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Hyperfine Interactions and Relaxation Effects in Laves-Phase Intermetallic Compounds of Neptunium

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Studies of magnetic properties of cubic Laves-phase compounds of Np have been performed using the Mössbauer effect of the 59.5-keV transition in ^{237}Np. The compounds studied were $NpAl_2$, $NpCo_2$, $NpNi_2$, $NpFe_2$, and $NpIr_2$. Hyperfine-interaction parameters and ordering temperatures were deduced from these measurements. If the values of $H(T)/H(0)$ are plotted as a function of T/T_C, the points (except those of $NpFe_2$) lie on the molecular-field-theory curve for $S=1/2$. Quadrupole interactions were found to be very small. This behavior is consistent with the assumption that the ground crystalline state in these compounds is an isolated Kramers doublet. Relaxation phenomena were observed in the spectra. The spectra could be fitted by assuming relaxation effects within the Kramers doublet with a relaxation time of $\sim 4\times 10^{-11}$ sec. Isomer shifts were measured and found to change regularly with the size of the unit cell.

I. INTRODUCTION

A detailed study of the magnetic properties of cubic Laves-phase intermetallic compounds of neptunium has been performed utilizing the Mössbauer effect of the 59.5-keV transition in ^{237}Np. Recoilless absorption spectra were obtained for NpM_2 (M = Al, Co, Ni, Fe, Ir) compounds at various temperatures from 1.9 K to above the respective ordering temperatures. From the spectra obtained, the magnetic hyperfine fields acting on the ^{237}Np nuclei in the various compounds at different temperatures and the ordering temperatures could be determined. The fields at magnetic saturation were found to vary significantly from one compound to the other. The diversity of the values found for the hyperfine fields indicates that the behavior of the $5f$ ions is quite different from that of the $4f$ (rare-earth) ions in similar compounds. In the rare-earth region, the crystalline-electric-field interactions are weak relative to the spin-orbit interaction and J is a good quantum number. In ordered rare-earth intermetallic compounds at low temperatures the exchange interaction is usually stronger than the crystalline-field interaction and the ground state of the rare-earth ion is almost a pure $J_z=J$ state. This leads to an effective magnetic field at the nucleus, which is close to the free-ion field. In the actinide compounds, on the other hand, the exchange interaction is usually not large compared to the crystalline-field interaction. The hyperfine field may depend therefore on the size of the crystalline-field parameters B_4 and B_6 and on the size of the exchange field. The crystalline-field interactions are expected to be not very weak compared to the spin-orbit interaction and J mixing might be present in the various ionic levels. The situation in Np (and other actinide) metallic compounds might even be more complicated. For compounds with relatively small Np-Np distances (as, e.g., in α-Np),[1] the $5f$ electrons are probably not localized, but are hybridized into rather wide conduction bands.[2] In such cases the Np ions may even lose their paramagnetic character. In addition, in magnetic metallic compounds, one should expect a contribution to the hyperfine fields from polarized conduction electrons, which might be quite large and different in the various compounds. It is therefore not surprising that the hyperfine fields vary significantly from one Np compound to the other.

In the experimental spectra obtained in the present work, some of the individual absorption lines are significantly broadened and indicate clearly the existence of relaxation phenomena. The spectra cannot be fitted assuming the existence of one static effective magnetic field acting on the Np nuclei. *A priori*, very little is known about the nature of the ionic levels associated with the observed relaxation phenomena. We have therefore used in the first stage a general relaxation model described by Wegener[3] for the analysis of the experimental spectra. In this model, no specific assumptions concerning the character of the ionic levels are made. Relatively good fits to the experimental spectra were obtained using this model. This model introduces an average time-independent field H_{eff} and a time-dependent fluctuating field $h(t)$ so that the field acting on any nucleus at any time is given by $H(t)=H_{\text{eff}}+h(t)$. It is based on the following three assumptions: (i) The influence of the nuclear spin on the ionic spin is negligible. This is, in fact, the assumption of the validity of the effective-field approximation. (ii) The precession of the electronic spin around the direction of the external (or exchange) field is so fast, that only the component of the internal field in the direction of the external (or exchange) field acts on the nucleus. This assumption is equivalent to taking into account instantaneous fluctuations of the longitudinal hyperfine field only, and neglecting transverse fluctuating hyperfine fields. (iii) Relaxation times are short compared to the nuclear Larmor time: $\nu(m_e, m_0)H_{eff}\tau/h \ll 1$, where $\nu(m_e, m_0) = (g_e m_e - g_0 m_0)\mu_N$, g_e and g_0 are the nuclear g factors, and m_e and m_0 are the magnetic quantum numbers of the excited and ground nuclear levels, respectively. μ_N is the nuclear magneton and h is the Planck constant. According to this model, the recoilless absorption spectrum is a superposition of lines of Lorentzian shape, the positions of which are given by

$$E(m_e, m_0) = E_0 - \nu(m_e, m_0)H_{eff} + \Delta(m_e, m_0) \ , \quad (1)$$

where E_0 is the nuclear transition energy taking into account isomer shifts and possible quadrupole interactions, ν and H_{eff} were defined before, and $\Delta(m_e, m_0)$ is an energy shift of the line caused by relaxation phenomena. The intensity of each absorption line is proportional to the square of the appropriate Clebsch–Gordan coefficient for the (m_e, m_0) transition, and the full width at half-maximum (FWHM) of each line is given by

$$\Gamma = \Gamma_0 + \gamma_L(m_e, m_0), \quad (2)$$

where Γ_0 is the FWHM of a Mössbauer absorption line in the absence of relaxation broadening and

$$\gamma_L(m_e, m_0) = 2\nu^2(m_e, m_0)\langle h_L^2\rangle \tau_L/\hbar \quad (3)$$

is the broadening of the individual absorption lines caused by relaxation effects. $\langle h_L^2\rangle$ is the average of the square of $h_L(t)$ and τ_L is the relaxation time. $\Delta(m_e, m_0)$ was found to be negligible in all our spectra. (The same expressions were obtained by van der Woude and Dekker,[4] though they employed a different approach to deal with the relaxation phenomena.) Gabriel[5] and Levinson and Luban[6] used other approaches to include the effect of relaxation phenomena on recoilless absorption spectra. They arrive at explicit expressions for Mössbauer spectra for short relaxation times. The first assumption of Wegener is made by them too, but they drop Wegener's second assumption. They obtain, therefore, an additional broadening of the individual absorption lines caused by transverse relaxation processes. Following Wegener's notation of fluctuating fields $h(t)$ at the nucleus, we assume a longitudinal component $h_L(t)$ as defined above and a transverse component $h_T(t)$. If we denote the transverse relaxation time by τ_T, we then obtain, according to Gabriel[5] and Levinson and Luban,[6] an additional line broadening, given by

$$\gamma_T(m_e, M_0) = 2\mu_N^2 \langle h_T^2\rangle \tau_T [g_e^2(I_e^2 + I_e - m_e^2) + g_0^2(I_0^2 + I_0 - m_0^2)]/h, \quad (4)$$

where g_e, g_0, m_e, and m_0 were defined above and I_e and I_0 are the spins of the nuclear ground and excited state, respectively.

The expression for the line broadening as obtained by Gabriel[5] and Levinson and Luban[6] owing to longitudinal relaxation effects is identical to the expression derived by Wegener[3] and the total width of an absorption line is given by

$$\Gamma = \Gamma_0 + \gamma_L(m_e, m_0) + \gamma_T(m_e, m_0) . \quad (5)$$

It was found experimentally in the present work that γ_L is at least ten times larger than γ_T, but nevertheless, taking into account the transverse relaxation process in theoretically constructed spectra, improves somewhat the fit to the experimental spectra. Gabriel[5] finds also a small second-order energy shift, which was neglected by the authors. It is assumed to be very small in all cases and was not taken into account in our analysis.

From the analysis of the experimental spectra, the temperature dependence of H_{eff} for the various compounds could be determined. It was found that the temperature dependence for each of the compounds: $NpCo_2$, $NpIr_2$, $NpNi_2$, and $NpAl_2$ was to a good accuracy identical with that expected theoretically for an isolated Kramers doublet split by the magnetic exchange interaction. We have tried therefore to fit the experimental spectra by assuming relaxation within an isolated Kramers doublet. A least-square-fitting procedure based on the closed form relaxation formulas given by Nowik and Wickman[7] for the case of a Kramers doublet in a magnetically ordered compound was used. In order to explain the fact that even at low temperatures the spectra cannot be explained by one well-defined hyperfine magnetic field, we had to modify Nowik and Wickman's formulas. The nature of the modifications is discussed in Secs. II–IV.

II. EXPERIMENTAL DETAILS

The source used for the recoilless absorption measurements of the 59.5-keV γ ray of ^{237}Np was ^{241}Am in the form of 6-at.% Am in Th. This source gives, even at low temperatures, an unsplit emission line.[8] The narrowest absorption line obtained with the source had a FWHM of 1.7 mm/sec. It was obtained, for example, with the source at 4.2 K and a $NpIr_2$ absorber at 77 K.

The Np cubic Laves-phase compounds were prepared by arc melting stoichiometric amounts of the metals under a dry-argon atmosphere. Metallo-

TABLE I. Crystal parameters, isomer shifts, ordering temperatures, and hyperfine interaction constants of NpM_2 compounds.

Compound	Unit cell (Å)	Isomer shift[a] (cm/sec)	T_C (K)	$g_0\mu_N H_{eff}(0)/h$ (MHz)	$eqQ/4h$ (MHz)
$NpAl_2$	7.795 ± 0.005	0	57.0 ± 1.0	2570 ± 20	10 ± 10
$NpNi_2$	7.115 ± 0.005	−1.79 ± 0.04	28.0 ± 2.0	1960 ± 20	50 ± 25
$NpFe_2$	7.135 ± 0.005	−2.4 ± 0.1	>300	1420 ± 20	135 ± 20
$NpIr_2$	7.50 ± 0.01	−1.08 ± 0.04	5.8 ± 0.2	1040 ± 20	0 ± 10
$NpCo_2$	7.055 ± 0.005	−2.25 ± 0.04	8.4 ± 0.2	860 ± 10	20 ± 20

[a] Relative to $NpAl_2$. The isomer shift of $NpAl_2$ relative to NpO_2 is 0.61 ± 0.04 cm/sec.

graphic and x-ray-diffraction measurements showed that single phases were obtained. The lattice constants were determined and are summarized in Table I. The Np metal was produced by reducing NpF_4 with Ca metal.

The absorber material, in powder form, was embedded between two thin copper foils and encapsulated in a double Lucite container. The copper foils ensure the homogeneity of the absorber temperature. A 0.08-in.-diam gold-chromel thermocouple was embedded inside the absorber powder. The double Lucite container was used in order to minimize the possibility of any contaminations. All the absorbers were about 150 mg/cm thick.

Measurements were carried out for absorber temperatures between 1.9 and 125 K. The oven used for heating the absorber to temperatures above 4 K has been previously described.[9] The heating current was controlled by a temperature stabilizer. The temperature stability was better than ± 0.1 K. Temperatures below 4.2 K were obtained by pumping above liquid helium.

A constant-acceleration Mössbauer drive system was used. In measurements below 4.2 K the velocity was transferred into the cryostat through an "Edwards Wilson seal." Calibrations with a Co^{57} in Pt source and a Fe_2O_3 absorber, with and without the seal, proved that the seal did not have any effect on the motion of the source. The 59.5-keV

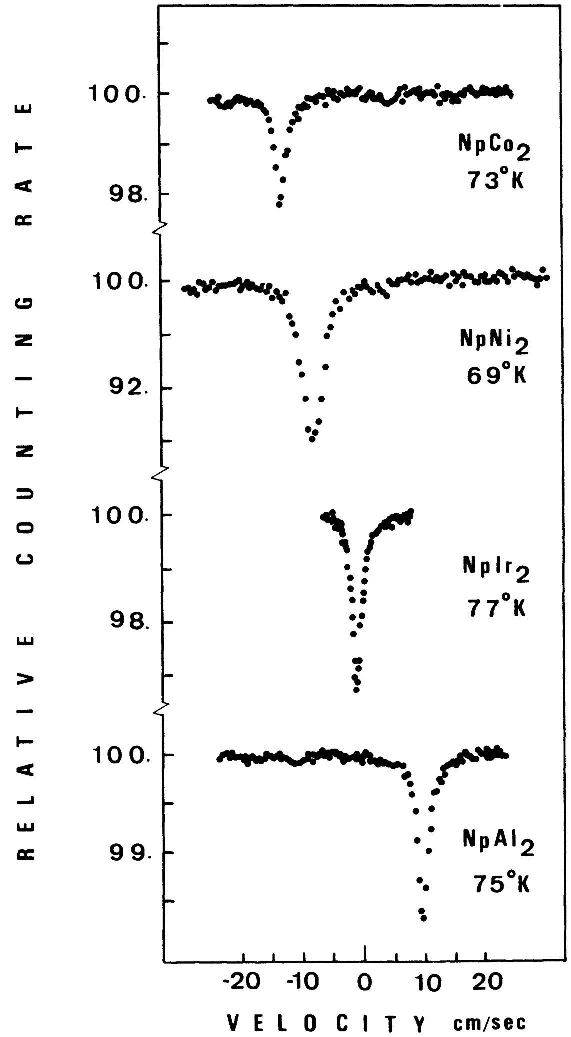

FIG. 1. Unsplit recoilless absorption spectra of the 59.5-keV γ rays of ^{237}Np in $NpCo_2$, $NpNi_2$, $NpIr_2$, and $NpAl_2$.

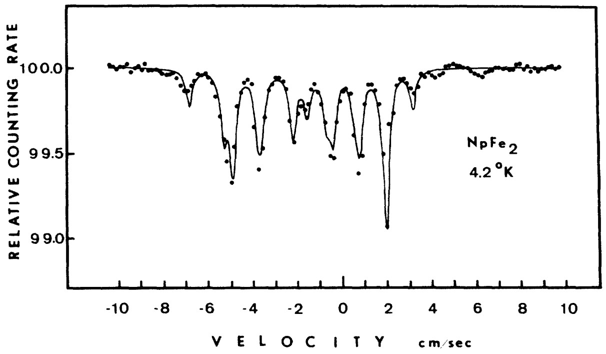

FIG. 2. Recoilless absorption spectrum of the 59.5-keV γ rays of ^{237}Np in $NpFe_2$ at 4.2 K. The solid line is the theoretical spectrum using the parameters given in Table I.

γ radiation was detected by a 3/8×2-in. NaI(Tl) scintillation counter with a Be window.

III. EXPERIMENTAL RESULTS

All the compounds investigated in the present work ($NpIr_2$, $NpCo_2$, $NpNi_2$, $NpFe_2$, and $NpAl_2$) were found to be magnetically ordered at low temperatures. The experimental spectra of $NpAl_2$ obtained in this work are very similar to those obtained previously by Dunlap *et al.*[10] and by Stone and Pillinger.[11]

The absorption spectra of $NpCo_2$, $NpNi_2$, $NpIr_2$, and $NpAl_2$ at temperatures above their respective ordering temperature are shown in Fig. 1. From these spectra the linewidths and isomer shifts were determined. The results obtained are summarized in Table I. Because of the high ordering temperature of $NpFe_2$, we could not carry out measurements above its Curie temperature. The isomer shift of $NpFe_2$ was determined from a split spectrum obtained at low temperatures. The spectrum of $NpFe_2$ at 4.2 K is shown in Fig. 2. The narrowest linewidth FWHM was obtained with the $NpIr_2$ absorber. Its FWHM was 1.71 ± 0.05 mm/sec. This is about 25 times the natural linewidth ($2\Gamma_0$) as calculated from the half-life of the 59.5-keV level of ^{237}Np. The FWHM obtained in $NpNi_2$ is more than twice the linewidth obtained in $NpIr_2$. This broadening is probably caused by relaxation times not fast enough to narrow the line to its natural width.

The isomer shifts of the NpM_2 compounds relative to a NpO_2 absorber are between $+0.61$ and -2.8 cm/sec (see Table I). If these shifts are compared to those obtained in Np salts,[12] it is seen that they lie between the regions corresponding to 4+ and 5+ charge states of Np. This tends to indicate that the Np ions in the Laves-phase intermetallic compounds are probably in a 4+ state,[10] the extra shift being caused by the conduction-electron density at the nucleus.

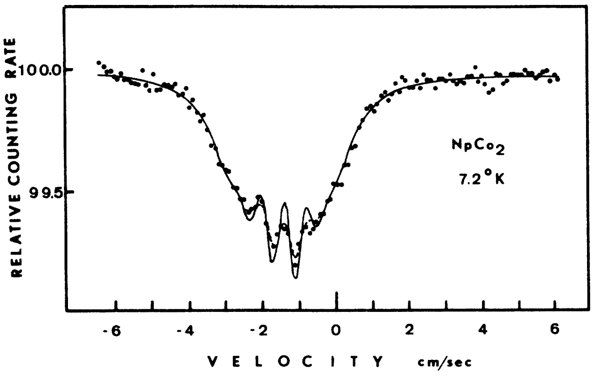

FIG. 3. Recoilless absorption spectrum in $NpCo_2$ at 7.2 K. The solid line is the best fit obtained using Wegener's theory. The dashed line is the best fit taking into account transverse relaxation effects.

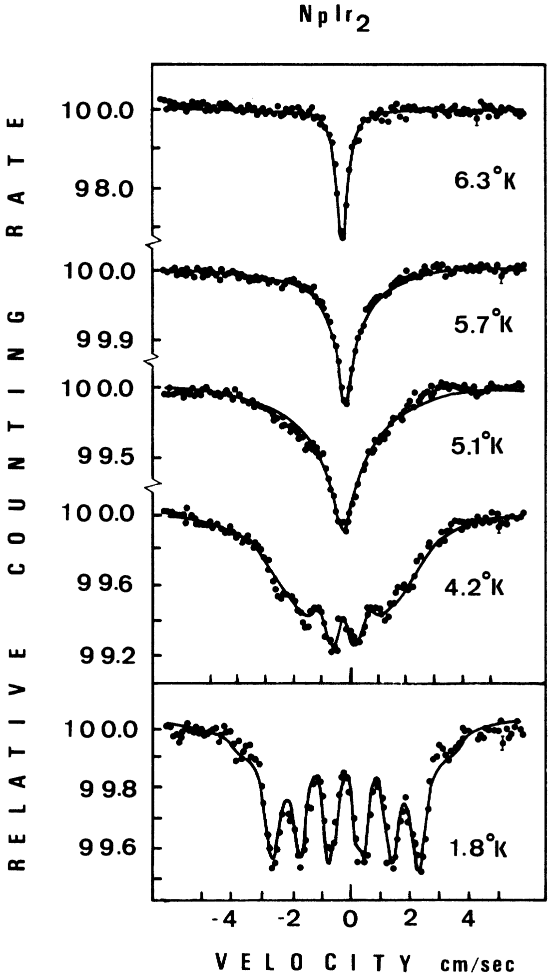

FIG. 4. Recoilless absorption spectra in $NpIr_2$. The solid lines are the theoretical best fits using Gabriel's theory. The parameters of the fits are given in Table II.

The shapes of most of the spectra clearly reveal the effects of relaxation phenomena. Only the $NpAl_2$ up to 25 K and $NpFe_2$ spectra at low temperatures could be fitted by assuming the existence of one static effective magnetic field and an electric field gradient (EFG) acting on the Np nuclei. Least-square computer fits to these spectra were performed: The position of a line corresponding to the transition between the sublevel m_e and the sublevel m_0 is

$$E(m_e, m_0) = \Delta E + \nu(m_e, m_0) H_{\text{eff}} + \frac{eQ_e[3m_e^2 - I_e(I_e+1)]}{4I_e(2I_e-1)} - \frac{eQ_0[3m_0^2 - I_0(I_0+1)]}{4I_0(2I_0-1)} , \quad (6)$$

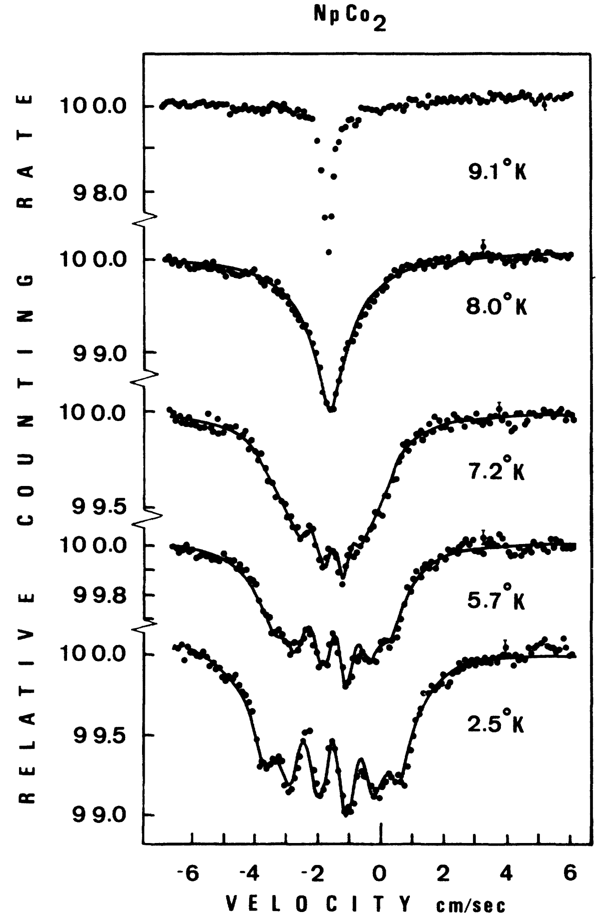

FIG. 5. Recoilless absorption spectra in NpCo$_2$. The solid lines are the theoretical best fits using Gabriel's theory. The parameters of the fits are given in Table III.

where Q_e and Q_0 are the quadrupole moments of the nuclear excited and ground states, respectively, ΔE is the isomer shift, H_{eff} is the magnetic hyperfine field, and q is the EFG acting on the Np nuclei. All other parameters were defined in Sec. I. In the analysis, the values of g_e/g_0 were taken as 0.537 and the value of Q_e/Q_0 was taken as 1.0.[11] Nuclear-polarization effects (the different population of the nuclear levels at low temperatures) were taken into account in all fittings.

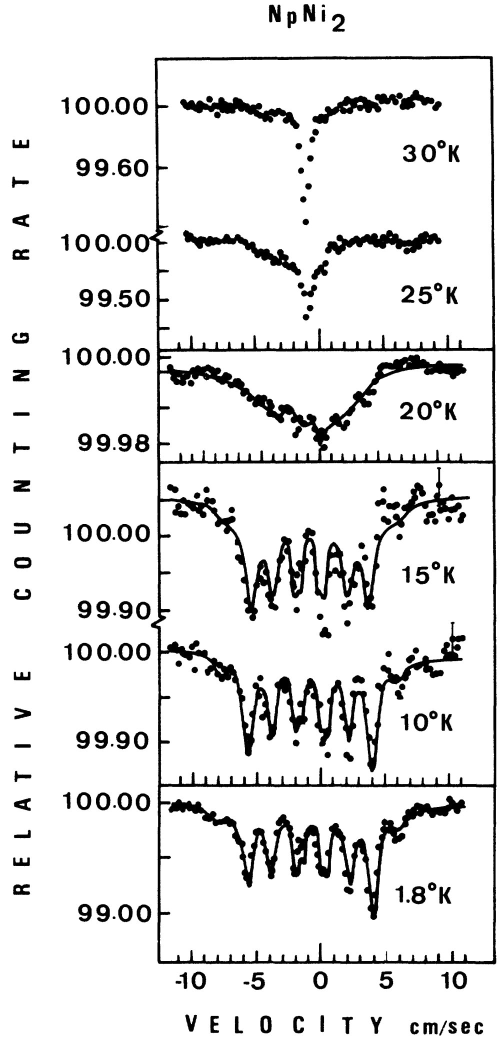

FIG. 6. Recoilless absorption spectra in NpNi$_2$. The solid lines are the theoretical best fits using Gabriel's theory. The parameters of the fits are given in Table IV.

For the least-square fits to all other experimental spectra, relaxation phenomena had to be taken into account. The experimental spectra were first analyzed by applying the theory developed by Wegener,[3] discussed in Sec. I. The fits obtained using Wegener's theory were quite good (for example,

TABLE II. Hyperfine interaction and relaxation parameters of NpIr$_2$.

T (K)	$g_0\mu_N H_{eff}/h$ (MHz)	$\nu_{0L}^2\tau_L$ (MHz)	$\nu_{0T}^2\tau_T$ (MHz)	$eqQ/4h$ (MHz)	$\frac{T}{T_C}$	$\frac{H(T)}{H(0)}$
1.9	1040 ± 20	120 ± 15	2.5 ± 1.0	0 ± 10	0.33 ± 0.02	1.00 ± 0.02
2.6	1040 ± 20	140 ± 20	2.5 ± 1.0	0 ± 20	0.45 ± 0.03	1.00 ± 0.02
4.2	840 ± 20	430 ± 40	15 ± 2	5 ± 20	0.72 ± 0.03	0.81 ± 0.03
5.1	580 ± 140	1250 ± 300	40 ± 10	...	0.88 ± 0.04	0.56 ± 0.15
5.7	~40	...	...	...	0.98 ± 0.05	~0.04

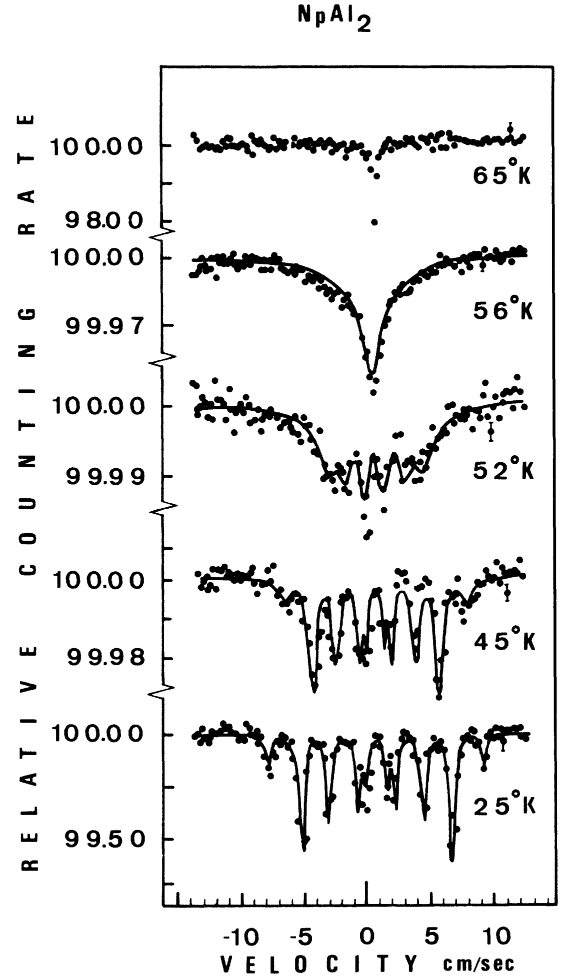

FIG. 7. Recoilless absorption spectra in NpAl$_2$. The solid lines are the theoretical best fits using Gabriel's theory. The parameters of the fits are given in Table V.

the solid line in Fig. 3), but Γ_0 could not be kept constant for the various spectra analyzed. By including transverse relaxation effects, as suggested by Gabriel[5] and Levinson and Luban,[6] Γ_0 could be kept constant and somewhat better fits were obtained (for example, the dashed line in Fig. 3). The solid lines in Figs. 4–7 are the theoretical spectra obtained by least-square fitting to the experimental spectra, using Eqs. (3)–(6) given in Sec. I. From these least-squares fits, the following parameters were deduced: $g_0\mu_N H_{\text{eff}}$, $\frac{1}{4}eqQ$, $4\pi g_0^2 \mu_N^2 \langle h_L^2 \rangle \tau_L / h^2 = \nu_{0L}^2 \tau_L$, and $4\pi g_0^2 \mu_N^2 \langle h_T^2 \rangle \tau_T / h^2 = \nu_{0T}^2 \tau_T$. The values of these parameters are summarized in Tables II–V. The same values for $g_0\mu_N H_{\text{eff}}$ and $\frac{1}{4}eqQ$ were obtained using either Wegener or Gabriel's methods of analysis. $\nu_{0T}^2 \tau_T$ is always much smaller than $\nu_{0L}^2 \tau_L$.. As can be seen from Figs. 4–7 the fits are quite good, though some of them are not perfect. In Table I, the values of the hyperfine constants at 0 K (obtained by extrapolation) are summarized. As seen from Table I, the quadrupole interactions are very small in NpAl$_2$, NpIr$_2$, NpCo$_2$, and NpNi$_2$ and are larger in NpFe$_2$. The point symmetry of the Np nuclei in the Laves compounds is cubic, so that only the polarized 5f electrons may contribute to the electric field gradients. The magnetic fields at the Np nuclei are very different in the various compounds. The largest field (which is about half of the free-ion value for Np^{4+}) is obtained in NpAl$_2$. This field is about three times as large as the field in NpCo$_2$ at 1.9 K.

In Figs. 8 – 10, the values of $g_0\mu_N H_{\text{eff}}$ and the values of $\nu_{0L}\tau_L$ are plotted as a function of temperature. From these figures the ordering temperature of the various compounds and the effective magnetic fields at 0 K, as summarized in Table I, were determined. As can be seen from Tables II – V and Figs. 8 – 10, $\nu_{0L}^2 \tau_L$ rises first slowly with temperature. Near the ordering temperature a sharp increase of this parameter is seen. The increase of the parameter is probably due to the increase of the time-dependent fluctuation field. In Fig. 11 the reduced effective fields $[H(T)/H(0)]$ are plotted as a function of the reduced temperature T/T_C, where T_C is the magnetic ordering temperature. As seen from Fig. 11, all points lie within

TABLE III. Hyperfine interaction and relaxation parameters for NpCo$_2$.

T (K)	$g_0\mu_N H_{\text{eff}}/h$ (MHz)	$\nu_{0L}^2 \tau_L$ (MHz)	$\nu_{0T}^2 \tau_T$ (MHz)	$eqQ/4h$ (MHz)	$\frac{T}{T_C}$	$\frac{H(T)}{H(0)}$
1.9	870 ± 10	200 ± 20	8 ± 3	20 ± 20	0.23 ± 0.01	1.01 ± 0.02
2.5	850 ± 10	220 ± 20	8 ± 3	20 ± 20	0.30 ± 0.02	0.99 ± 0.02
4.2	860 ± 10	220 ± 20	8 ± 3	15 ± 20	0.50 ± 0.02	1.00 ± 0.02
5.7	735 ± 15	250 ± 25	8 ± 4	50 ± 50	0.68 ± 0.03	0.85 ± 0.02
7.0	655 ± 20	280 ± 30	8 ± 4	50 ± 50	0.83 ± 0.03	0.76 ± 0.02
7.2	586 ± 15	300 ± 30	10 ± 5	25 ± 50	0.86 ± 0.04	0.68 ± 0.03
8.0	312 ± 70	580 ± 100	8 ± 8	0	0.95 ± 0.04	0.36 ± 0.08
8.2	~30	•••	•••	•••	0.98 ± 0.04	~0.04

TABLE IV. Hyperfine interaction and relaxation parameters for $NpNi_2$.

T (K)	$g_0\mu_N H_{\rm eff}/h$ (MHz)	$\nu_{0L}^2\tau_L$ (MHz)	$\nu_{0T}^2\tau_T$ (MHz)	$eqQ/4h$ (MHz)	$\frac{T}{T_C}$	$\frac{H(T)}{H(0)}$
1.9	1910 ± 20	130 ± 15	12 ± 5	60 ± 20	0.07 ± 0.01	0.97 ± 0.02
4.2	1950 ± 20	200 ± 20	24 ± 5	80 ± 20	0.15 ± 0.01	1.00 ± 0.02
10.0	1960 ± 20	150 ± 20	14 ± 5	40 ± 20	0.36 ± 0.03	1.00 ± 0.02
15.0	1870 ± 30	240 ± 50	19 ± 5	50 ± 25	0.54 ± 0.04	0.95 ± 0.03
20.0	1370 ± 100	800 ± 100	60 ± 20	50 ± 30	0.71 ± 0.05	0.70 ± 0.08

the limits of error on the solid line, which represents the theoretical curve of $H(t)/H(0)$ as a function of T/T_C assuming $J=\frac{1}{2}$ in the molecular-field approximation $[H(T)/H(0)]=B_{1/2}(\Delta/2kT)$, where $\Delta = 2kT_C H(T)/H(0)$. For comparison the theoretical curve for $J=\frac{9}{2}$ (corresponding to a Np^{4+} free ion) is also shown in Fig. 11. Such a temperature dependence is expected theoretically for an isolated Kramers doublet split by an exchange interaction. The fact that the quadrupole interactions are almost negligible in the cases studied (except in $NpFe_2$) lends support to the assumption that we are dealing, to a good approximation, with an isolated Kramers doublet. If the Np ions in the Laves-phase compounds were tetravalent, the lowest levels in a cubic crystalline field for $J=\frac{9}{2}$ would be a Γ_6 doublet.[13] A weak exchange interaction might split this doublet without appreciable mixing of higher states into the ground doublet. Even if J is not a good quantum number, the lowest level in the cubic crystalline field could still be a Kramers doublet. For such an isolated doublet in a cubic crystalline field, the quadrupole interaction would be identically zero and the temperature dependence of $H(T)/H(0)$ would follow the solid curve in Fig. 11.

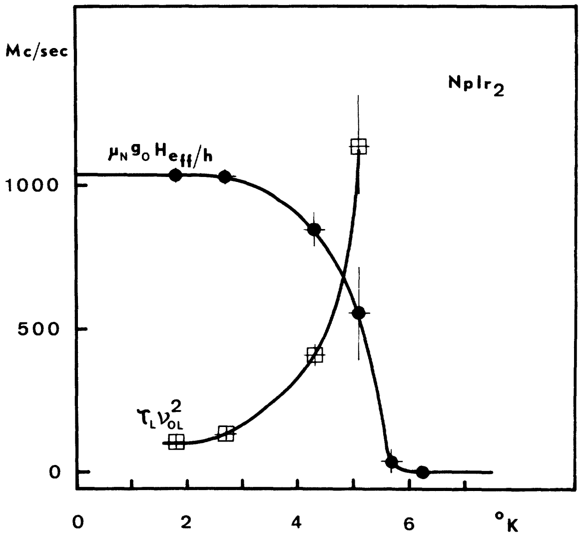

FIG. 8. Values of $\mu_N g_0 H_{\rm eff}/h$ and $\tau_L \nu_{0L}^2$ for $NpIr_2$ (given in Table II) as function of temperature.

If this assumption of an isolated Kramers doublet were rigorously true, well-defined spectra with unbroadened lines, showing no relaxation effects, would be obtained at 1.9 K (as only the lower level of the split doublet would be populated at this temperature). This is obviously not the case for $NpCo_2$, $NpIr_2$, and $NpNi_2$. We have to assume, therefore, some kind of mechanism which causes a spread in the hyperfine fields even at low temperatures. The spectra obtained for $NpCo_2$, $NpIr_2$, and $NpNi_2$ were reanalyzed, making the following two assumptions:

(i) The lowest ionic Np state in these compounds is an isolated Kramers doublet split by the exchange interaction. At temperatures below T_C, only this doublet is populated. Effects of relaxation within the Kramers doublet are calculated by using the closed relaxation formulas (based on the modified Bloch equations) derived by Nowik and Wickman[7] for such a case.

(ii) A small spread in the values of the average hyperfine magnetic field, $H(T)$ exists. This spread is responsible for the broadening of the lines in the spectra at 1.9 K and has an effect on the shapes of the spectra at higher temperatures. As mentioned before, the spectra at 1.9 K can be analyzed by assuming that the positions of a line corresponding to a $m_e \rightarrow m_0$ transition is given by Eq. (6). Each line has a Lorentzian shape with a width $\Gamma(m_e, m_0)$ given

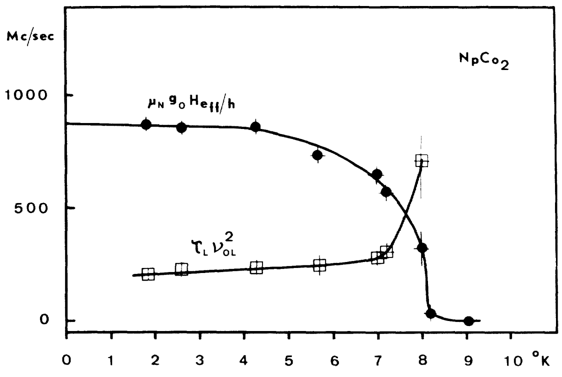

FIG. 9. Values of $\mu_N g_0 H_{\rm eff}/h$ and $\tau_L \nu_{0L}^2$ for $NpCo_2$ (given in Table III) as function of temperature.

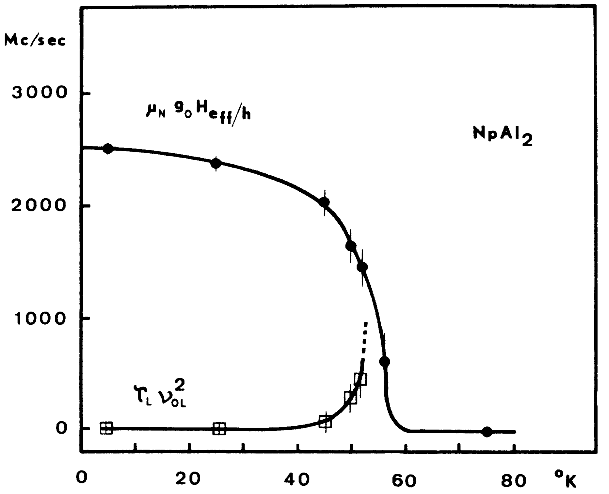

FIG. 10. Values of $\mu_N g_0 H_{eff}/h$ and $\tau_L \nu_{0L}^2$ for NpAl$_2$ (given in Table V) as function of temperature.

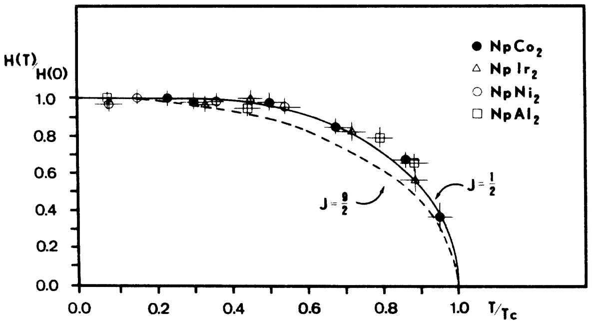

FIG. 11. Values of $H_{eff}(T)/H_{eff}(0)$ as function of T/T_C for NpCo$_2$, NpIr$_2$, NpAl$_2$, and NpNi$_2$. Values of $H_{eff}(T)$ are taken from Tables II–V. The solid line is the theoretical curve for $J=\frac{1}{2}$. The dashed line is the theoretical curve for $J=\frac{9}{2}$.

by

$$\Gamma(m_e, m_0) = \Gamma_0 + B(m_e g_e/g_0 - m_0)^2 . \qquad (7)$$

B is a broadening factor constant for all the lines of a spectrum and Γ_0 is the narrowest experimental linewidth observed, determined by the width of the emission line. In the present analysis we attribute the broadening of the lines at 1.9 K to a spread in H and not to relaxation effects. Equation (7) is a good approximation for the broadening effects due to a spread in H. (It is exact if the initial lines have Gaussian shapes, the spread in H is Gaussian and $\Gamma - \Gamma_0$ is small compared to Γ_0.) The values of B (in mm/sec) which fit the spectra at 1.9 K are given in Table VI.

According to Nowik and Wickman's formulas,[7] the relaxation spectrum is a function of the following parameters: (i) $g_0\mu_N H_{eff}(0)$ — the magnetic hyperfine interaction constant corresponding to each of the two levels of the Kramers doublet; (ii) Δ — the splitting of the doublet in the exchange field; (iii) τ — the relaxation time between the two sublevels of the doublet; (iv) $\Gamma(m_e, m_0)$ — the widths of the spectral lines in the absence of relaxation effects. In the analysis of the spectra, the value of $g_0\mu_N H(0)$ for each compound was assumed to be equal to the value found for $g_0\mu_N H_{eff}$ at 0 K (Table I). It was also assumed that the values of $\Gamma(m_e, m_0)$ are given by Eq. (7). B, Δ, and τ were taken as free parameters in the least-square analysis. Relatively good fits were obtained. The fits obtained for NpCo$_2$ at 5.7, 7.2, and 8 K are shown in Fig. 12. The fits for NpIr$_2$ at 4.2 and 5.1 K are shown in Fig. 13 and the fit for NpNi$_2$ at 15 K is shown in Fig. 14. The values of the parameters which gave the best fits to the experimental results are summarized in Table VI. From the values of $\Delta(T)$ derived from the fits, values of $H(T)$ were determined using the relation $H(T)/H(0) = \tanh[\Delta(T)/2kT]$. If these values of $H(T)/H(0)$ for NpCo$_2$, NpIr$_2$, and NpNi$_2$ are plotted as a function of T/T_C, the points are found to lie very well on the theoretical curve corresponding to $J=\frac{1}{2}$ shown in Fig. 11. The good agreement between the experimental values of $H(T)/H(0)$ determined for NpCo$_2$ and NpNi$_2$ and the molecular field, $S=\frac{1}{2}$, theoretical values show that the Co-Np and the Ni-Np exchange interactions are small in these compounds compared to the Np-Np exchange interactions. Magnetization measurements of the RNi$_2$ compounds,

TABLE V. Hyperfine interaction and relaxation parameters of NpAl$_2$.

T (K)	$g_0\mu_N H_{eff}/h$ (MHz)	$\nu_{0L}^2\tau_L$ (MHz)	$\nu_{0T}^2\tau_T$ (MHz)	$eqQ/4h$ (MHz)	$\frac{T}{T_C}$	$\frac{H(T)}{H(0)}$
4.2	2570 ± 20	15 ± 15	0	0 ± 20	0.07 ± 0.01	1.00 ± 0.03
25.0	2405 ± 20	20 ± 20	0	15 ± 20	0.44 ± 0.03	0.94 ± 0.03
45.0	2035 ± 50	75 ± 25	7 ± 10	15 ± 20	0.79 ± 0.04	0.79 ± 0.03
50.0	1700 ± 50	290 ± 50	10 ± 5	15 ± 20	0.88 ± 0.05	0.66 ± 0.03
52.0	1460 ± 100	360 ± 100	10 ± 5	15 ± 20	0.91 ± 0.05	0.57 ± 0.06
56.0	~550	•••	•••	•••	0.98 ± 0.05	~0.21

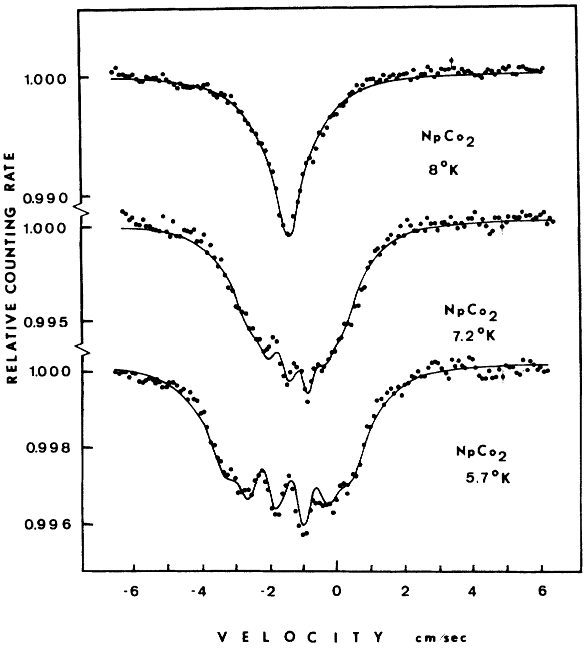

FIG. 12. Recoilless absorption spectra in $NpCo_2$. The solid lines are the theoretical best fits assuming relaxation effects within an isolated Kramers doublet. The parameters of the fits are given in Table VI.

where R is a rare-earth ion, have shown that the Ni ion in these compounds has no magnetic moment.[14]

It is seen from Table VI that the values of B are about the same for all the cases analyzed [(3 ± 1) mm/sec]. The values of τ for $NpCo_2$, $NpIr_2$, and $NpNi_2$ are $\sim 3\times10^{-11}$, $\sim 4.5\times10^{-11}$, and $\sim 7\times10^{-12}$ sec, respectively.

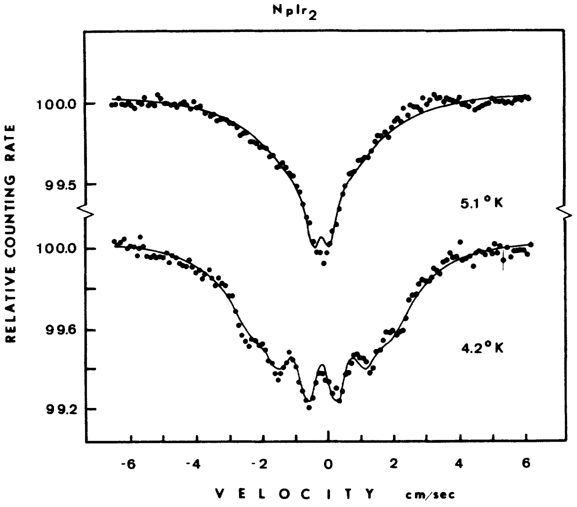

FIG. 13. Recoilless absorption spectra in $NpIr_2$. The solid lines are the theoretical best fits assuming relaxation effects within an isolated Kramers doublet. The parameters of the fits are given in Table VI.

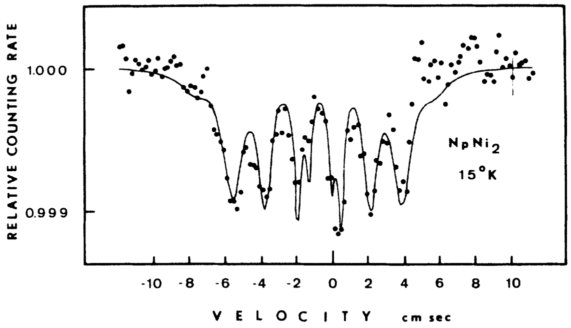

FIG. 14. Recoilless absorption spectrum in $NpNi_2$ at 15 K. The solid line is the theoretical best fit assuming relaxation effects within an isolated Kramers doublet. The parameters of the fits are given in Table VI.

IV. CONCLUSIONS

The experimental results for the temperature dependence of $H(T)$ and for the size of the quadrupole interactions in $NpCo_2$, $NpNi_2$, and $NpAl_2$ are consistent with the assumption that the ionic ground state of Np in these compounds is essentially an isolated Kramers doublet split by a relatively weak exchange interaction. Similar results were obtained by Dunlap *et al.*[15] for $NpOs_2$. In $NpFe_2$ the exchange field acting on the Np ion is large, as proved by the fact that the value of H_{eff} (77 K) is very close to the value of H_{eff} (4 K). For such a large exchange interaction, the ionic ground state of Np cannot be considered as an isolated Kramers doublet.

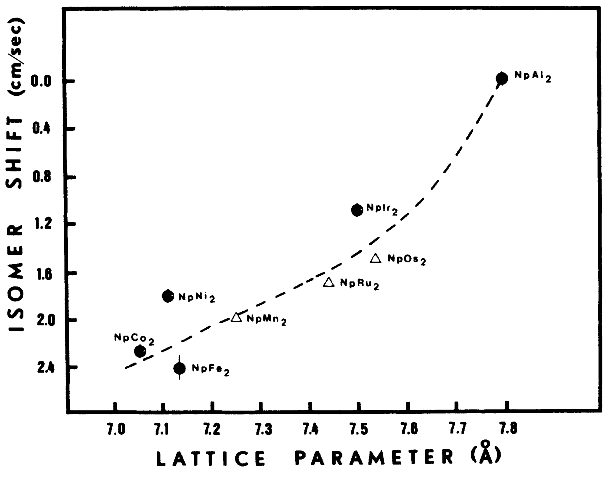

FIG. 15. Isomer shifts of NpM_2 compounds as a function of the size of their respective unit cells. (The points for $NpOs_2$, $NpMn_2$, and $NpRu_2$ are taken from Ref. 15.)

TABLE VI. Values of parameters derived for $NpCo_2$, $NpIr_2$, and $NpNi_2$ assuming relaxation effects within an isolated Kramers doublet.

Compound	Temp. (K)	$eqQ/4h$ (MHz)	Relaxation time (10^{-11} sec)	Δ (K)	B (mm/sec)
$NpCo_2$	1.7	20 ± 20	⋯	⋯	4.0 ± 0.5
	5.7	40 ± 20	3 ± 1	14.8 ± 0.4	2.0 ± 0.5
	7.2	30 ± 20	3 ± 1	10.8 ± 0.4	1.5 ± 0.5
	8.0	30 ± 20	3 ± 1	5.0 ± 0.2	2.0 ± 0.5
$NpIr_2$	1.7	0	⋯	⋯	2.5 ± 0.5
	4.2	0	4 ± 1	9.0 ± 0.4	2.6 ± 0.5
	5.1	0	5 ± 1	5.6 ± 0.3	4.0 ± 0.5
$NpNi_2$	1.7	50 ± 25	⋯	⋯	2.5 ± 0.5
	15	50 ± 25	0.7 ± 0.2	15 ± 0.5	2.3 ± 0.5

The experimental spectra obtained at 1.9 K show that even at this low temperature H_{eff} is not perfectly well defined. There exists a small spread in the values of H_{eff} which is responsible for the observed line broadenings. The reasons for this spread are not clear. Possible explanations for this phenomenon are the following:

(i) A small spread in the stoichiometric composition of the samples is investigated. Some of the lattice positions which should be occupied by the M atoms (M = Ir, Co, Ni, Al, or Os) may be vacant and the local stoichiometric composition of the sample may be NpM_x with a small spread in $x \sim 2$. The value of H_{eff} may then be a function of x and not be the same for all parts of the sample. (ii) The temperature of the absorber is not uniform. The ^{237}Np nuclei are α emitters. The α particles and the recoiling nuclei cause a temporary local heating of their immediate environment. H_{eff} is a function of temperature and a spread in temperature in the various parts of the absorbers may reveal itself as a spread in the hyperfine magnetic fields. (iii) There is a new physical effect. It is possible that even for constant soichiometry and uniform temperature throughout the samples, a spread in H_{eff} at very low temperatures would exist. Such a spread may be associated with the nonlocalized behavior of the electrons in the actinide compounds. The exact mechanisms which may be responsible for such an effect are not yet clear.

The present experimental results show that the values of $H_{eff}(0)$ at the Np nuclei differ significantly in the various Np Laves-phase compounds. If J were a good quantum number, the wave functions of the ground-state doublets of the Np ions in the various NpM_2 compounds (excluding $NpFe_2$) would be identical (wave function of a Γ_6 doublet) and one would expect the same contribution of the $5f$ electrons to H_{eff} in all NpM_2 compounds. The diversity in the values of H_{eff} is probably mainly due to the fact that J is not a good quantum number. The wave functions of the ground doublets depend therefore on the crystalline-field parameters which vary from one NpM_2 compound to the other. The values of H_{eff} produced by the $5f$ electrons may therefore not be the same in all NpM_2 compounds. In addition, the contributions of the polarized conduction electrons to H_{eff} are not expected to be the same in the various compounds.

The isomer shifts of all the measured Np Laves-compounds fall within the region corresponding to Np^{4+} or Np^{5+} salts. It is therefore very likely that the Np ions are tetravalent in these compounds with the additional shifts being caused by the conduction electrons. This assignment is consistent with our analysis which assumes that the ground crystalline state of the Np ion in these compounds is an isolated Kramers doublet. In Fig. 15 the values of the isomer shifts are plotted as a function of the lattice parameters of the NpM_2 compounds. (The figure includes three points taken from Ref. 15). It is seen that the size of the isomer shifts changes regularly with the size of the unit cell, being the most negative for the smallest unit cell. This indicates that the smaller the Np-Np distance, the larger is the density of s (or $p_{1/2}$) electrons at the Np nuclei. According to Dunlap *et al.*, [15] the dependence of the isomer shift on lattice spacing is associated with the change in the degree of localization of the $5f$ electrons as a function of the Np-Np distance. When the Np-Np distance is relatively small, the overlap between the $5f$ electrons of neighboring atoms is large and the $5f$ electrons are not well localized. Hence, by decreasing the Np-Np distance, $5f$ electrons are effectively removed from the ion and shield less the s (or $p_{1/2}$) electrons from the nuclear charge, resulting in a larger electron density at the nucleus.

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