An analogous cancellation is well-known in free-electron spin resonance of alkali metals. In the presence of a magnetic field, the electron gas is spin polarized. An exchange field thus exists which alters the energy required to flip the spin of a particular electron. This exchange field is analagous to Overhauser's periodic potential. If the spin-resonance frequency is calculated without including back flow, it is altered by the exchange field. In actual fact, since the total spin angular momentum commutes with the Hamiltonian, exchange does not alter the spin-resonance frequency, and "backflow" precisely cancels the exchange correction to the spin-resonance frequency. In both cases the cancellation is a necessary consequence of the observables in question, the current and spin, respectively, commuting with the total Hamiltonian.

Under some circumstances, "at $k=0$" and "the limit $\mathbf{k}\rightarrow 0$" are not the same in the presence of long-range interactions. In both Overhauser's case and the case of the spin in an electron gas, the relevant excitation has no charge-density fluctuation in the limit $k\rightarrow 0$, so "the limit $k\rightarrow 0$" and "at $k=0$" are synonymous. [Overhauser uses a $k\rightarrow 0$ limiting process, but only to show the relation between the power absorption and $\epsilon_2(\omega)$].

This discussion does not bear on the correctness of the spin-density wave ground state in potassium. Were potassium to have such a ground state, other mechanisms (pinning of the spin-density wave or anomalous skin effect) could result in optical absorption displaying the spin-density wave. The Overhauser calculation, however, of a one-parameter optical-absorption shape based on a free-electron gas and the long-wavelength limit seems to be incorrect.

PHYSICAL REVIEW VOLUME 139, NUMBER 2A 19 JULY 1965

Nuclear Magnetic Resonance of ^{61}Ni in Nickel Metal*

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The zero-applied-field nuclear magnetic resonance of ^{61}Ni in high purity, well-annealed Ni metal has been investigated at room temperature. The technique of rotary saturation is used to obtain a value for the domain-wall enhancement factor $\eta=1600$. Fast passage and saturation effects are observed and interpreted according to theories developed by Portis for inhomogeneously broadened spin systems. This analysis leads to a value for the longitudinal relaxation time $T_1=0.16$ msec, and to an observed nuclear dispersion-to-absorption ratio in the power absorbed of $\beta_0=0.5$ at low rf levels. Fast-passage effects are used to obtain a tracing of the distribution of nuclear magnetic fields in the sample.

INTRODUCTION

ZERO-applied-field nuclear magnetic resonance signals observed at low rf levels in the ferromagnetic metals, Co,[1,2] Ni,[3,4] and Fe,[5–8] arise from nuclei in the domain walls of the sample. Because of the motion of the domain walls under the influence of the applied rf magnetic field, the rf-field amplitude at the site of a nucleus in the wall is enhanced by a factor $\sim 10^3$ over the applied field. The strength of the observed signal is also enhanced. Because of a modulation of the intrinsic losses in the sample by the nuclear susceptibility, the detection of the resonance with spectrometers sensitive only to power absorbed leads to signals which are mixtures of nuclear absorption and dispersion. Spin echo experiments and other less direct techniques have shown that these lines are inhomogeneously broadened.[9,10] Rapid-passage effects have been observed and used to interpret some of the characteristics of the resonances in Co[1] and Fe.[8]

This paper presents the results of an investigation of the nuclear magnetic resonance of ^{61}Ni in pure, well-annealed, unenriched Ni powder at room temperature. The technique of rotary saturation[11] is used to find directly a value for the domain-wall enhancement

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factor η. A study of the resonance signal as the rf level and modulation frequency are varied has been interpreted in terms of theories developed by Portis for saturation and fast-passage effects in systems with spectral distributions.[12,13] This gives a check on the value found for η, and leads to values for the spin lattice relaxation time and the amount of mode mixing. The fast-passage effects are used to plot directly the distribution of nuclear magnetic fields in the sample.

EXPERIMENTAL TECHNIQUES

The sample used in this experiment was prepared from carbonyl Ni of 99.99% purity. A solid slug of bulk density was formed from the carbonyl Ni by pressing and sintering at 1200°C under a dry hydrogen atmosphere. This process removes oxygen and carbon impurities. This slug was filed, and those filings which passed through a 250-mesh sieve were annealed under hydrogen to remove the strain produced by filing.[14] The filings were then sealed in a test tube under oil.

The oscillator used in these experiments is a modified version of one described by Knight.[15] This oscillator is designed to operate at high rf levels and is sensitive only to power absorbed. It is frequency modulated and the output is recorded after phase-sensitive detection at the modulation frequency.

All experiments were carried out at room temperature.

EXPERIMENTAL RESULTS

A. Rotary Saturation

The linearly polarized rf field $2H_1 \cos\omega t\mathbf{i}$ applied in a nuclear resonance experiment, can be divided into two oppositely rotating components. Only one of these rotating components induces transitions between the Zeeman levels of the system and, except for the very rare circumstance where H_1 is comparable to the static field $H_n\mathbf{k}$, the other rotating component can be neglected. If we transform to a coordinate system rotating with the circularly polarized component of the applied rf field which induces transitions,[16] the nuclear spin system finds itself in a time-independent effective magnetic field $H_e=(H_n-\omega/\gamma)\mathbf{k}+H_1\mathbf{i}$. If H_1 is sufficiently large, the nuclear magnetization will align itself approximately along H_e, precessing about it at a frequency $\omega_a=\gamma H_e$.[17,18] When ω is near resonance, $H_e\approx H_1\mathbf{i}$ and the nuclear magnetization lies nearly at right angles to the applied static field.

If a second alternating field $H_a \sin\omega_a t\mathbf{k}$ is simultaneously applied to the spin system, the effect on the observed signal can be understood by repeating the above analysis beginning in the rotating frame with $H_e\approx H_1\mathbf{i}$ playing the role of the static field and transforming to a second rotating coordinate system. When the condition $\omega_a\approx\gamma H_1$ is satisfied, transitions in the rotating frame will be induced by the second applied field and the projection of the nuclear magnetization along H_1 will be reduced. Since this projection is directly proportional to χ', the observed signal decreases. This effect, called rotary saturation, was predicted and verified by Redfield[17] and has been used to calibrate rf levels.

In a ferromagnetic metal the time-varying field seen by the nucleus depends on the domain-wall enhancement η defined by the expression $H_1=\eta H_x/2$. H_x, the peak field from the oscillator, can be calculated from coil geometry and the measured rf voltage across the coil. Thus a measure of H_1 by rotary saturation yields a value for the enhancement factor η.

In our experiment it is not feasible to apply an audiofrequency magnetic field in the same direction as H_n. However, the field in the rotating coordinate system has a Z component $(H_n-\omega/\gamma)$, and a modulation of the oscillator frequency is equivalent to a modulation of the magnetic field along the Z axis. The experiment consists of tuning the oscillator to the center of the resonance signal, modulating weakly at a low frequency which serves to provide a signal for the phase-sensitive detector, and simultaneously modulating at a second frequency which plays the role of the second alternating magnetic field. This experiment was carried out on the nuclear resonance of ^{57}Fe in pure Fe metal as a test of the method. The experimental results gave $\eta\sim 2000$ in excellent agreement with the previous results for η in Fe.[8]

Figure 1 shows the results of rotary saturation in a Ni sample at two different rf levels. For small H_1, Abragam[18] discusses two important sources of error in

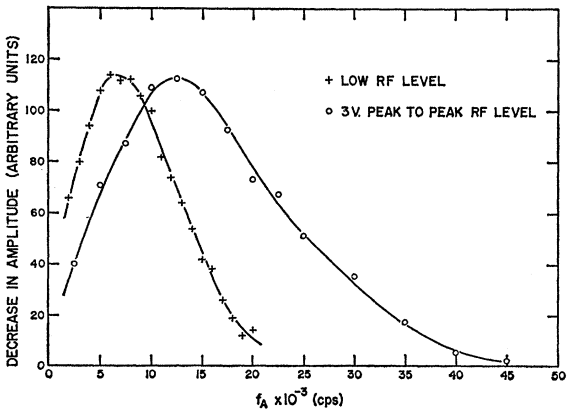

FIG. 1. Rotary saturation in Ni. $\omega_m/2\pi=1$ kc/sec., 90° phase, $\gamma H_m/2\pi=3$ kc/sec, $\gamma H_a/2\pi=4.5$ kc/sec.

[12] A. M. Portis, Techn. Note No. 1, Sarah Mellon Scaife Radiation Laboratory, University of Pittsburgh, 1955 (unpublished). See also, M. Weger, Bell System Tech. J. **39**, 1013 (1960).
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this experiment, both of which tend to shift the maximum of the signal change to values of ω_a greater than γH_1. The first is the Bloch-Siegert shift, and the second arises because the modulation used for detecting the resonance holds all the nuclei in an average effective field somewhat greater than H_1. These effects are important corrections for the Ni data labeled "low rf level." As H_x increases, the maximum signal decrease moves smoothly to higher values of ω_a. At the level 3 V peak-to-peak, both corrections are small. From our coil geometry we compute that 3 V peak-to-peak corresponds to $H_x=42$ mG. Using the value for the nuclear gyromagnetic ratio of ^{61}Ni, $\gamma=2.3\times10^3$ sec^{-1} G^{-1}, we conclude that in Ni, $\eta=1600$.[19]

The detailed line shape traced out in this experiment depends on the nature of the nuclear resonance line. For an inhomogeneously broadened line the expected behavior to the first approximation would be no change in signal amplitude when $\omega_a<\gamma H_1$, a sharp drop at $\omega_a\approx\gamma H_1$, and a slow return to the original level at high ω_a. The initial drop might extend over 4–5 kc/sec in our experiment because H_a is large. We observe a much slower approach to the minimum and believe this is due to a distribution of enhancement factors throughout the sample.

We are able to observe the effects of rotary saturation while monitoring the signal in either the slow-passage or fast-passage mode as long as $\epsilon=(\omega_m H_m T_1)/H_1\lesssim1$ (see the next section of this paper). The second alternating field is most effective in reducing the magnetization of those packets near resonance, but under slow-passage conditions these packets make only a small contribution to the total nuclear magnetization. Because of this the rotary saturation is much more pronounced in the fast-passage mode. The data shown in Fig. 1 were taken under fast-passage conditions.

B. Fast Passage and Saturation

The results of spin-echo experiments in pure unenriched Ni at room temperature indicate that the resonance line is inhomogeneously broadened and that $T_1\approx T_2$.[9] Furthermore, steady-state experiments show that there is an appreciable contribution to the power absorption from the dispersion mode of the nuclear susceptibility. We expect that Protis' analysis of saturation and fast passage for inhomogeneously broadened lines will be appropriate for a spin system of this type.[12,13]

Portis' results on saturation of an inhomogeneously broadened spin system allow us to write, for the power absorbed from the oscillator, $dW/dt\propto H_1(\chi''/\beta+\chi')$ where χ'' and χ' are the unsaturated nuclear absorption and dispersion susceptibilities. The form of β is $\beta=\beta_0\{1+\gamma^2H_1^2T_1^2\}^{1/2}$, where β_0 is a constant giving the ratio of the amount of nuclear dispersion to absorption in the power absorbed at low rf levels.

[19] P. R. Locher and S. Geschwind, Phys. Rev. Letters **11**, 333 (1963); see also R. L. Streever, Phys. Rev. Letters **10**, 232 (1963).

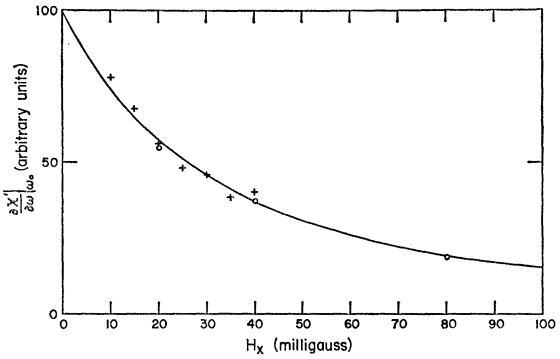

FIG. 2. Amplitude of the derivative of the nuclear dispersion susceptibility in Ni as a function of applied rf-field amplitude. These points have been corrected for oscillator characteristics. The solid curve is the expected variation for a Lorentzian line with $\eta=1650$.

Streever and Bennett[4] have examined the resonance in well-annealed Ni as a function of rf level from $H_x=2.8$ to about 17 mG and find reasonable agreement with a linear variation of β with H_1, with $\beta=0.75$ at $H_x=3.8$ mG. We have repeated these experiments from $H_x=7$ mG up to quite high rf levels and find results in good agreement with Streever and Bennett's results and with Portis' theory. We find $\beta\approx1.2$ at $H_x=7$ mG.

At higher rf levels the dispersion signal begins to saturate because of a broadening of the inhomogeneous envelope by the rf field. Assuming a Lorentzian envelope we expect at high rf levels that $d\chi'/d\omega|_{\omega_0}\propto1/(1+\gamma\eta H_x/2\Delta\omega)^2$. In Fig. 2 we show the measured $d\chi'/d\omega|_{\omega_0}$ as a function of H_x. The solid curve is the predicted variation using the value $\eta=1650$. The agreement with the rotary saturation value for η is excellent, no doubt fortuitously good.

The mode mixing effect is sufficiently strong in Ni, and the inhomogeneous broadening is great enough that it is feasible to work at rf levels where the signal arises almost entirely from the dispersion mode of the nuclear susceptibility, and the inhomogeneous envelope is still not badly broadened by the rf field. Under these conditions one can observe Portis' fast-passage effects which are described by the equation

$$\chi'(\omega)=\frac{\pi}{2}\chi_0\omega\frac{\partial}{\partial\omega_0}\left\{\frac{2}{\pi}\int_0^\infty\frac{\omega' h(\omega',\omega_0)d\omega'}{\omega'^2-\omega^2}\right\}\gamma H_m\cos\omega_m t$$
$$+\tfrac{1}{4}\pi\chi_0\omega\epsilon[1+(\omega_m T_1)^2]^{-1}$$
$$\times h(\omega,\omega_0)\sin(\omega_m t-\tan^{-1}\omega_m T_1)+O(\epsilon^3)$$

where $h(\omega,\omega_0)$ is the normalized distribution of local fields, ω_m and γH_m are the audio modulation frequency and amplitude, respectively, and the expression is valid for $\epsilon=(H_m\omega_m T_1/H_1)<1$. We have examined the resonance signals at various rf levels, at modulation frequencies from 40 cps to 3 kc/sec, and at 0° and 90° phase settings between modulation and detection, and

observed all the qualitative features expected from Portis' theory. Figure 3 shows a trace $h(\omega,\omega_0)$, the distribution of magnetic fields in our sample, plotted by utilizing the fast-passage effects. The line is symmetrical but is neither quite Lorentzian nor Gaussian. The half-width at half-height is $\Delta\omega/2\pi=19$ kc/sec. At 25.6°C the maximum is at 26.096 Mc/sec.

The relaxation time can be determined by examining the amplitude of the signal observed at 90° phase setting as a function of modulation frequency at fixed rf level and modulation amplitude. From Portis' theory we expect $\chi'(90°)\propto\omega_m T_1/[1+(\omega_m T_1)^2]$. The experimental results are shown in Fig. 4. The maximum in the neighborhood $\omega_m/2\pi=1$ kc/sec indicates $T_1\approx 0.16$ msec.

Using the value $T_1=0.16$ msec and $\eta=1600$, we can make a detailed comparison of experiment with Portis' theory. With the assumption of Lorentzian line shape the ratio of the signal amplitude at 90° to that at 0° was measured for modulation frequencies from 40 cps to 3 kc/sec, and the results agree with the predicted values within about 20% in all cases examined. Care was taken to assure that the conditions necessary for Portis' theory were satisfied. Since there are relatively few spin packets under the inhomogeneous line we believe the agreement is very satisfactory.

As a final test we have observed the transiton of the signal into a true fast-passage signal. At higher modulation frequencies the expansion parameter ϵ can be made greater than 1 while satisfying the adiabatic condition. When this occurs we find that the fast-passage part of the signal does not increase as fast as linearly with the modulation amplitude. This is the characteristic behavior of fast-passage signals in inhomogeneous lines when spin-spin interactions are weak.

DISCUSSION

We have mentioned that our data for the amount of mode mixing in Ni are in agreement with those of

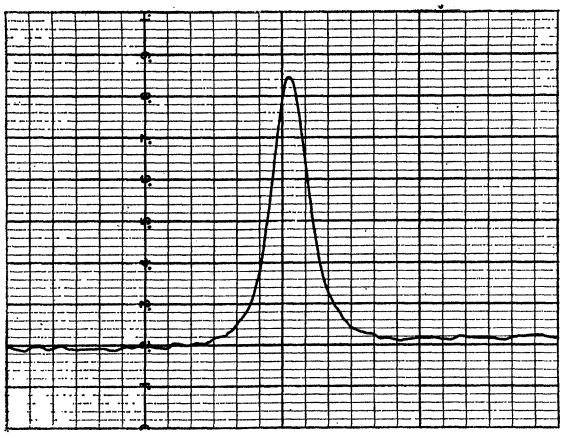

FIG. 3. Fast-passage resonance signal in Ni. $H_x=28$ mG, $\omega_m/2\pi=1$ kc/sec, 90° phase setting. This is a plot of $h(\omega,\omega_0)$, the inhomogeneous broadening envelope of the resonance. The full width at half height is 38 kc/sec.

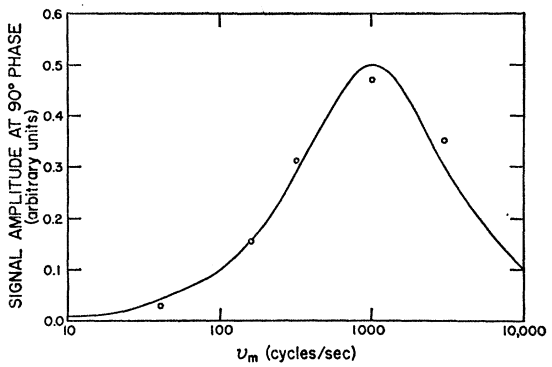

FIG. 4. Signal amplitude observed with 90° phase setting between modulation and phase-sensitive detection, as a function of modulation frequency. $H_x=28$ mG. H_m is the same for all points and $\epsilon<1$ for all points. The solid curve is the predicted behavior assuming that $T_1=0.16$ msec.

Streever and Bennett.[4] Since their experiments were done in a sample with considerably smaller particle size, and a different heat treatment, this suggests that β_0 is not a particularly structure-sensitive quantity. Our numbers for η and T_1 allow us to calculate the mode-mixing parameter expected at low rf level from the high rf level experimental results, and we find $\beta_0\sim 0.5$. This is appreciably smaller than the values found for Fe($\beta_0\approx 3$),[8] or Co($\beta_0>1$).[2]

A measure of the mode mixing as a function of rf level can give a value for a product $\beta_0\{1+(\gamma\frac{1}{2}\eta H_x T_1)^2\}^{1/2}$ but only careful measurements both above and below saturation can give β_0 and T_1 separately. Neither our measurements nor Streever and Bennett's measurements in their well-annealed sample extend to low enough rf level to do this. Streever and Bennett, however, extrapolated their data with the aid of measurements taken at lower rf level but in a different sample.[4] This second sample was unannealed and stated by them to be under some strain, which is known to affect the mode mixing.[4] Using the spin-echo value of $T_1=0.35$ msec, they concluded[9] that $\beta_0\approx 0.1$ and $\eta\approx 7000$.[4]

The value we find for the relaxation time $T_1=0.16$ msec is about a factor of 2 smaller than the value given by spin-echo experiments.[9] This seems completely reasonable since the spin-echo experiments are performed at appreciably higher rf levels. Associated with some of the spread in enhancement factors will be a spread in relaxation times. Operation at higher rf levels increases the contribution from nuclei with low enhancement factors and would be expected to give longer average relaxation times.

The value found for the domain-wall enhancement in Ni, $\eta=1600$, is nearly the same as that found in identically prepared samples of Fe($\eta=2000$). This would seem to be consistent with Portis and Gossard's[2] model which predicts $\eta\propto D(H_n/M_s)(d\theta/dZ)$, where $(d\theta/dZ)$ is the rate of change of spin direction inside a domain wall in a direction normal to the wall, D is a typical domain width, H_n is the hyperfine field at the

nucleus, and M_s is saturation magnetization. We observe first that the ratio (H_n/M_s) is nearly the same for Fe, Ni, and Co so that a difference in η must come from a difference in domain and domain-wall structure. Fe and cubic Co have very similar magnetic properties and, as expected, their enhancement factors are about the same (for Co, $\eta \approx 1500$).[2] The magnetic properties of Ni are different. Nonetheless a rough calculation indicates that $D(d\theta/dZ)$ should be nearly the same for Ni as for Fe. The dimension D for the underlying domain structure of a ferromagnetic particle is determined by competition between domain-wall energy and surface energy. Since our filings have surfaces which are randomly oriented with respect to the crystalline axes, either free magnetic poles will form on the surface or domains of closure must form along hard directions of magnetization. For materials, like Fe and Ni, having weak anisotropy, we expect the surface energy will be of the form $E_s \propto K_1 D\{1+C(K_1/M_s^2)\}$, where K_1 is the anisotropy constant and C is a number of order of magnitude 1 or smaller. (The simple closure structure described by Friedel and deGennes[20] leads to values for $C<0.1$. Since K_1/M_s^2 is small and only changes by a factor of about 0.7 on going from Ni to Fe, the closure structure will be similar in the two materials and the details of closure are not very important. An elementary calculation then gives $D(d\theta/dZ) \propto (K_1/JS^2)^{1/4}$, where J is the exchange constant and S the ion spin. This expression for $D(d\theta/dZ)$ is about 20% smaller for Ni than for Fe.)

Finally, we would like to point out the advantages in observing this kind of resonance in the fast-passage mode at 90° phase setting. Not only is the quantity $h(\omega,\omega_0)$ more easily interpreted than the derivative of the susceptibility, but the 90° phase setting makes for an improved signal-to-noise ratio because of the high stability.

Note added in proof. (*1*) Professor A. M. Portis has informed us that the paper, A. C. Gossard, A. M. Portis, M. Rubenstein, and R. H. Lindquist, Phys. Rev. **138**, A1415 (1965) contains a theoretical discussion of the mode mixing in ferromagnetic materials. The analysis suggests that $\beta_0=2\omega\tau$, where τ is the relaxation time of the domain wall.

Note added in proof. (*2*) Dr. R. L. Streever has informed us that in an unpublished extension of the work reported in R. L. Streever, Phys. Rev. **134**, A1612 (1964) he has measured T_1 in pure well-annealed Ni metal at room temperature and found that T_1 is about 0.16 msec although the accuracy of the measurement was poor. In addition he has found T_1 to depend on the state of anneal of the metal. He has found T_1 to be 0.35 msec in a sample which was not carefully annealed.

[20] J. Friedel and P. G. deGennes, Compt. Rend. **251**, 1283 (1960).

PHYSICAL REVIEW VOLUME 139, NUMBER 2A 19 JULY 1965

Electric and Magnetic Translation Group

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A set of translation operators is defined which commute with the combination of operators occurring in the time-dependent Schrödinger equation for an electron in potentials periodic in time and space, with uniform applied electric and magnetic fields in arbitrary directions. It is shown that the operators form a group. The group is made finite by imposing periodic boundary conditions, and restrictions on the electric and magnetic fields are obtained. All irreducible representations of the group, and corresponding basis functions are generated. The limit of these functions is found as the distance between boundaries becomes infinite and the restrictions on the fields disappear.

I. INTRODUCTION

WHEN there are no applied fields, the Hamiltonian for an electron in the periodic potential of a crystal lattice is invariant under a symmetry translation $\mathbf{R}_n$ of the lattice. A group of translation operators of the form $\exp(\mathbf{R}_n\cdot\nabla)$ may then be defined, and it may be shown that the wave functions take the form of Bloch functions, $\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$, where $\mathbf{k}$ is a wave vector and $u_{\mathbf{k}}(\mathbf{r})$ has the period of the lattice. However, when uniform electric or magnetic fields are present, the Hamiltonian may contain terms linear in $\mathbf{r}$ or t and hence it no longer retains the translational symmetry of the lattice.

It was pointed out by Wannier and Fredkin[1] that a uniform field physically does not destroy the translational invariance of the crystal, since the physical environment of the electron is the same at all sites whose positions differ by a lattice vector $\mathbf{R}_n$. Thus it follows, as noted by Brown,[2] that a type of translation

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