

since one here requires the use of trial functions whose flexibility is restricted by the physically unnatural conditions mentioned above (the exact function does *not* satisfy those conditions) there is a limitation on the accuracy of the bound that can be obtained. In fact, it may well not be possible to find the appropriate number of trial functions Φ_{ni} of the prescribed restricted form (i.e., we might *necessarily* have $T' < T$) in which case the bound obtained on η will be too low by approximately $(T - T')\pi$.

It should be emphasized that while we obtain valid results using (restricted) trial energy eigenfunctions Ω is nevertheless not an allowable trial function in an energy eigenvalue problem. The difficulty has been bypassed by the use of the associated potential strength

eigenvalue problem as the starting point. The point is that in this latter approach one places conditions only upon the oscillatory term, through having specified the phase shift $\delta(\mu_n)$; no restrictions are placed on the amplitudes of the virtually excited decaying states.

The primary purpose of the present paper is the derivation of Eqs. (4.2), (4.3), and (4.4). The analysis of previous work presented in this section is simply a byproduct. We have presented the analysis for two reasons. Firstly, it sheds some light on the methods of the present paper as well as on previous work. Secondly, there will be occasions when for practical reasons one would use trial functions of the restricted form; that is what was done, for example, in the analysis of the scattering of positrons by hydrogen atoms.⁷

Isotope Shift in the Arc Spectrum of Nickel*†

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The isotope shift in 31 spectral lines in the nickel arc spectrum has been determined by the use of a Fabry-Perot interferometer. The normal mass shifts were calculated ($\approx +0.025$ cm⁻¹ between Ni⁵⁸ and Ni⁶⁴) and subtracted from the observed isotope shifts. The differences were attributed to the specific mass and field effects. The relative shifts of levels of four configurations were deduced from the observed line shifts, these being the "complex" configurations $3d^84s^2$ and $3d^84s4p$ and the two-electron configurations $3d^94s$ and $3d^94p$. It was shown that the shifts due to the specific mass effect are a significant part of the observed shifts. Perturbations due to interconfiguration interactions were postulated to explain some of the observed shifts. The isotope shift to be expected between Ni⁵⁸ and Ni⁶⁴ on the basis of field effect calculations is about -0.02 cm⁻¹ for a single $4s$ electron, while the

shifts observed are as large as $+0.190$ cm⁻¹. A large fraction of this shift must therefore be attributed to the specific mass effect. By noting the deviations of the relative shifts between adjacent pairs of even isotopes from those predicted by mass effect theory, it was possible to deduce the relative field effect. The relative level shift resulting from the field effect is nearly the same for the adjacent isotope pairs 60-62 and 62-64 while the relative level shift for the isotope pair 58-60 is approximately 0.004 cm⁻¹ larger than that for the other adjacent isotope pairs. The arrangement of neutrons in the outermost nuclear shells is believed to account for this difference. Within the experimental error the level shift of the Ni⁶⁴ relative to the neighboring even isotopes is such that there is no odd-even staggering of the levels.

INTRODUCTION

ISOTOPE shift of spectral lines can be divided into two classes, that caused by the mass effect and that resulting from the field effect. The mass effect consists of two parts, normal and specific, and results from the nucleus having a finite mass. The normal mass effect can be calculated exactly while the specific mass effect, present in spectra of atoms with more than one electron, is very difficult to calculate precisely. Both of these effects decrease with increasing Z . The field effect, which increases with increasing Z , arises because of the

deviation of the nuclear electric field from a Coulomb field and can be used to study details of nuclear structure. This is probably the most important consequence of isotope shift studies.

In the very light elements the mass effect dominates and can account qualitatively for the observed shifts. In the heaviest elements the mass effect is negligible and the field effect can roughly account for the observed shifts. In the elements of intermediate mass the two effects are comparable. As a result, the shifts observed are small because the mass and field effects within the levels are often in such a direction as to oppose one another. In order to use the field effect in the determination of nuclear properties, it is necessary that the contributions of the mass and field effects to the observed shifts be known. For elements of intermediate mass it is difficult to determine experimentally the relative contributions of these two effects.

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TABLE I. Isotope shifts (in units of 10^{-3} cm^{-1}) and ratios of line shifts in nickel grouped according to transition type.

Transition	σ (cm^{-1})	Measured shifts ^a				Normal shift 58-64	Residual shift 58-64	Ratios of shifts ^b	
		58-60	60-62	62-64	58-64			(58-60)/(62-64)	(60-62)/(62-64)
$3d^9 4s^2 3D_3 - 3d^8 4s 4p^5 D_4$	25 548.8	-38.4	-37.5	-35.8	-111.8	22.5	-134.3	1.07 ± 0.06	1.05 ± 0.06
$3d^9 4s^2 1D_2 - 3d^8 4s 4p^5 F_3$	26 422.9	-32.5	-29.9	-29.6	-91.8	23.2	-115.0	1.10 ± 0.07	1.01 ± 0.07
$3d^9 4s^2 3D_3 - 3d^8 4s 4p^5 D_3$	26 461.2	-40.7	-38.9	-34.0	-113.6	23.3	-136.9	1.20 ± 0.06	1.14 ± 0.06
$3d^9 4s^2 3D_3 - 3d^8 4s 4p^5 D_2$	27 209.8	-39.3	-35.5	-35.6	-110.1	23.9	-134.0	1.10 ± 0.06	1.00 ± 0.06
$3d^9 4s^2 3D_2 - 3d^8 4s 4p^5 G_3$	27 698.3	-36.3	-37.7	-32.4	-106.0	24.4	-130.4	1.11 ± 0.06	1.16 ± 0.06
$3d^9 4s^2 3D_3 - 3d^8 4s 4p^5 F_4$	28 879.6	-20.6	-18.2	-18.6	-57.2	25.4	-82.6	1.11 ± 0.10	0.98 ± 0.10
$3d^9 4s^2 3D_2 - 3d^8 4s 4p^5 F_3$	28 953.0	-31.3	-27.3	-29.3	-87.8	25.5	-113.3	1.07 ± 0.07	0.93 ± 0.07
$3d^8 4s^2 3F_4 - 3d^8 4s 4p^5 D_3$	26 665.9	18.5	20.4	19.6	58.7	23.5	35.2	0.94 ± 0.09	1.04 ± 0.10
$3d^8 4s^2 3F_3 - 3d^8 4s 4p^5 G_4$	26 735.9	19.9	21.0	21.2	62.3	23.5	38.8	0.94 ± 0.09	0.99 ± 0.10
$3d^8 4s^2 3F_3 - 3d^8 4s 4p^5 G_3$	27 245.9	19.2	21.5	21.3	62.4	24.0	38.4	0.90 ± 0.09	1.01 ± 0.10
$3d^8 4s^2 3F_4 - 3d^8 4s 4p^5 G_5$	27 580.4	17.7	21.3	20.3	59.5	24.3	35.2	0.87 ± 0.09	1.05 ± 0.10
$3d^8 4s^2 3F_4 - 3d^8 4s 4p^5 G_4$	28 068.1	18.6	21.7	20.8	61.2	24.7	36.5	0.89 ± 0.09	1.04 ± 0.10
$3d^8 4s^2 3F_4 - 3d^8 4s 4p^5 F_5$	28 542.1	18.1	22.5	21.3	61.9	25.1	36.8	0.85 ± 0.09	1.06 ± 0.10
$3d^8 4s^2 3F_4 - 3d^8 4s 4p^5 F_4$	29 084.5	36.5	37.6	37.1	111.3	25.6	85.7	0.98 ± 0.06	1.01 ± 0.06
$3d^9 4s^2 1D_2 - 3d^9 4p^3 F_3$	25 911.0	2.7	6.4	3.1	12.4	22.8	-10.4		
$3d^9 4s^2 1D_2 - 3d^9 4p^3 D_3$	26 259.0	-1.9	0.6	0.0	-1.3	23.1	-24.4		
$3d^9 4s^2 1D_2 - 3d^9 4p^3 F_3$	27 621.1	6.7	10.0	9.2	26.3	24.3	2.0		
$3d^9 4s^2 1D_2 - 3d^9 4p^3 D_2$	28 031.7	6.0	5.6	7.6	19.4	24.7	-5.3		
$3d^9 4s^2 3D_3 - 3d^9 4p^3 P_2$	28 364.4	14.1	17.2	18.1	49.3	25.0	24.3	0.78 ± 0.11	0.95 ± 0.13
$3d^9 4s^2 3D_2 - 3d^9 4p^3 F_3$	28 440.9	4.1	7.3	4.5	15.9	25.0	-9.1		
$3d^9 4s^2 3D_1 - 3d^9 4p^3 P_0$	28 479.2	15.3	18.5	17.0	50.9	25.1	25.8	0.90 ± 0.11	1.09 ± 0.13
$3d^9 4s^2 3D_2 - 3d^9 4p^3 P_1$	28 620.8	13.5	17.1	16.7	47.6	25.2	22.4	0.81 ± 0.11	1.02 ± 0.13
$3d^9 4s^2 3D_1 - 3d^9 4p^3 F_2$	28 906.3	3.1	4.1	4.0	11.5	25.4	-13.9		
$3d^9 4s^2 3D_2 - 3d^9 4p^3 D_2$	29 008.7	1.5	2.7	3.6	7.9	25.5	-17.6		
$3d^9 4s^2 3D_3 - 3d^9 4p^3 F_3$	29 115.9	4.6	5.6	5.7	16.1	25.6	-9.5		
$3d^9 4s^2 3D_1 - 3d^9 4p^3 D_1$	29 199.7	-2.9	-0.2	-0.7	-3.8	25.7	-29.5		
$3d^9 4s^2 1D_2 - 3d^9 4p^3 P_1$	29 572.3	16.4	20.4	18.7	55.8	26.0	29.8	0.88 ± 0.11	1.09 ± 0.13
$3d^8 4s^2 3F_2 - 3d^8 4p^3 D_2$	27 672.0	58.6	60.6	58.3	177.4	24.3	153.1	1.01 ± 0.06	1.04 ± 0.06
$3d^8 4s^2 3F_3 - 3d^8 4p^3 F_3$	27 988.6	66.2	62.5	60.8	189.4	24.6	164.8	1.09 ± 0.07	1.03 ± 0.06
$3d^8 4s^2 3F_2 - 3d^8 4p^3 D_1$	28 696.3	56.1	54.4	56.0	166.6	25.3	141.3	1.00 ± 0.07	0.97 ± 0.07
$3d^8 4s^2 3F_4 - 3d^8 4p^3 F_4$	29 481.0	50.5	50.4	50.0	151.3	25.9	125.4	1.01 ± 0.08	1.01 ± 0.08

^a The mean spread in each set of observations is 0.002 cm^{-1} . Thus, the uncertainty in each measurement given is taken to be $\pm 0.001 \text{ cm}^{-1}$, except in the case of the weak $3d^8 4s^2 - 3d^8 4p$ transitions where it is $\pm 0.002 \text{ cm}^{-1}$. The average number of independent measurements contributing to each of the 58-60, 60-62, 62-64, and 58-64 shifts is 3, 2, 4, and 4, respectively. Different independent measurements here denote values of the shift obtained from measurements on different plates.

^b Since the error limits on the ratios increase as the shifts decrease, the ratios of the shifts are given only when $|58-64| > 0.04 \text{ cm}^{-1}$.

In this investigation the contribution of a field effect to the observed shifts in Ni has been established. By considering the deviations of the ratios of the shifts between adjacent pairs of even isotopes from those predicted by the mass effect, it has been possible to determine the relative, but not the absolute, field effect among the Ni isotopes. In this case the absolute field effect is defined as the field shift between two isotopes given explicitly in cm^{-1} , while the relative field effect is defined as only the difference in the field shifts between different pairs of isotopes. It is possible to determine the absolute field effect only if the mass effect is negligible or if the mass effect can be calculated explicitly. In general, neither of these situations holds for the elements of intermediate mass. However, knowledge of the relative field effect can be useful in the determination of nuclear properties, as will be pointed out later. This investigation has also shown that for certain types of transitions the specific mass effect is the principal cause of isotope shift in Ni. This conclusion agrees with other isotope shift investigations on elements in this part of the periodic table.^{1,2}

¹ S. Wagner, Z. Physik **141**, 122 (1955).

² M. F. Crawford, W. M. Gray, F. M. Kelly, and A. L. Schawlow, Can. J. Research **A28**, 138 (1950).

EXPERIMENTAL PROCEDURE

The apparatus consisted of a Fabry-Perot etalon mounted externally in front of a Littrow-type quartz spectrograph. The Fabry-Perot plates were coated with dielectric multilayer coatings consisting of alternate layers of antimony trioxide and cryolite with a maximum measured coefficient of reflection of 87% at $28\,000 \text{ cm}^{-1}$. To ensure constancy of optical conditions during a set of exposures the interferometer was enclosed in a gas-tight chamber and the experiment was carried out in a room in which the temperature stayed nearly constant for periods of many hours. Spacers of 10, 15, and 25 mm were used in the Fabry-Perot etalon.

Samples of highly enriched Ni isotopes ($A=58, 60, 61, 62, 64$), obtained in the form of NiO from the Oak Ridge National Laboratory, were excited in hollow cathode tubes which are a modification of an earlier design.³ (A description of this modified design is to be published later.) Each of the tubes was charged with 5 mg of an enriched isotope and gave a strong Ni spectrum for several hours when operated at a current

³ H. Kopfermann, H. Krüger, and H. Öhlmann, Z. Physik **126**, 760 (1949).

of 10–20 ma. Neon was used as the carrier gas and the tubes were cooled in liquid air during operation. Each of the samples of an even isotope had a purity greater than 95%; the Ni⁶¹ sample had a purity of 83%. Thus, only in the case of the Ni⁶¹ was the contamination of other isotopes an important factor.

The spectra of three different isotopes could be recorded on a single plate by moving the plateholder between exposures. An exposure of a Hg¹⁹⁸ lamp was superposed on each of the nickel spectra and was used as a check on the constancy of the optical conditions. The arrangement was such that the time lapse from the end of one exposure to the beginning of an exposure on the same plate of a different Ni isotope was only a few minutes. Measurements were made only of the shifts between isotopes whose spectra were recorded on the same plate. Measurements were made only on lines in the region 25 000 to 30 000 cm⁻¹.

RESULTS

The isotope shift in 31 lines was measured with the results tabulated in Table I. The sign convention used is that which denotes the direction of the normal mass shift as positive. All of the shifts are given in units of millikaysers (1 mkyser=0.001 cm⁻¹). Most of the

TABLE II. Relative level shifts in nickel as deduced from the observed line shifts and grouped according to configuration.

Configuration	Level	Level value in cm ⁻¹	Level shift	Normal shift	Residual shift
			58–64	(in 10 ⁻³ cm ⁻¹) 58–64	58–64
3d ⁸ 4s ²	³ F ₄	0	0 ^a	54.2	-54
3d ⁸ 4s ²	³ F ₃	1332	1	53.0	-52
3d ⁸ 4s ²	³ F ₂	2216	-1	52.5	-54
3d ⁹ 4s	³ D ₃	205	-170	54.0	-224
3d ⁹ 4s	³ D ₂	880	-170	53.5	-224
3d ⁹ 4s	³ D ₁	1713	-171	52.7	-224
3d ⁹ 4s	¹ D ₂	3410	-174	51.2	-225
3d ⁸ 4s4p	⁵ D ₄	25 754	-58	31.5	-90
3d ⁸ 4s4p	⁵ D ₃	26 666	-57	30.7	-88
3d ⁸ 4s4p	⁵ D ₂	27 415	-60	30.0	-90
3d ⁸ 4s4p	⁵ G ₅	27 580	-60	29.9	-90
3d ⁸ 4s4p	⁵ G ₄	28 068	-61	29.5	-91
3d ⁸ 4s4p	⁵ F ₅	28 542	-62	29.0	-91
3d ⁸ 4s4p	⁵ G ₃	28 578	-62	29.0	-91
3d ⁸ 4s4p	⁵ F ₄	29 084	-113	28.6	-142
3d ⁸ 4s4p	⁵ F ₃	29 833	-82	28.0	-110
3d ⁹ 4p	³ P ₂	28 569	-219	29.0	-248
3d ⁹ 4p	³ F ₃	29 321	-187	28.4	-215
3d ⁹ 4p	³ F ₄	29 481	-151	28.2	-179
3d ⁹ 4p	³ P ₁	29 501	-218	28.2	-246
3d ⁹ 4p	³ D ₃	29 669	-173	28.0	-201
3d ⁹ 4p	³ D ₂	29 889	-178	27.9	-206
3d ⁹ 4p	³ P ₀	30 192	-221	27.6	-249
3d ⁹ 4p	³ F ₂	30 619	-183	27.2	-210
3d ⁹ 4p	³ D ₁	30 913	-167	27.0	-194
3d ⁹ 4p	¹ F ₃	31 031	-200	26.9	-227
3d ⁹ 4p	¹ D ₂	31 442	-193	26.5	-220
3d ⁹ 4p	¹ P ₁	32 982	-230	25.2	-255

^a The shift in this level is arbitrarily set equal to zero.

measurements were made on the photoelectric comparator at the Argonne National Laboratory.⁴ This comparator was recently modified so that the measurements can be recorded on IBM-cards, thus facilitating reduction of the data. There was no error analysis made other than giving the mean spread in the measurements as indicated in Table I. Since each of the shifts between adjacent even isotopes was measured directly, it is not necessary that the sum of the partial shifts in Table I be equal to the 58–64 shift, which was also measured directly.

It is more important to consider the relative level shifts than the line shifts. From the tabulated line shifts the relative level shifts were deduced by arbitrarily assigning a zero shift to one of the levels. This choice is arbitrary since the actual level shifts cannot be determined. The deduced level shifts are tabulated in Table II, which indicates only the gross features of the relative shifts. The detailed features of the relative spacings between adjacent pairs of even isotopes will be considered later in terms of the ratios given in Table I.

The normal mass shift ΔT in a level is calculated by using the relation $\Delta T/T = m\Delta M/M_1M_2$, where T is the term value in cm⁻¹ of the level as measured from the ionization limit, m is the electron mass, M_1 and M_2 are the isotopic masses, and ΔM is the mass difference of the isotopes. The normal mass shift in a line is just the difference of the normal shifts in the corresponding levels. The residual shifts in Table I, obtained by subtracting the calculated normal mass shifts from the measured shifts, can then be attributed to the specific mass and field effects.

DISCUSSION OF RESULTS

There are a number of interesting features which are apparent from a study of Table I. Some of the features are present as regularities in the observed shifts, while some of the more interesting features are apparent deviations from regularity.

Some of the observed regularities are the following: (1) Large negative shifts occur in lines resulting from transitions from the d^8sp to the d^9s configuration. (2) Very large positive shifts occur in lines resulting from transitions from the d^9p to the d^8s^2 configuration. (3) There are relatively small shifts in lines arising from transitions from the d^9p to the d^9s configuration. (4) The shifts in the transitions from the d^8sp ⁵L levels ($L=D, G$) to levels of the d^8s^2 configuration are approximately equal. (5) The shifts in the transitions from the d^9p ³P levels to the d^9s ³D levels are approximately equal.

Some of the apparent deviations from regularity are as follows: (1) There are differences in the observed shifts in lines resulting from transitions from the various d^9p ³L and d^9p ¹L levels ($L=D, F$) to the d^9s levels. (2) There are differences in the shifts in lines of transitions from the d^8sp ⁵F_J terms ($J=3, 4, 5$) to lower levels

⁴ F. S. Tomkins and M. Fred, J. Opt. Soc. Am. 41, 641 (1951).

having the same level shift. (3) There are deviations in the ratios of the observed shifts from the ratios predicted by the mass effect theory.

The regularities in the observed wave number shifts noted above are more easily seen by considering the relative residual level shifts given in Table II. As indicated earlier, only the differences between the residual shifts have meaning. Table II shows a clear distinction between the "complex" d^8sp and d^8s^2 configurations and the two-electron configurations d^9p and d^9s . It will be shown that this distinction must arise because of the specific mass effect.

On the basis of volume effect calculations, it was possible to estimate roughly the size of the field effect shift in nickel due to one $4s$ electron, neglecting the effect of the $4p$ electron. It was assumed that the charge is distributed uniformly in the nucleus and that the nuclear radius $r_0 = R_0 M^{1/3}$, where $R_0 = 1.20 \times 10^{-13}$ cm and M is the mass number. Calculations based on these assumptions lead to a field shift between Ni^{58} and Ni^{64} of about -0.02 cm^{-1} for one $4s$ electron. This value is probably an upper limit since the observed shifts in heavy elements are generally less than the calculated shifts based on this model. A study of Table I shows clearly that the residual shifts cannot be accounted for solely by this field effect shift and hence the specific

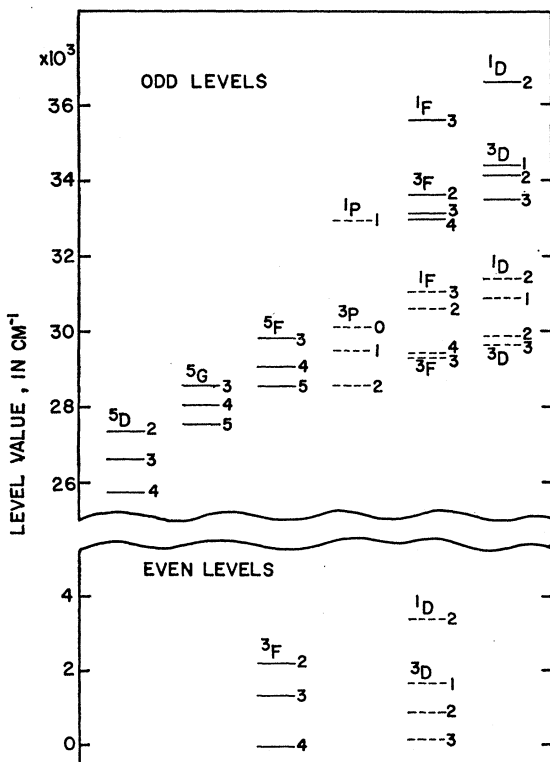


FIG. 1. Energy level diagram of nickel. The simple configurations $3d^94s$ and $3d^94p$ are shown by dashed lines; the complex configurations $3d^84s^2$ and $3d^84s4p$ (only partly recorded) by full lines.

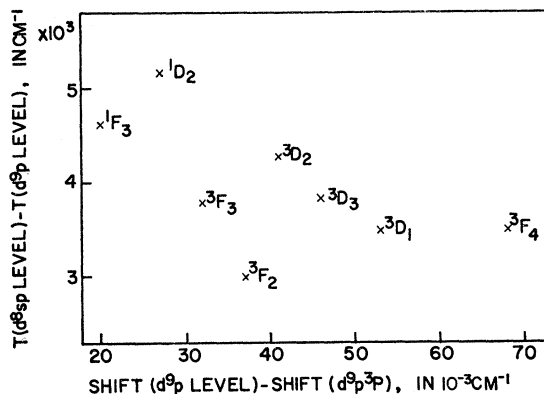


FIG. 2. Shifts of perturbed $3d^94p$ levels relative to the shift of the unperturbed $3d^94p \ ^3P$ term. The differences of the level values of interacting levels are given on the vertical axis.

mass shift is a significant factor. For transitions of the type $d^9s - d^8sp$ the resultant field shift is zero and the residual shift is due entirely to the specific mass effect. For the remaining transitions the sign of the residual shift is generally opposite to that of the field shift and so the specific mass shift must be a significant part of the residual shift. In particular, for transitions between one of the complex configurations and one of the two-electron configurations the specific mass effect is dominant.

Calculations of the relative specific shifts in the configurations of nickel were made following the procedure described by Vinti.⁵ In the case of nickel the calculated specific shift is the same for all the terms of the $3d^94s$ configuration. It is also the same for each of the quintet terms of the $3d^84s4p$ configuration. In addition, the specific shift is the same for all the terms of the $3d^94p$ configuration except for the 1P term. These statements are true on the assumption that LS coupling describes the terms. A study of levels of these configurations by Mack⁶ indicates that the coupling scheme is nearer to LS coupling than to jj coupling. The residual shifts tabulated in Table II indicate agreement with these predictions except for the terms $d^8sp \ ^5F$, $d^9p \ ^3F$, $d^9p \ ^3D$, $d^9p \ ^1F$, and $d^9p \ ^1D$. The discrepancies for these terms can be accounted for entirely on the basis of perturbations due to interconfiguration interactions.

According to second-order perturbation theory the necessary conditions for interaction between two nearby atomic states are that these states have the same J value and same parity. The effect is greatest when these states have the same L and S values in LS coupling and results in a mixing of the properties of the states. Study of the energy level diagram for nickel in Fig. 1 indicates that under the assumptions of the two conditions above, the following terms should be essentially unperturbed: $3d^94s \ ^3D$, 1D , $3d^84s^2 \ ^3F$, $3d^84s4p \ ^5D$, 5F , 5G , and $3d^94p \ ^3P$, 1P . The results in Table II combined with

⁵ J. P. Vinti, Phys. Rev. **56**, 1120 (1939).

⁶ J. E. Mack, Phys. Rev. **34**, 17 (1929).

the predictions of the specific effect theory stated above do indicate that all of these terms except the 5F can be considered as unperturbed. This apparent exception of the 5F term will be considered below. Those terms which Fig. 1 indicates are perturbed are the $3d^94p\ {}^3F$, 3D , 1F , 1D terms. This is shown by the presence of nearby terms arising from the $3d^84s4p$ configuration which can perturb those $3d^94p$ terms. Since there are no nearby states which can perturb the $3d^94p\ {}^3P$ and $3d^84s4p\ {}^5G$ terms, it is possible to use the relative shifts in these unperturbed terms as a basis for comparison. Table II shows that the shifts of the perturbed levels of these configurations lie between the shifts of the two unperturbed terms noted above.

Since the interaction between two states varies inversely as the energy difference, the result is that the shift of a level of the $3d^94p$ configuration lying nearest its perturbing level is changed the most with respect to the shift of the unperturbed term $3d^94p\ {}^3P$. This effect is clearly shown in the plot in Fig. 2. The upward displacement of the points for the D terms relative to the points for the F terms can be attributed to different interaction matrices for the terms of different L value. The point for the 3F_4 level does not fall where expected. This is explained by an interaction between the $3d^94p\ {}^3F_4$ and $3d^84s4p\ {}^5F_4$ levels. This also explains the relative shift of the 5F_4 level as compared with that of the unperturbed $3d^84s4p\ {}^5G$ term. A small effect is also indicated between the $3d^94p\ {}^3F_3$ and $3d^84s4p\ {}^5F_3$ levels. By comparison the shift in the $3d^84s4p\ {}^5F_5$ level should be the same as that of the 5G term and this is indeed the case.

The final feature noted at the beginning of this section is the deviation of the ratios of the observed shifts from the ratios expected if the shifts were due only to the mass effect. By ascribing these deviations to the field effect it has been possible to deduce the

relative field effect shift, that is, the difference in the field shift between levels of different pairs of adjacent even isotopes. According to the theory of the mass effect, both normal and specific, the relative line shifts are given⁷ by the relation $\Delta\sigma_{12}/\Delta\sigma_{23} = M_3/M_1$, where $\Delta\sigma_{12}$ is the line shift between isotopes of mass numbers M_1 and M_2 , $\Delta\sigma_{23}$ the shift between isotopes of mass numbers M_2 and M_3 , and $M_1 - M_2 = M_2 - M_3$. According to this relation the line shifts for nickel should be in the following ratios: $(58-60)/(62-64) = 62 \cdot 64/58 \cdot 60 = 1.14$; $(60-62)/(62-64) = 64/60 = 1.07$. If the measured shifts satisfy these relations, then it can be assumed that the shifts due to the field effect are negligible. A study of Table I shows clearly that, well within the experimental error, ratios different from 1.14 are obtained for 3 of the 4 transition types. Another feature is that for 2 of these transition types, d^9s-d^9p and $d^8s^2-d^8sp$, the 58-60 difference is a smaller positive number than the 62-64 difference. This is important because the differences are significant even though the ratios are meaningless for those lines whose total shift is small. For transitions of the type d^9s-d^8sp the resultant field effect is zero and the measured $(58-60)/(62-64)$ ratios roughly agree with 1.14. The disagreements with the number 1.14 occur in transitions where the lower electron configuration has 1 or 2 more s electrons than the upper configuration.

As the total shift in a line increases, due to an increase of the mass effect, the relative effect of a given superposed field shift will be less. Thus, the ratios of the shifts will be nearer to the ratios predicted by the mass effect theory when the mass shift is relatively larger than the field shift. This explains the small effect of the field shift due to two s electrons on the ratios of shifts of the transition type $d^8s^2-d^9p$, as compared with the effect of one s electron on the ratios for the transitions d^9s-d^9p and $d^8s^2-d^8sp$.

It is not possible to determine uniquely both the relative spacings between adjacent isotopic levels and the total shift due to the field effect. The procedure used was to assume a certain total field shift S_F and to determine the relative spacings for this total shift. This evaluation was then carried out for different assumed values of S_F . The observed shift between Ni^{58} and Ni^{64} is $S = S_M + S_F$, where S_M is the mass shift, S_F is the field shift due to one or two $4s$ electrons, and where $S_M > 0$, $S_F < 0$. A schematic diagram of the shift is shown in Fig. 3 from which it is clear that if $S = S_M + S_F$, then $S = (A+a) + (B+b) + (C+c)$. Since for a particular transition type S is known and a value of S_F is assumed, S_M is also determined. The values of A , B , and C can now be found since $A/C = 1.14$, $B/C = 1.07$. Various combinations of a , b , and c (for fixed S_F) are now combined with the known A , B , and C to obtain the ratios $(A+a)/(C+c)$ and $(B+b)/(C+c)$ which can be compared with the measured

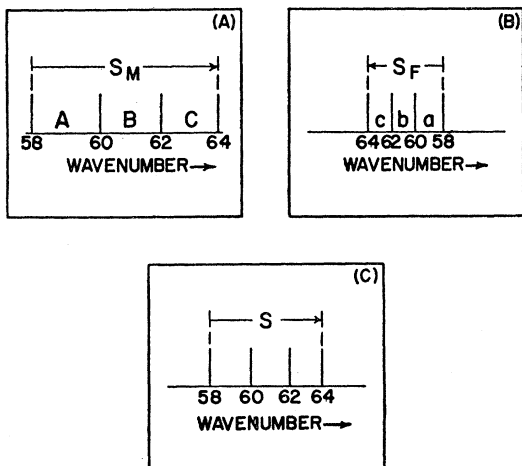


FIG. 3. Schematic breakdown of the isotope shift in nickel. In (A), S_M is the line shift due to the mass effect only, $S_M > 0$; In (B), S_F is the line shift due to the field effect only, $S_F < 0$; In (C), S is the observed line shift, $S = S_M + S_F$.

⁷H. Kopfermann, *Nuclear Moments* (Academic Press, Inc., New York, 1958), 2nd ed.; English translation, p. 165.

TABLE III. Summary of field effect calculations as derived from the ratios of measured shifts.

Transition	Total ^a shift S	Mass shift S_M	Field shift S_F	a^b	b	c	Deduced	Meas. ^c	Deduced	Meas. ^c
	(in 10^{-3} cm^{-1})						(58-60)/ (62-64)	(58-60)/ (62-64)	(60-62)/ (62-64)	(60-62)/ (62-64)
$d^3_s \ ^3D - d^3_p \ ^3P, \ ^1P$	49	84	-35	-15	-10.5	-9.5	0.83	0.84 ± 0.11	1.02	1.04 ± 0.13
$d^8_{s^2} \ ^3F - d^8_{sp} \ ^5D, \ ^5G$	61	96	-35	-15	-10.5	-9.5	0.94	0.91 ± 0.09	1.05	1.02 ± 0.10
$d^8_{s^2} \ ^3F - d^8_p \ ^3D$	171	241	-70	-30	-21	-19	0.99	1.01 ± 0.07	1.06	1.01 ± 0.07
$d^3_s \ ^3D - d^3_p \ ^3P, \ ^1P$	49	74	-25	-12	-7	-6	0.84	0.84 ± 0.11	1.04	1.04 ± 0.13
$d^8_{s^2} \ ^3F - d^8_{sp} \ ^5D, \ ^5G$	61	86	-25	-12	-7	-6	0.91	0.91 ± 0.09	1.06	1.02 ± 0.10
$d^8_{s^2} \ ^3F - d^8_p \ ^3D$	171	221	-50	-24	-14	-12	0.96	1.01 ± 0.07	1.05	1.01 ± 0.07
$d^3_s \ ^3D - d^3_p \ ^3P, \ ^1P$	49	64	-15	-8	-4	-3	0.87	0.84 ± 0.11	1.02	1.04 ± 0.13
$d^8_{s^2} \ ^3F - d^8_{sp} \ ^5D, \ ^5G$	61	76	-15	-8	-4	-3	0.92	0.91 ± 0.09	1.03	1.02 ± 0.10
$d^8_{s^2} \ ^3F - d^8_p \ ^3D$	171	301	-30	-16	-8	-6	0.98	1.01 ± 0.07	1.04	1.01 ± 0.07

^a The number of line shifts from which this average S is derived is 4, 6, and 2, respectively, for the transition types $d^3_s - d^3_p$, $d^8_{s^2} - d^8_{sp}$, and $d^8_{s^2} - d^8_p$.

^b The values of a , b , and c are the assumed intervals due to the field effect only for 58-60, 60-62, and 62-64, respectively.

^c The measured ratio given is the mean of the ratios of the corresponding transitions used.

ratios. These values of a , b , and c are combined with each of the three different S_M (one for each transition type) and varied until the best fit is obtained with the ratios of all three of the transition types whose relative shifts are affected by the field effect. The results of this procedure are summarized in Table III for each of three different assumed values of S_F . The values of a , b , and c given in Table III can be changed by $\pm 0.0005 \text{ cm}^{-1}$ without altering the ratios drastically.

Within the experimental error of the measured ratios, the deduced field effect in Table III shows the following features: (1) On account of the field shift only, the (60-62) interval is about 0.001 cm^{-1} larger than the (62-64) interval. (2) The (58-60) interval is substantially larger than the (60-62) interval, the difference being $0.0045 \pm 0.001 \text{ cm}^{-1}$.

According to nuclear shell theory⁸ the neutron shell from $N=28$ to $N=50$ is expected to be filled in the following order: $3p_{3/2}$, $4f_{5/2}$, $3p_{1/2}$, and $5g_{3/2}$. The two neutrons added to Ni^{58} to form Ni^{60} complete the $p_{3/2}$

subshell, while the subsequent neutrons added to form Ni^{62} and Ni^{64} are $f_{5/2}$ neutrons. This theory and the results on the relative field effect above suggest that the relatively larger (58-60) interval is due to the differences of outermost neutrons between the various isotopes. No calculations have been carried out with respect to this suggestion.

The hyperfine structure of Ni^{61} was not resolved. The isotope shift between Ni^{61} and the neighboring even isotopes was measured for 16 lines. The measurements are more uncertain than those between lines of even isotopes because of the unresolved hyperfine structure but within the experimental error the levels of Ni^{61} lie midway between the levels of Ni^{60} and Ni^{62} .

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⁸ M. G. Mayer and H. D. Jensen, *Elementary Theory of Nuclear Shell Structure* (John Wiley & Sons, Inc., New York, 1955), p. 58.