shift	$\frac{1}{2}e^2qQ$
90	1.22 ± 0.04	2.63 ± 0.08	0.57 ± 0.10	1.19 ± 0.12
169	1.17 ± 0.04	2.52 ± 0.09	0.54 ± 0.10	1.17 ± 0.15
295	1.08 ± 0.04	2.41 ± 0.07	0.54 ± 0.10	1.04 ± 0.18
345	1.03 ± 0.03	2.36 ± 0.06	0.54 ± 0.10	1.03 ± 0.15
400	0.99 ± 0.04	2.23 ± 0.07	0.51 ± 0.10	1.00 ± 0.08
500	0.88 ± 0.04	2.08 ± 0.09	0.44 ± 0.10	0.97 ± 0.08

IV. DISCUSSION

A. Absorber

The magnitude of the room-temperature isomer shift is in good agreement with the values measured by several others.[3-7] The quadrupole splitting agrees best with the values of Stampfl *et al.*[7] while the values obtained by others bracket it.

The magnitude of the isomer shift as well as the magnitude and temperature independence of the quadrupole splitting indicate that this absorber spectrum is due to Fe^{3+}, in agreement with EPR experiments.[8-10] EPR shows that the great majority of Fe^{3+} substitutes for Ti^{4+} with all the nearest O and Ti neighbors present when the doping is above the hundredths-of-a-percent range. Some type of lattice defect must result to preserve neutrality, either Ti^{4+} interstitials or O^{2-} vacancies. The Ti lattice site in rutile is quite noncubic, so that the large 3+ quadrupole interaction of 0.70 mm/sec is not surprising. The large linewidth can be ascribed to a variety of similar, but not identical, defect configuration, e.g., oxygen vacancies at the two next-nearest-neighbor positions, 3.46 and 3.58 Å from the Fe^{3+} ion. The measured Mössbauer Debye temperature of 430 K is much lower than the calometric value of 778 K,[11] as is to be expected from the many optical modes present.

B. Percent sources

The isomer shift of these sources identifies the spectrum as due to Fe^{3+}. There have been no previous Mössbauer studies of TiO_2:^{57}Co. However, EPR work[13,14] indicates that when Co is doped into rutile above the hundredths-of-a-percent level, the great majority of the Co substitutes for Ti^{4+} as Co^{2+}, again with all nearest O and Ti neighbors present. Thus, in percent sources, Co^{2+} always converts to Fe^{3+} after electron capture.

The close relationship of the percent source and percent absorber is shown in the equal Debye temperature of 430 K. This is reasonable, as both percent source and absorber involve Fe^{3+} at the same site with the same nearest neighbors according to EPR results. However, the isomer shift and especially the quadrupole splitting differences between these sources and the absorber indicate that the total surroundings of the Fe^{3+} in source and absorber are not the same. The defects induced in the crystal to preserve charge neutrality are such that the electric field gradient in the percent-Co-doped samples is unusually small at the time of the γ-ray emission, possibly by a partial cancellation of the electric field gradient of the ideal rutile crystal by terms due to the somewhat different defect configurations required by the stable Fe^{3+} and the parent Co^{2+}. The narrower percent-source lines then reflect the smaller resulting quadrupole interactions for all of the existing defect configurations.

C. ppm sources

1. Spectrum a

The isomer shift of this spectrum is in the range expected for Fe^{2+} with a considerable 4*s* admixture.[17] The narrowness of the doublet lines suggest an unusually well-defined site free of local defects. This site would not seem to be the ordinary substitutional one for Co in rutile as the spectrum is completely different from the percent source spectrum and disappears upon annealing. A possible configuration might be diffusing ions trapped at interstitial sites[18] by rapid cooling. Since reasonable fits to the data were arrived at by assuming constant parameters for spectra *b* and *c*, the center responsible for spectrum *a* does not appear to interact strongly with those responsible for *b* and *c* during its existence.

2. Spectra b and c

The isomer shift of spectrum *b* is in the range expected for Fe^{2+} with a small 4*s* admixture, while, within a comparatively large uncertainty, the shift of spectrum *c* can be ascribed to Fe^{2+} with a large 4*s* admixture. The quadrupole splittings of both spectra appear to have the temperature dependence characteristic of Fe^{2+}, with spectrum *c* exhibiting the smaller quadrupole splitting expected from a decrease in the *d* character of the orbitals caused by the large 4*s* admixture.

The predominance of Fe^{2+} in these ppm-^{57}Co sources is reasonable. It has been suggested[19] that the charge state of the iron daughter after the electron-capture decay of the ^{57}Co parent is strongly related to the charge state of iron in the analogous iron-containing compound. Since work on ppm of Fe in rutile[11,12] indicates that most of the Fe forms complexes with the normal crystalline defects and is found in the charge state Fe^{2+}, the present Fe^{2+} may readily be expected. Even at high doping levels, Fe^{3+} can be converted to Fe^{2+} in rutile if more defects are introduced by reduction.[7]

The broad lines of spectra *b* and *c*, as well as the preparation dependence of their intensity ratio, suggest that the spectra are related to a variety of defects. The variety of defects can also be seen in the number of different weak spectra seen in the EPR work of both Fe and Co in rutile.[10-15]

The behavior of the emissions *b* and *c* with temperature is complex. The separate spectra cannot be fitted by unique Mössbauer Debye temperatures. Θ_D, in a reasonable way, especially at the higher temperatures. If, instead, a single Θ_D is assumed for the sum of the two spectra, $\Theta_D = 330$ K is obtained. This is 100 K below the Θ_D of the absorber and percent sources, which is reasonable in view of the looser binding of the iron at the ppm sites due to more nearby defects. The single Θ_D for the sum of the two spectra implies that *b* states can be reversibly thermally exicted to *c* states. The fits for the separate spectra shown in Fig. 5 require a thermal activation energy of 0.09 eV, five or six *c* states available for every *b* state, and some *c* states filled even at the lowest temperatures. All of these results are consistent with the expected surroundings of the Fe^{3+} daughter ion.

V. CONCLUSIONS

The source and absorber results for ^{57}Fe and ^{57}Co in rutile can now be reviewed and compared. When rutile is doped in the percent range with Fe or Co, the results are reasonably related, i.e., the source and absorber spectra show the same Fe^{3+} charge state and the same Θ_D, while showing somewhat different isomer shifts and quite different quadrupole interactions. That the first two are the same is satisfying, since the lattice site and the nearest neighbors of the resulting iron are the same for both absorber and source, and since the charge stabilization energies may be expected to be very similar.[19] That the isomer shift and the quadrupole interaction differ should be no surprise. In the Mössbauer absorber, rutile is doped with Fe which finds its place as Fe^{3+} in the crystal and establishes its extrinsic defect concentrations to compensate for its trivalent state. In the percent Mössbauer source, rutile is doped not with Fe but with Co which finds its place as Co^{2+} and established different extrinsic defect complexes to compensate for its divalent state. Although the divalent state is ionized to a trivalent state as Co^{2+} decays to Fe^{3+}, the surrounding defects are still related to the Co^{2+} doping and not the Fe^{3+} doping; and in rutile apparently remain different, at least during the 10^{-7} sec lifetime of the excited Fe^{57} Mössbauer state.

When rutile is doped with Co^{57} in the ppm range, the resulting Mössbauer spectra differ considerably from both the percent absorber and percent source spectra. The connection between the various spectra appears to lie in the state of iron when doped into rutile. Fe in the ppm range enters as Fe^{2+} and associates with nearby intrinsic lattice defects, while the Co in the annealed-ppm samples appears to also associate with nearby intrinsic lattice defects and to decay to Fe^{2+}. Fe in the percent range enters as Fe^{3+} associated with nonlocal extrinsic defects required by charge neutrality, as seen in the percent absorber, while the Co in the percent Co samples also associates with nonlocal extrinsic defects and decays to Fe^{3+}

It has been shown that in rutile the source and absorber spectra and the spectra obtained by percent and ppm doping all have fundamental differences. This may well hold in other materials. These results clearly bring out the fact that great care must be exercised in making comparisons between source and absorber Mössbauer data, and that a distinction must be made between the behavior of Mössbauer sources at low doping levels and at high doping levels when defects are involved.

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