

sonably good quantum number to even specify the Stark split levels of Sm^{3+} except for the above mentioned levels. In this group of levels, which orig-

inates from three different J manifolds ${}^6F_{1/2}$, ${}^6H_{15/2}$, and ${}^6F_{3/2}$, the effect of J mixing is considerable, i. e., probably due to the closeness of these levels.

[†]Work supported by the National Research Council and the Defense Research Board of Canada.

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¹M. J. Weber and R. W. Bierig, *Phys. Rev.* **134**, A1492 (1964); R. W. Bierig, M. J. Weber, and S. I. Warshaw, *ibid.* **134**, A1504 (1964).

²N. Rabbiner, *Phys. Rev.* **130**, 502 (1963); *J. Opt. Soc. Am.* **57**, 1376 (1967).

³S. T. Pai, Ph.D. thesis, University of Windsor, 1970 (unpublished).

⁴W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.* **49**, 4424 (1968).

⁵Slightly deformed symmetries from pure O_h , C_{4v} and C_{3v} are also possible.

⁶M. Nerenberg and M. Schlesinger, *Phys. Letters* **26A**, 109 (1968); M. Schlesinger and M. Nerenberg, *Phys. Rev.* **178**, 568 (1969).

⁷M. A. H. Nerenberg, G. A. Behie, and M. Schlesinger, *Phys. Letters* **31A**, 212, (1970).

⁸B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).

⁹If we are only interested in a certain energy range, then the sizes are even more reduced. For example, the sizes are only 12×12 in the energy region up to

$11\,000\text{ cm}^{-1}$ in which we are interested in the present paper.

¹⁰The vectors of Carnall *et al.* are not really for the free ion, but are instead vectors for aqueous solution involving some loosely bonded species. We also assume that the free-ion E_k and ζ values do not depend on coordination, environment, etc.

¹¹We are much indebted to Dr. W. T. Carnall for providing us with the detailed information about the free-ion energy states of the Sm^{3+} ion. Actually, we have recalculated the free-ion energy states of Sm^{3+} by employing the same parameters given by Carnall *et al.* (Ref. 4) in order to avoid the possibility of making trivial errors in transcribing the data.

¹²C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for p^n , d^n , and f^n Configurations* (MIT Press, Cambridge, Mass., 1964).

¹³G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5.

¹⁴ Γ_5 and Γ_6 form Kramer's pair in the case of C_{3v} symmetry.

¹⁵J. Sierro, *J. Chem. Phys.* **34**, 2183, (1961).

¹⁶J. S. Prener and J. D. Kingsley, *J. Chem. Phys.* **38**, 667 (1963).

Positron Annihilation Rates in Lanthanum Hydrides[†]

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(Received 1 June 1970)

Positron annihilation rates λ_1 and λ_2 are reported for a series of lanthanum hydride samples of compositions from $\text{LaH}_{2.0}$ to $\text{LaH}_{2.9}$. From $\text{LaH}_{2.0}$ to $\text{LaH}_{2.7}$, λ_1 was approximately constant at 3.36 nsec^{-1} . At higher compositions, λ_1 increased with increasing hydrogen content. A slower rate component λ_2 was observed for annihilation in lanthanum hydrides, but the associated intensity was very low. New data are also reported for lithium hydride as follows: $\lambda_1 = 3.12\text{ nsec}^{-1}$, $\lambda_2 = 0.68\text{ nsec}^{-1}$, and $I_2 = 6.30\%$.

INTRODUCTION

Positron annihilation provides an attractive approach to the study of bonding in solids. Two types of measurements have been extensively used to characterize the annihilation process in solids: the measurement of positron lifetimes and the measurement of the two-photon angular correlations. Positronium formation is precluded in ionic solids.¹ The formation of a positron-anion bound

state remains a subject of discussion^{2,3} and has been most extensively treated for the case of the hydride ion. Gol'danski *et al.*⁴ treated a bound state consisting of a positron-hydride-ion pair in relation to the fast component of the lifetime spectrum of lithium hydride. Ivanovna and Prokop'ev⁵ attempted to account for additional lifetime components in lithium hydride in terms of additional excited states of this bound state. More recently,

Lebeda and Schrader⁶ have reported an improved variational wave function for positronium hydride. These authors emphasize the importance of including positron-electron correlation in such calculations. They find positronium hydride to be stable to the extent of 0.657 eV and calculate an annihilation rate of 2.095 nsec⁻¹ or 2.265 nsec⁻¹, depending on the exact choice of wave functions used. Gainotti *et al.*⁷ reported lifetimes for several ionic and metallic hydrides and, for group-IA and -IIA hydrides, found a linear dependence of annihilation rate on molecular density within each series. On the basis of this dependence of lifetime on molecular density, these authors suggest that in the bound state the positron interacts with more than one hydride ion. Brandt *et al.*⁸ have treated the importance of interactions with the lattice for the angular correlation of 2 γ annihilation radiation in lithium hydride.

We report here new experimental results which are of some importance in the context of this current discussion. For lanthanum hydrides, we report annihilation rates as a function of composition. In addition, we report new values for the rates of annihilation in lithium hydride.

A unique feature of lanthanum hydrides is the wide range over which their composition can be varied. From LaH_{1.9} to LaH₃, lanthanum hydrides are face-centered cubic with respect to the lanthanum atoms, with the lattice expanding by only about 1% over this composition range.⁹ Chouinard *et al.*¹⁰ have recently reported angular correlation studies of 2 γ positron annihilation in the closely similar hydrides of cerium, but annihilation rates have not been previously reported for any system of this type.

EXPERIMENTAL

Lanthanum hydride samples were prepared by the direct reaction of the metal (99.9% pure) with hydrogen by the procedure previously described.¹¹ Reagent-grade lithium hydride was used as received. Compositions were determined gravimetrically to ± 0.05 atom-ratio units. The positron sources used were about 10 μ Ci of sodium-22 chloride sandwiched between two 5-mm layers of sample in cylindrical Lucite capsules: 10 mm diam, 10 mm height, and of 1 mm wall thickness. The quantity of sample used was thought adequate to ensure that a negligible fraction of the positrons escaped from the sample to annihilate in the Lucite capsule material. The handling and sealing of hydride samples were carried out under an argon atmosphere.

The electronic circuit used to obtain the lifetime measurements was of conventional design, incorporating an Ortec 437A time-to-pulse height converter, 1.5 \times 1-in. Naton 136 plastic scintillators mounted on 56AVP photomultipliers and a PIP 400-channel analyzer. The instrument was calibrated using

fixed lengths of delay cables and was found to be very linear. This calibration led to a value of 0.114 nsec per channel with an uncertainty of less than 1%.

The experimental data were fitted to the equation

$$n = n_1 e^{-\lambda_1 t} + n_2 e^{-\lambda_2 t} + b$$

using Paul's program.¹² In that part of the program where values for λ_1 and λ_2 are obtained, data within several channels of the maximum in the plot of counts versus channel number were excluded from the computation. Figure 1 illustrates the experimental results and the fit of the calculated curve to a typical set of data points.

RESULTS

Table I summarizes measured annihilation rates for several materials and compares the present results with data from the literature. Error limits shown are those computed by the program and represent the standard deviations in the slopes of the plot of log counts vs channel number for a given set of data points. Independent determinations for a given material usually agreed with each other within these error limits for λ_1 and λ_2 but larger differences were found for I_2 . In all but one case, that of lithium hydride, the agreement of these results

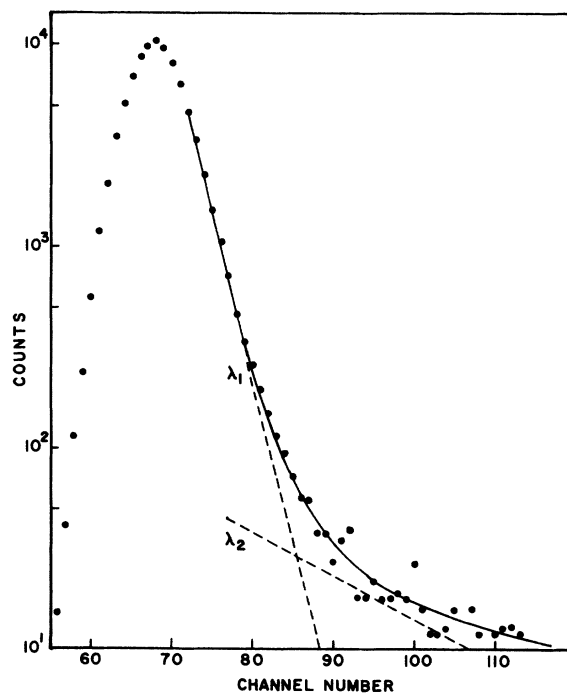


FIG. 1. Time spectrum of positrons annihilating in LaH_{2.00}. The solid circles represent the experimental data, the dotted lines the calculated slopes corresponding to λ_1 and λ_2 , and the solid line the total calculated count.

TABLE I. Comparison of some positron annihilation rates from the present work with those previously reported in the literature.

Material	λ_1 (nsec ⁻¹)	λ_2 (nsec ⁻¹)	I_2	Reference
H ₂ O	2.25 ± 0.04	0.509 ± 0.011	20.8 ± 1.1	. . .
	2.44	0.535	21.5	13
	2.38	0.562	21 ± 5	14
LiH	3.12 ± 0.04	0.68 ± 0.024	6.30 ± 0.53	
	4.76 ± 0.68	0.658 ± 0.035	6.4 ± 0.4	15
	5.71 ± 0.33	0.312 ± 0.015	65 ± 10	7
Sc	3.68 ± 0.03	0.338 ± 0.020	0.20 ± 0.34	
	3.61 ± 0.01			16
Y	3.37 ± 0.04	0.634 ± 0.24	0.65 ± 0.51	
	3.37 ± 0.02			16
La	3.35 ± 0.05	0.576 ± 0.13	2.24 ± 0.51	
	3.39 ± 0.02			16

with the literature is satisfactory. This gives us some confidence that the value which we report here for λ_1 in lithium hydride is also accurate. The very high value for I_2 reported by Gainoth *et al.*⁷ casts real doubt on the validity of their results. Substantially different lifetime values have since been reported¹⁷ for several of the compounds reported earlier by Bisi *et al.*¹⁵ New data for lithium hydride were not, however, included in the more recent report. This new value is of significance in relation to the considerable attention given to positron annihilation in lithium hydrides from both an experimental and a theoretical point of view.^{2-5,7,8}

For the metals reported in Table I, the intensity associated with the slower observed annihilation rate, λ_2 , was of the order of 2%. It is unlikely that the occurrence of this slow component is an intrinsic property of the metals. It is probably due to surface effects.¹⁸ The metals used being quite reactive, the surfaces of the samples were unavoidably contaminated by some oxide.

Three features of our annihilation results for lanthanum hydrides are especially noteworthy. These are (i) the variation of λ_1 with composition, (ii) the magnitude of λ_1 , and (iii) the intensity associated with λ_2 .

The dependence of λ_1 and λ_2 on composition is shown in Fig. 2. The curves shown there were visually fitted to the data points. From LaH_{2.0} to about LaH_{2.7}, no significant change was observed in λ_1 . Beginning at about LaH_{2.7}, λ_1 increases with increasing hydrogen content. The greater scatter of λ_2 data points makes it difficult to treat the dependence of λ_2 on hydrogen content. As discussed below, there may be some question as to the nature of the process associated with λ_2 .

For λ_1 in lanthanum hydrides, values of about 3.36 nsec⁻¹ are characteristic of compositions below LaH_{2.7}. A value of 3.72 nsec⁻¹ was observed for the highest composition studied, LaH_{2.89}. These values may be compared to the value 3.12 nsec⁻¹

which we have measured for lithium hydride and the values 2.09 and 2.26 nsec⁻¹ calculated by Lebeda and Schrader⁶ for positronium hydride without taking interactions with the crystal lattice into account.

For lithium hydride, we found λ_2 to occur to the extent of 6.3%. For the lanthanum hydride samples, I_2 varied irregularly between 1.1 and 2.6%. The values of λ_2 and I_2 for lanthanum hydrides are comparable to those observed for lanthanum metal. These considerations suggest that, for the hydrides, the occurrence of a slow component may be due to oxide contamination of the surfaces of the powdered samples. Thus, it is difficult to establish with certainty that the slower component observed for lanthanum hydrides is of any real significance.

DISCUSSION

We take the hydrogen in lanthanum hydrides to be hydridic^{11,19,20} rather than protonic.^{21,22} Chouinard *et al.* took the opposite view in interpreting their angular-correlation results for cerium hydrides.¹⁰ They observed broader angular correlations for cerium hydrides than cerium metal. Such broadening would be expected if the hydrogen were protonic with the electrons lost by the hydrogen going to fill the conduction band of the metal.

Chouinard *et al.* assume that if the hydrogen were hydridic in cerium hydrides, annihilation would occur primarily with the electrons of the hydride ions. They then calculate the angular correlation for cerium hydrides on the basis of the interaction of a positron with a single hydride ion. This calculation predicts narrower angular correlations for cerium hydrides, if they are hydridic, than for cerium metal. We feel that this argument is not conclusive because the calculation for the case of hydridic model was overly simplified. The an-

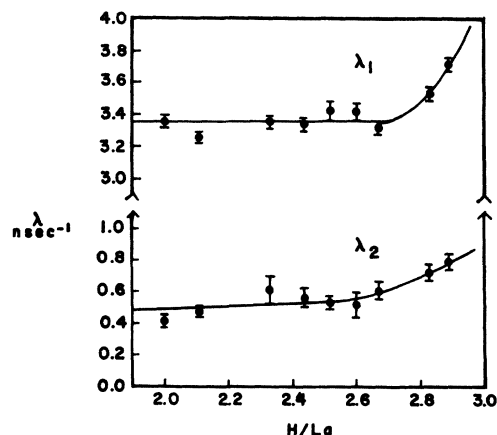


FIG. 2. Positron annihilation rates as a function of hydrogen content for lanthanum hydrides.

gular correlation measured by Chouinard *et al.* for lithium hydride is significantly broader than that predicted by this calculation. Differences between lithium hydride and cerium hydrides, other than that of bonding, might well account for the additional breadth of the cerium hydride angular correlation. The importance of taking the crystallographic environment of the bound system into account has been illustrated by Brandt *et al.*⁸ in their treatment of positron annihilation in lithium hydride.

At least for $\text{CeH}_{1.8}$ and $\text{CeH}_{2.2}$ there is a significant point of similarity between cerium hydrides and lithium hydrides: The angular correlations are approximately parabolic in shape. We conclude that the angular correlation results by no means preclude the hydridic model. Other evidence^{11,19,20} is persuasive in support of the hydridic model and we adopt it as a basis for the discussion of the lifetime data presented here.

The observation that λ_1 does not vary significantly with hydrogen content over the range $\text{LaH}_{2.0}$ – $\text{LaH}_{2.7}$ is consistent with the view that annihilation occurs primarily within a positron–hydride-ion pair. Indeed, it is rather surprising that more of a change is not observed in λ_1 over this range. According to the hydridic model, as the number of hydride ions increases from 2.0 to 2.7 per metal atom the number of conduction electrons decreases from 1.0 to 0.3. Here we distinguish one of the factors that may be acting to keep the effect of hydrogen concentration on λ_1 small. On a very local level, the environment of the bound states may be much the same over the composition range $\text{LaH}_{2.0}$ – $\text{LaH}_{2.7}$. The lanthanum hydride lattice becomes rather crowded at higher compositions and the bound state may form preferentially around those hydride ions which do not have a full set of nearest-neighbor hydride ions. Spatial requirements for the formation of bound states have been discussed in relation to ionic compounds for some time. Ferrell¹ cited as one criterion for the formation or nonformation of positronium in solids the availability of adequate space for this particular bound system. That there is not adequate space in closely packed ionic crystals may be one factor which prevents the formation of positronium in this type of solid.²³ Spatial

considerations as they apply to positron-anion bound states have been discussed by Bussolati *et al.*¹⁷ for the case of alkali halides.

Up to $\text{LaH}_{2.0}$, the hydrogen is accommodated in the tetrahedral interstices of the face-centered-cubic lanthanum sublattice.⁹ Beyond this composition, additional hydrogen is statistically distributed among the octahedral interstices, filling these completely at the composition LaH_3 . Each tetrahedral hydrogen has four equivalent octahedral hydrogen neighbors very near to it. The occupancy of one or more of the octahedral sites surrounding a given tetrahedral hydrogen may not leave room for the formation of a bound state. Every octahedral hydrogen would, of course, be in a crowded environment. At $\text{LaH}_{2.5}$ one tetrahedral hydrogen out of sixteen would still have no octahedral neighbor. At $\text{LaH}_{2.75}$, only one tetrahedral hydrogen in 256 would have no octahedral neighbor. The increase observed for λ_1 at higher H/La ratios may be a result of the fact that tetrahedral hydrogens without octahedral neighbors are present in smaller and smaller numbers. If bound states form with hydrogens that do have near neighbors, the effect of this change in surroundings may lead to a faster annihilation rate. It is also possible that at higher hydrogen contents a different sort of bound state forms not involving hydride ions or that annihilations which do not involve a bound state at all become dominant.

At about $\text{LaH}_{2.7}$, where an increase in λ_1 begins to become evident, lanthanum hydride loses its metallic character.² Below this composition, it is a paramagnetic metallic conductor; above it is a diamagnetic semiconductor.²⁴ Libowitz and Pack²⁰ have suggested that the remaining conduction electrons become localized at vacant octahedral sites and act as electron donors in the semiconducting hydrides. Having thus been localized, these electrons could form a positroniumlike bound state with a different characteristic annihilation rate than that of the positron–hydride-ion system.

ACKNOWLEDGMENT

The authors are grateful to Professor D. A. L. Paul for making his computer program available to us and for his assistance in adapting it to our use.

[†]Work supported in part by National Science Foundation Grant No. GP-9218 and in part by National Aeronautics and Space Administration Sustaining University Program Grant No. NGR-002-005.

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¹R. A. Ferrell, *Rev. Mod. Phys.* **28**, 208 (1956).

²W. Brandt, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), pp. 155–182.

³A. Fiorentini, in *Positron Annihilation*, edited by

A. T. Stewart and L. O. Roellig (Academic, New York, 1967), pp. 81–94.

⁴V. J. Gol'danski, A. V. Ivanovna, and E. P. Prokop'ev, *Zh. Eksperim. i Teor. Fiz.* **47**, 659 (1964) [*Soviet Phys. JETP* **20**, 440 (1965)].

⁵A. V. Ivanovna and E. P. Prokop'ev, *Zh. Eksperim. i Teor. Fiz.* **48**, 1155 (1965) [*Soviet Phys. JETP* **21**, 771 (1965)].

⁶C. F. Lebeda and D. M. Schrader, *Phys. Rev.* **178**, 24 (1969).

⁷A. Gainotti, C. Ghezzi, M. Manfredi, and L. Zecchina,

Nuovo Cimento **56B**, 47 (1968).

⁸W. Brandt and L. Eder, Phys. Rev. **142**, 165 (1966).

⁹W. L. Korst and J. C. Warf, Inorg. Chem. **5**, 1719 (1966).

¹⁰M. P. Chouinard, D. R. Gustafson, and R. C. Heckman, J. Chem. Phys. **51**, 3554 (1968).

¹¹T. P. Abeles, W. G. Bos, and P. J. Ouseph, J. Phys. Chem. Solids **30**, 2159 (1969).

¹²D. A. L. Paul and P. C. Strangøby, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), pp. 417-419.

¹³C. Bussolati, S. Cova, and L. Zappa, Nuovo Cimento **50B**, 256 (1967).

¹⁴J. E. Jackson and J. D. McGervey, J. Chem. Phys. **38**, 300 (1963); J. D. McGervey, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 144.

¹⁵A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev.

131, 1023 (1963).

¹⁶J. L. Rodda and M. G. Stewart Phys. Rev. **131**, 255 (1963).

¹⁷C. Bussolati, A. Dapasquier, and L. Zappa, Nuovo Cimento **52B**, 529 (1967).

¹⁸H. Kugel, E. Funk, and J. Mihelich, Phys. Letters **20**, 364 (1966).

¹⁹W. G. Bos and H. S. Gutowsky, Inorg. Chem. **6**, 552 (1967).

²⁰G. G. Libowitz and J. G. Pack, J. Chem. Phys. **50**, 3557 (1969).

²¹D. S. Schreiber, Phys. Rev. **137**, A860 (1965).

²²R. C. Heckman, J. Chem. Phys. **46**, 2158 (1967).

²³J. Green and J. Lee, *Positronium Chemistry* (Academic, New York, 1964), p. 39.

²⁴B. Stalinski, Bull. Acad. Polon. Sci., Classe III **5**, 997, (1957); **5**, 1001 (1957).

PHYSICAL REVIEW B

VOLUME 3, NUMBER 1

1 JANUARY 1971

Fe⁵⁷ Nuclear Magnetic Resonance and Some Dynamical Characteristics of Domain Walls in α -Fe₂O₃ †

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(Received 10 August 1970)

Steady-state Fe⁵⁷ nuclear magnetic resonance (NMR) signals in α -Fe₂O₃ have been re-examined using large good-quality synthetic single crystals. It has been confirmed that strong signals originate in domain walls. The detected signal is related to the electronic loss modulated by the real part of the susceptibility of the nuclear spins, χ'_n . The total loss detected in a coil is proportional to $1 + m\chi'_n$, where m is the modulation index. It is shown theoretically that for a domain wall with a wall resonance frequency $\nu_0 > \nu_N$, where ν_N is the NMR frequency, m is positive; while for a wall with $\nu_0 < \nu_N$, m is negative. This effect has been observed experimentally and correlated with domain-pattern observations, magnetization measurements, and also pulsed-NMR experimental results.

INTRODUCTION

Several years ago one of the present authors, with his co-workers, studied the characteristics of Fe⁵⁷ nuclear magnetic resonance (NMR) signals in the weak ferromagnet α -Fe₂O₃.¹ It was concluded that the NMR signals were mainly due to nuclei within the domain walls. Their experiments, however, used polycrystalline natural samples, and detailed information on the characteristics of domain walls, for example, could not be obtained.

Another of the present authors, with his co-workers, has studied the domain structure by domain-pattern observations.² There now seems to be a somewhat clearer understanding of magnetic domains and domain walls in this material.

It is well known that NMR signals in ferromagnetic materials are strongly enhanced. When the enhancement of NMR signals is considered, not only the enhancement of the applied rf field, but also the back reaction of the nuclear spin system on the electronic spin system should be treated properly. Such a re-

fined theory has been developed by Portis *et al.*³ However, until now the validity of their results has not been carefully checked, especially in the case of domain-wall enhancement.

Therefore, it seemed worthwhile to reexamine the Fe⁵⁷ NMR signals in α -Fe₂O₃ using good-quality synthetic single-crystal samples. The purposes of the present experiments were the following. The first experiment was to check whether or not the Fe⁵⁷ NMR signals really come from the nuclei within the domain walls. Then, if the NMR signals do indeed come from nuclei within the domain walls, a second experiment was to test Portis's refined expression for the intensity of NMR absorption by the domain-wall enhancement mechanism. Finally, a further investigation was made to determine what particular kind of information can be obtained about domains and domain walls.

Recently several papers have appeared which treat the same subjects.⁴⁻⁶ However, judging from the data on the temperature dependence of the NMR sig-