

L Fluorescence Yields in Heavy Elements*

J. WOODS HALLEY AND D. ENGELKEMEIR
Argonne National Laboratory, Argonne, Illinois
 (Received 31 July 1963)

L x-ray fluorescence yields for the Ra, Th, U, Pu, and Cm daughters of even-even alpha emitters were measured by three methods. Internal conversion of *E2* gammas from the decay of these nuclides produces approximately equal numbers of *L*_{II} and *L*_{III} vacancies and practically no *L*_I vacancies; the yields reported here are, therefore, averages of the *L*_{II} and *L*_{III} shell yields. The results are: Ra, 0.480±0.012; Th, 0.488±0.008; U, 0.478±0.009; Pu, 0.540±0.009; and Cm, 0.531±0.010.

INTRODUCTION

THE *L* fluorescence yield ω_L is the number of *L* x rays emitted per *L* vacancy created. Only a small number of *L* x-ray fluorescence yield measurements have been reported¹⁻³ for elements with $Z \geq 90$. Reliable fluorescence yields in this region are needed to help interpret heavy-element nuclear spectra.

In the alpha decay of even-even heavy nuclei about 25% of the decays lead to a low-lying 2+ level in the daughter nucleus. This 2+ level decays to the 0+ ground state by means of a highly converted *E2* transition. Internal conversion in the *L* shell produces vacancies which are filled either with the emission of *L* x rays or Auger electrons. In the experiments reported here, the number of *L* x rays emitted per *L* vacancy created was measured in the Ra, Th, U, Pu, and Cm daughters of the even-even nuclides Th²³⁰, U²³², Pu²³⁸, Cm²⁴⁴, and Cf²⁵². The decay schemes of these nuclides are similar and are all well known⁴; that of U²³² is shown in Fig. 1. Three methods were used to determine the number of *L* vacancies.

In the *L* x-ray spectra, x rays due to vacancies in different *L* shells were not resolved. Theoretical computa-

tions⁵ of the internal conversion coefficients α_L and our conversion electron spectra (Fig. 4) indicate that $\alpha_{LII} \approx \alpha_{LIII}$ and $\alpha_{LI}/\alpha_{LII} < 2\%$. The results, therefore, represent an average of the *L*_{II} and *L*_{III} fluorescence yields.

EXPERIMENTAL METHODS

For all the x-ray measurements, thin (<100 μg/cm²) samples of the alpha emitters were sublimed onto 1.8-mg/cm² aluminum foils and mounted in a collimator which precisely defined the fraction of the emitted x rays which was detected. In the collimator, the sample faced a 0.9988±0.0004-in. hole in a 0.010-in.-thick platinum sheet mounted 1.183±0.002 in. from the sample. The x-ray detector, a 1½-in.-diam by 1-in.-long NaI(Tl) scintillator with a 0.020-in. Be window, was mounted 3 mm beyond the platinum sheet. The platinum was thick enough to absorb x rays not passing through the hole. The solid angle subtended by this collimator is 3.936% of 4π sr for a point source and 3.911% for a ¼-in.-diam uniformly spread source. Since source diameters ranged from ⅛ to ⅜ in., spread-source solid angles were computed for each source.

A. L X-Ray Singles Method

All the *L* x rays detected by the scintillator were counted, giving a total *L* x-ray emission rate $N_x/\Omega_x t_x$, where N_x is the observed rate, Ω_x is the fraction of *L* x rays admitted to the detector by the collimator, and t_x is the x-ray transmission of the detector window. The total alpha emission rate N_α was measured with a low-geometry alpha counter. The rate at which *L* vacancies are produced is $B_{2+} N_\alpha \alpha_L / (1 + \alpha)$ where B_{2+} is the branching ratio or fraction of alpha decays leading to the 2+ excited state, and α and α_L are the total and *L*-shell conversion coefficients, respectively. The *L* fluorescence yield ω_L , by this method, is then

$$\omega_L = \frac{N_x (1 + \alpha)}{\Omega_x t_x \alpha_L N_\alpha B_{2+}} \quad (1)$$

The ratio α_L/α was found by beta spectroscopy as dis-

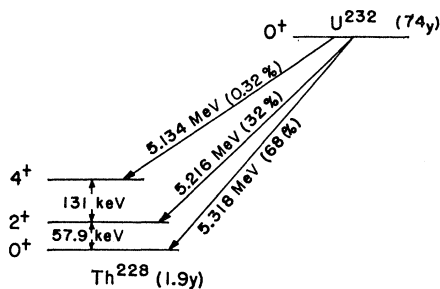


FIG. 1. Decay scheme for U²³². The decay schemes for the other nuclides studied are similar. Much less than 1% of the alpha decays go to excited levels of the daughter higher than the 4+ level.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ B. B. Kinsey, Can. J. Res. **26**, 404 (1948).

² B. L. Robinson and R. W. Fink, Rev. Mod. Phys. **27**, 424 (1955); **32**, 117 (1960).

³ L. Salgueiro, J. G. Ferreira, J. J. H. Park, and M. A. S. Ross, Proc. Phys. Soc. (London) **B77**, 657 (1961).

⁴ D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys. **30**, 585 (1958), and references cited there.

⁵ M. E. Rose, *Internal Conversion Coefficients* (North-Holland Publishing Company, Amsterdam, 1958).

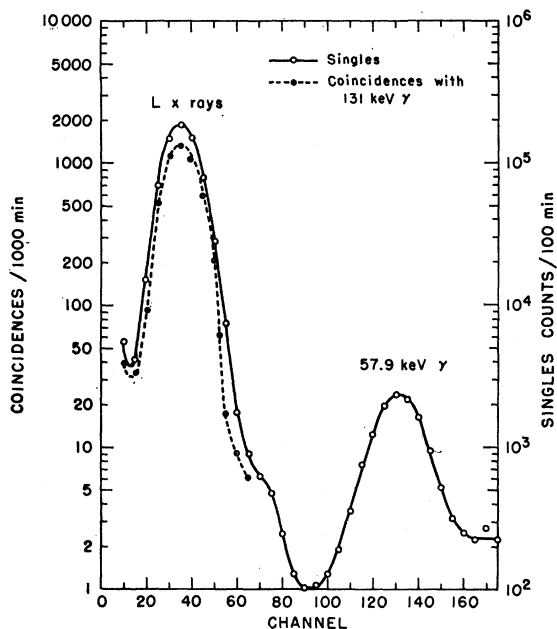


FIG. 2. L_x singles and L_x - γ coincidence spectra for U^{232} . Beryllium window NaI(Tl) scintillator $1\frac{1}{2}$ in. in diameter and 1 in. high. Five-channel sums are plotted.

discussed below. Published values⁶ for B_{2+} and α were used. The L x-ray singles spectrum from U^{232} appears as the solid curve in Fig. 2. N_x was found by integrating the area under the L x-ray peak. The second peak in the curve is due to unconverted 57.9-keV gammas from the $2+$ to ground-state transition (Fig. 1).

It was not possible to use the singles method for Cf^{252} because of the high background in the L x-ray region caused by spontaneous fission in the source.

B. (L X Ray)-Gamma Coincidence Method

Only x rays in coincidence with gammas emitted in the $4+$ to $2+$ transition of the daughter nucleus were counted. The gammas were detected by another NaI(Tl) scintillator behind the sample and selected by a single-channel analyzer. For each such gamma, $\omega_L\alpha_L/(1+\alpha)$ L x rays are emitted. The fluorescence yield is then

$$\omega_L = \frac{N_{x\gamma} (1+\alpha)}{N_\gamma \Omega_{xL} \alpha_L} \quad (2)$$

Here $N_{x\gamma}$ is the coincidence rate and N_γ is the rate at which the $4+$ to $2+$ gammas were detected by the second NaI(Tl) scintillator and single-channel analyzer. The dashed curve in Fig. 2 is the spectrum of x rays in coincidence with these gammas for U^{232} . $N_{x\gamma}$ is found

⁶ For B_{2+} see references in Table I; for α see below; Th^{230} : Ref. 7; U^{232} : G. Scharff-Goldhaber, E. der Mateosian, G. Harbottle, and M. McKeown, Phys. Rev. **99**, 180 (1955); Pu^{238} : F. Asaro and I. Perlman, Phys. Rev. **94**, 381 (1954); Cm^{244} : F. Asaro and I. Perlman, cited in Ref. 4; Cf^{252} : F. Asaro, F. S. Stevens, B. G. Harvey, and I. Perlman, Phys. Rev. **100**, 137 (1955).

by integrating the area under the L x-ray peak in the dashed curve.

In the Th^{230} (L x ray)-gamma determination a small correction (1%) was made for the partial detection of a 253-keV gamma which crosses over the $2+$ level. Although the single-channel analyzer was set to select the photopeak of the 142-keV gamma populating the $2+$ level, part of the Compton distribution from the 253-keV gamma was also counted. Alpha branching to the $4+$ level is too low to permit reliable measurements by the (L x ray)-gamma method for Pu^{238} , Cm^{244} , and Cf^{252} .

C. (L X Ray)-Alpha Coincidence Method

In this method⁷ L x rays in coincidence with alphas leading to the $2+$ state were counted. Alphas were detected with a Si-Au surface-barrier counter mounted behind the sample. The alpha spectrum (Fig. 3) was recorded on a multichannel analyzer which was coincidence gated by L x-ray pulses selected by a single-channel analyzer. The window of the single-channel analyzer was wide enough to accept at least 99.5% of the L x-ray pulses. The coincidence spectrum shows only the alpha group to the $2+$ level; low-intensity alpha groups to higher levels are below the region shown. The shoulder on the high-energy side of the peak is caused by simultaneous detection of alpha particles and conversion electrons. Since the alpha counter had good resolution (20 keV full width at half-maximum) the branch-

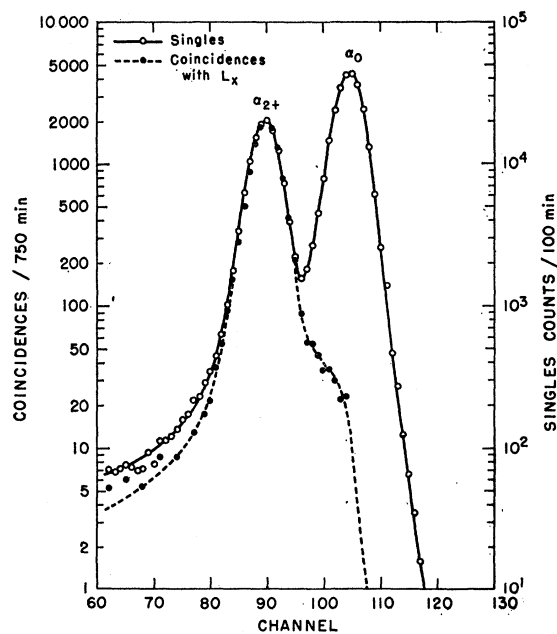


FIG. 3. Alpha singles and alpha- L_x coincidence spectra for U^{232} . Si(Au) solid-state detector.

⁷ A determination of ω_L for Ra^{226} by this method is described by E. Booth, L. Madansky, and F. Rasetti, Phys. Rev. **102**, 800 (1956).

TABLE I. Summary of measurements of the L fluorescence yield ω_L .^a

Daughter nuclide	Method	B_{2+}	$\alpha_L/(1+\alpha)$	No. of determinations	ω_L	Other work
Ra ²²⁶	L_x singles	0.259±0.005 ^b	0.701±0.014	12	0.482(0.003)	0.52 ±0.05 ^e 0.45 ^d
	L_x - α coinc.	0.259±0.005	0.701±0.014	5	0.485(0.003)	
	L_x - γ coinc.		0.701±0.014	7	0.473(0.004)	
				mean	0.480±0.012	
Th ²³²	L_x singles	0.320±0.020 ^e	0.731±0.007	5	0.495(0.001)	0.48 ^d
	L_x - α coinc.	0.316±0.003	0.731±0.007	4	0.485(0.001)	
	L_x - γ coinc.		0.731±0.007	3	0.483(0.006)	
				mean	0.488±0.008	
U ²³⁴	L_x singles	0.292±0.012 ^{f-h}	0.764±0.007	11	0.480(0.002)	0.45 ⁱ 0.50 ^d
	L_x - α coinc.	0.289±0.003	0.764±0.007	5	0.475(0.003)	
				mean	0.478±0.009	
Pu ²⁴⁰	L_x singles	0.233±0.003 ^b	0.710±0.007	6	0.544(0.001)	0.486±0.01 ^j
	L_x - α coinc.	0.232±0.003	0.710±0.007	5	0.536(0.004)	
				mean	0.540±0.009	
Cm ²⁴⁸	L_x - α coinc.	0.161±0.003	(0.731) ^l	5	0.531(0.002)	
		0.158 ^k		mean	0.531±0.010	

^a Except for Lay's result for uranium (footnote i) which includes contributions from the L_I shell, the yields listed are essentially the mean of the L_{II} and L_{III} subshell yields. The precision measure is the standard error of the mean.

^b J. P. Hummel, University of California Radiation Laboratory Report No. 3456, 1956. Other reported values have been obtained under conditions of poor resolution and were not included.

^c Reference 7.

^d Calculated from the yields given by Kinsey (Ref. 1) for equal numbers of vacancies in the L_{II} and L_{III} subshells and no vacancies in the L_I subshell.

^e F. Asaro and I. Perlman, Phys. Rev. **99**, 37 (1955).

^f F. Asaro and I. Perlman, Phys. Rev. **94**, 381 (1954).

^g F. Ajzenberg-Selove, Suppl. Nuovo Cimento **4**, 2 (1956).

^h L. N. Kondratév, G. I. Novikova, V. B. Dedov, and L. L. Goldin, Izvest. Akad. Nauk SSSR, Ser. Fiz. **21**, 907 (1957).

ⁱ Reference 11.

^j Reference 3.

^k Reference 6 for Cf²⁵².

^l Not measured for Cf²⁵²; the value of α_L/α used is an average of the other four measured values.

ing ratio to the $2+$ level was measured directly by resolving the total alpha spectrum into its components. Superposition of the coincidence peak on the total alpha spectrum facilitated its resolution. Branching ratios measured in this way were used in the L_x - α calculations and are listed opposite L_x - α in the B_{2+} column of Table I.

For each alpha detected, $B_{2+}\omega_L\Omega_x\alpha_L/(1+\alpha)$ coincidences with L_x rays were recorded. The fluorescence yield is then

$$\omega_L = \frac{N_{x\alpha}}{N_\alpha B_{2+}\Omega_x\alpha_L} \frac{(1+\alpha)}{\alpha_L}, \quad (3)$$

where $N_{x\alpha}$ is the coincidence rate and N_α is the total alpha singles rate of the alpha counter.

In the coincidence experiments, the chance coincidence rate was experimentally determined and subtracted from the observed coincidence rate before making the ω_L computations. Each method requires that the ratio of internal conversion coefficients $\alpha_L/(1+\alpha)$ be known. The ratio α_L/α was measured directly by conversion electron spectroscopy. Since the value⁶ of α for each nuclide is large, $\alpha_L/(1+\alpha)$ differs only slightly from α_L/α . For Th²³⁰, α is equal to 48 ± 7 ; for the other nuclides, α is greater than 100. To measure α_L/α , conversion electron spectra from the alpha emitters were measured on a double-lens beta spectrometer.⁸ Samples

were volatilized onto 200 $\mu\text{g}/\text{cm}^2$ aluminum backings. In all of the samples except Th²³⁰, the L conversion electrons were well resolved from those of higher shells. A momentum plot of a portion of the U²³² electron spectrum appears in Fig. 4. The ratio α_L/α was obtained from these data by numerical integration.

Benoist⁹ has pointed out that a directional correlation may exist between alphas and L_x rays emitted in the filling of the L_{III} shell. The maximum anisotropy theoretically possible for the transitions considered here (50% L_{III} vacancies) is $\sim 7.5\%$. In experiments¹⁰ on L_x rays coincident with alphas from the decay of Th²³⁰ no L_x -ray anisotropy was detected within an experimental precision of $\pm 4\%$. To determine if any directional correlation exists between gammas emitted in the $4+ \rightarrow 2+$ transition and L_x rays from the following $2+ \rightarrow 0+$ transition in even-even nuclides, the directional correlation was measured between 99-keV gammas and L_x rays in the decay of Pu²³⁸. The result is

$$\omega(180^\circ)/\omega(90^\circ) - 1 = -0.002 \pm 0.018.$$

The error is the standard deviation based on counting statistics and $\omega(\theta)$ is the γ - L_x coincidence rate. Thus, the x-ray emission is isotropic relative to the direction of gamma emission to within $\pm 2\%$.

⁹ P. Benoist, Compt. Rend. **238**, 1498 (1954).

¹⁰ P. Folk-Vairant, J. Teillac, G. Vallados, and P. Benoist, Compt. Rend. **238**, 1409 (1954).

⁸ F. Porter, M. S. Freedman, T. B. Novey, and F. Wagner, Phys. Rev. **103**, 921 (1956).

Since fluorescence yield measurements by coincidence techniques were made only at 180° , there is a possibility of errors of a few percent due to directional correlation effects.

RESULTS

Table I summarizes the results obtained and lists the factors entering into the calculations. The values of B_{2+} listed after the singles measurements are averages of the previously published values given in the references; the values of B_{2+} listed after the $L_x\text{-}\alpha$ measurements are those measured in the present experiments. The standard error in B_{2+} was calculated from replicate measurements of B_{2+} reported in the literature or from an estimate of the possible errors in the present B_{2+} measurements. The accuracy of $\alpha_L/(1+\alpha)$ is determined principally by the conversion electron spectrometric measurements of α_L/α . The error in α_L/α was estimated to be less than 1% for all nuclides except Th^{230} since the maximum amount of tail from the M, N, O, \dots lines under the L conversion lines was less than 1%. For Th^{230} the error could be as high as 2%. Counter backgrounds were less than 2% of the total singles or coincidence rates except in the (L x ray)-gamma measurements. In these measurements the background of the gamma counter (15 ± 1 counts per minute) was 30% of the gross singles gamma rate for Pu^{238} and 5-10% for Th^{230} and U^{232} . The standard deviation in the number of counts recorded for each determination is less than 0.5% for the singles measurements, less than 1% for $L_x\text{-}\alpha$ measurements, and from 0.7 to 2% for $L_x\text{-}\gamma$ measurements. The precision measure in parentheses after the ω_L result for each method is based solely on the internal consistency of the determinations and is the standard error of the mean.

An estimate of the reliability of these fluorescence yields was made by dividing the sources of error into two

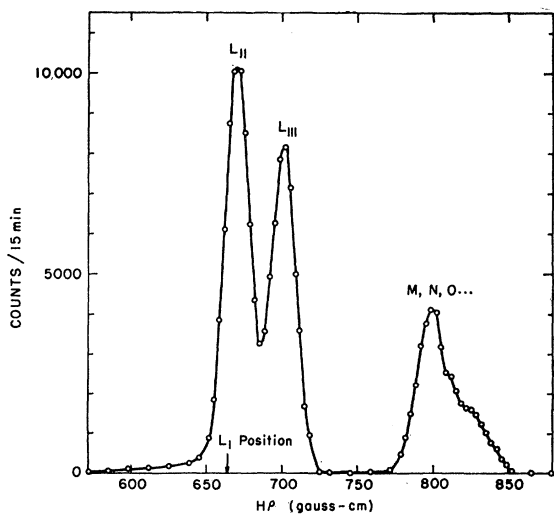


FIG. 4. Momentum plot of the conversion electrons of the 57.9-keV gamma from U^{232} .

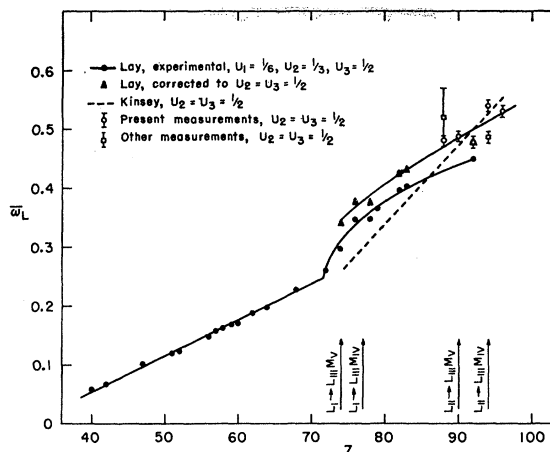


FIG. 5. L fluorescence yields.

categories: systematic errors common to all three methods and methodic errors which differed for the three methods. Systematic errors were estimated from a knowledge of the experimental conditions, whereas methodic errors were estimated from the differences in yield observed among the three methods. The principal systematic errors are in collimator solid angle (0.4%), x-ray absorption (0.5%), fraction of x-ray peak counted (1%), and $\alpha_L/(1+\alpha)(1-2\%)$; the numbers in parentheses are the estimated standard deviations. The principal methodic errors are in B_{2+} (not a factor for $L_x\text{-}\gamma$), directional correlation, and coincidence efficiency. Random errors due to counting statistics appear as methodic errors in the analysis.

The variance in yield was calculated for each element for which more than one method was used. These variances were combined to obtain a pooled estimate of the methodic error variance. This analysis gave values of 1.2, 0.8, and 0.7% for the methodic standard error of the mean when one, two, or three methods were used to measure the fluorescence yield. The standard error of the mean fluorescence yield for each element (listed after the mean yield) was calculated assuming that the systematic errors and the methodic standard error added randomly.

DISCUSSION

Other L fluorescence yield measurements of the elements considered here are shown in the last column of Table I. The Ra yield by Booth *et al.*⁷ is 8% higher than that reported here but is within the assigned errors. The careful yield measurement for Pu by Salgueiro *et al.*³ is 10% lower than the value found here, an amount well outside the assigned errors. Both of these measurements are directly comparable with this work since the method of excitation was the same, i.e., alpha decay of an even-even nuclide. The yields attributed to Kinsey¹ are not experimental values; they are averages of the L_{II} and L_{III} fluorescence yields which are based largely upon experimental and theoretical line widths. In Lay's meas-

urements¹¹ on uranium, L vacancies were produced by irradiating samples with x rays from molybdenum. This method of L vacancy production results in an appreciable proportion of L_I vacancies (15–20%), so this result is not directly comparable with the present work.

It may seem surprising that the L fluorescence yield measurements in this region do not appear to fall on a smoothly rising curve (see Fig. 5). It should be pointed out, however, that Coster-Kronig transitions of the $L_{II} \rightarrow L_{III}M_V$ type are energetically possible at $Z=90$ and above, and those of the $L_{II} \rightarrow L_{III}M_{IV}$ type at $Z=94$ and above. If the L_{II} and L_{III} subshell yields

are different, these Coster-Kronig transitions will introduce discontinuities in a plot of ω_L versus Z .

No theoretical computations of L fluorescence yields for these elements were found although a program was begun by Rose and Goertzel.¹² Theoretical computations of L fluorescence yields for elements with lower Z have been carried out by Pincherle.¹³

ACKNOWLEDGMENTS

The authors wish to thank Paul Day for assistance in the use of the beta spectrometer and A. H. Jaffey for advice on the statistical treatment of the data.

¹¹ H. Lay, *Z. Physik* **91**, 533 (1934).

¹² M. E. Rose (private communication).

¹³ L. Pincherle, *Nuovo Cimento* **12**, 81 (1935).

Nuclear Spin-Lattice Relaxation in Three-Spin Molecules*

L. K. RUNNELS†

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut
and

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana

(Received 20 August 1963; revised manuscript received 2 December 1963)

The free longitudinal relaxation of the nuclear magnetization of systems of three identical spins $\frac{1}{2}$ at the corners of an equilateral triangle is investigated using the semiclassical form of the density operator theory. The relaxation mechanism investigated is a fluctuating dipolar interaction between the spins. Assuming only that the symmetry of the thermal motion of the molecules preserves the complete equivalence of the three spins, the general relaxation equation is obtained before adopting models for this thermal motion. The effect of correlations between different pairwise interactions is studied; this effect can be more significant in the case of anisotropic reorientations possible in solids than for isotropic motion. For systems initially describable by a spin temperature, the effect of cross correlations always is to retard the relaxation. In general the relaxation is described by a sum of four exponentials, although three suffice for isotropic motion and two for the limit of long correlation times. An "effective relaxation time" is defined, the calculation of which is far simpler than that of the complete solution.

1. INTRODUCTION

THE THERMAL equilibration of nuclear spins with their surroundings often proceeds by means of a fluctuating magnetic dipolar interaction between the spins; the calculation of the longitudinal or spin-lattice relaxation has been much discussed.¹

It has been realized that the nuclear paramagnetism need not necessarily approach its equilibrium value exponentially—that is, there need not be a single relaxation time T_1 . For two important cases, however, the approach is exponential and T_1 is well defined: the first is an isolated pair of interacting spins; the second is a system of any number of spins with no correlations between the interactions of the various *pairs* of spins.^{1,2}

A more precise statement of this latter requirement will be made later.

The assumption of uncorrelated pair interactions is an attractive one, since it not only insures the existence of a single relaxation time T_1 but also facilitates its calculation since different dipolar interactions contribute additively to T_1^{-1} under this assumption.

Hubbard^{3,4} has examined carefully the problem of equivalent three- and four-spin molecules in a liquid with isotropic rotational diffusion of the molecules. He investigated the three-spin molecules at high temperatures and the four-spin molecules at many temperatures, finding two and three decaying exponentials involved in the approach of the nuclear magnetism to its equilibrium value at the "lattice" temperature. However, one of the relaxation times was found to be very close to the uncorrelated-pairs value and the other exponentials were found to be multiplied by small coef-

* The majority of this work was supported by the National Science Foundation.

† Present address: Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana.

¹ See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. VIII.

² P. S. Hubbard, *Rev. Mod. Phys.* **33**, 249 (1961).

³ P. S. Hubbard, *Phys. Rev.* **109**, 1153 (1958); **111**, 1746 (1958).

⁴ P. S. Hubbard, *Phys. Rev.* **128**, 650 (1962).