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## KNIGHT SHIFT AND ZERO-FIELD SPLITTING IN RHENIUM DETERMINED BY NUCLEAR ACOUSTIC RESONANCE

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Nuclear acoustic resonance signals have been observed in a single crystal of rhenium metal. From measurements of the resonance fields at different frequencies, values for the Knight shift and zero-field splitting at 4.2°K are obtained. The Knight shift, referred to aqueous NaReO<sub>4</sub>, is found to be  $(1.02 \pm 0.06)\%$ . The zero-field splitting,  $3e^2qQ/20h$ , is found to be  $40.6 \pm 0.35$  MHz for Re<sup>185</sup> and  $38.35 \pm 0.2$  MHz for Re<sup>187</sup>.

Effects which arise from a noncubic lattice structure are most easily studied in a single crystal. In this Letter, we report the first observation of nuclear acoustic resonance (NAR) in a noncubic metal. We have observed NAR in a single crystal of rhenium, which has the hexagonal close-packed structure, and we have determined the Knight shift and zero-field splitting.

In a noncubic crystal, there is a static electric field gradient (EFG) at the nuclear position. This EFG interacts with the nuclear electric quadrupole moment,  $eQ$ , to produce a splitting of the nuclear levels in the absence of a magnetic field. If  $eQ$  and the EFG are significant, as in rhenium metal, this splitting may be quite large. Rhenium has two naturally abundant isotopes, Re<sup>185</sup> and Re<sup>187</sup>, with electric quadrupole moments of 2.9 and 2.7 b, respectively. For each isotope,  $I = \frac{5}{2}$  and the Hamiltonian in the presence of a magnetic field is given by<sup>1</sup>

$$\mathcal{H} = h\nu_E [(3I_z'^2 - I^2) - \gamma(1+K)I_z], \quad (1)$$

where the  $z'$  axis is parallel to the crystalline  $c$  axis and the  $z$  axis is oriented along the dc magnetic field,  $\vec{H}_0$ . In this expression,  $h\nu_E$  is equal to  $e^2qQ/4I(2I-1)$  and  $eq$  is the  $z'z'$  component of the EFG tensor,  $K$  is the Knight shift, and  $\gamma$  is

equal to  $\gamma H_0/2\pi\nu_E$ , where  $\gamma$  is the nuclear gyromagnetic ratio. For rhenium metal, an average value of  $\nu_E$  has been determined by calorimetric measurements,<sup>2-4</sup> but there has been no nuclear magnetic resonance measurement of  $K$  or  $\nu_E$ . This is probably because of the severe line broadening caused by quadrupole effects in a powder, and the small rf skin depth in a single crystal. In an NAR experiment, however, the nuclear spins absorb energy from a sound wave propagating within a single crystal, and there is no rf skin depth problem. Therefore, NAR is an especially appropriate tool for the investigation of noncubic metals.

There are two reported NAR interaction mechanisms in metals. In aluminum metal,<sup>5</sup> the dominant coupling is between the oscillating magnetic field induced by the sound wave in the presence of a large magnetic field and the magnetic dipole moment of the nucleus. In tantalum metal,<sup>6</sup> the dominant coupling is between the oscillating EFG created by the sound wave and the electric quadrupole moment of the nucleus. We have calculated the acoustic absorption coefficient due to magnetic dipolar coupling and found it to be smaller than our noise level at the frequencies used in this experiment. The dominant interac-

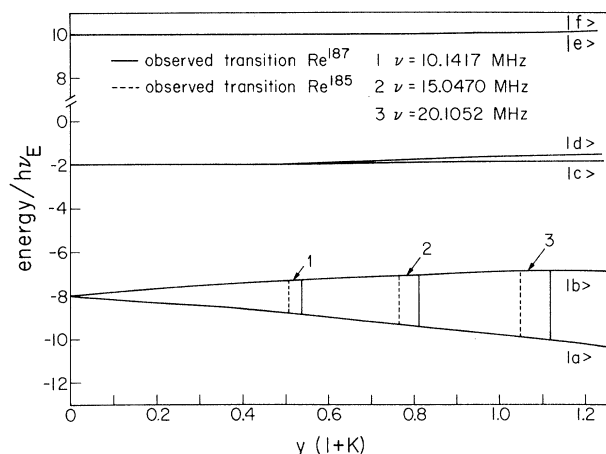


FIG. 1. Energy levels for a nuclear spin  $I = \frac{5}{2}$  when  $\vec{H}_0$  is perpendicular to the  $c$  axis. The ordinate represents the energy in units of  $h\nu_E$  and the abscissa is in dimensionless units proportional to  $H_0$ . When  $y(1+K)=1$ ,  $H_0$  corresponds to 6993.3 G for  $\text{Re}^{185}$  and 6534.1 G for  $\text{Re}^{187}$ .

tion mechanism in rhenium at these frequencies is probably the electric quadrupolar coupling.

The measurements were done with a marginal-oscillator ultrasonic spectrometer,<sup>7</sup> which records the derivative of the attenuation coefficient. The value of the resonant field was measured by monitoring the nuclear magnetic resonance frequency of  $\text{Li}^7$  and  $\text{F}^{19}$  in lithium fluoride powder inside two coils placed on either side of the rhenium sample. The  $c$  axis of the crystal<sup>8</sup> was oriented within  $0.5^\circ$  of the horizontal plane. The dc magnetic field is in the horizontal plane and may be oriented with an accuracy of better than  $0.2^\circ$ . The transverse sound wave propagates along the  $c$  axis and the polarization vector is in the basal plane. The measurements were done at 4.2°K.

For quadrupolar coupling, the transition probability is a maximum when  $\vec{H}_0$  is perpendicular to the  $c$  axis. Figure 1 shows the energy levels for the Hamiltonian of Eq. (1), in this orientation. These energy levels have been calculated with a computer program in which the eigenstates of  $\mathcal{H}$  are expressed as a linear combination of the eigenstates  $|m\rangle$  of  $I_z$ . For the experimentally observed transition frequencies, which are indicated in Fig. 1, the wave function  $|a\rangle$  is predominantly an  $m = \frac{5}{2}$  state and  $|b\rangle$  is a linear combination of  $m = \frac{3}{2}$ ,  $-\frac{1}{2}$ , and  $-\frac{5}{2}$  states each having approximately equal amplitude. The energy levels and the resonant field  $H_{\text{res}}$  for a particular frequency are strongly dependent upon the angle  $\theta$  between  $\vec{H}_0$  and the  $c$  axis. For the transition between the states  $|a\rangle$  and  $|b\rangle$ ,  $H_{\text{res}}$  is a minimum

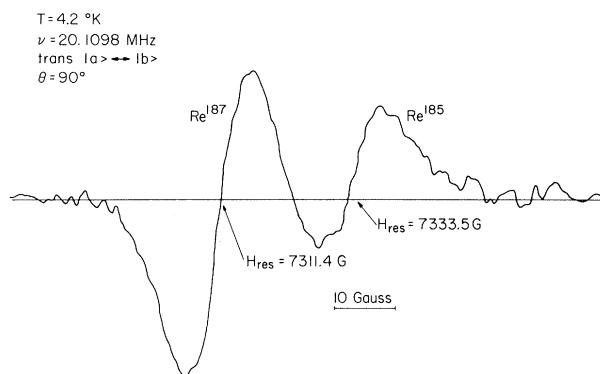


FIG. 2. Derivative of the attenuation coefficient. The modulation field is 4 G peak to peak and the time constant is equal to 3 sec. The polarization vector and  $\vec{H}_0$  are directed along a  $[11\bar{2}0]$  direction. The sound-wave vector is along the  $c$  axis.

when  $\theta = 90^\circ$ . We have used this fact to determine the orientation of the  $c$  axis in the horizontal plane within  $0.2^\circ$ . The uncertainty in  $H_{\text{res}}$  arising from misorientation is estimated to be less than 0.3 G for  $\theta \approx 90^\circ$ . The observed resonance line (Fig. 2) may be decomposed into two signals, each corresponding to one isotope. Within experimental error, the linewidths of these two signals are the same and the ratio of their amplitudes is consistent with the isotopic abundances. The width of each signal is independent of frequency and temperature between 1.3 and 77°K.

Measurements of  $H_{\text{res}}$  at two different frequencies determine the values of  $\nu_E$  and  $K$ . In Fig. 3, we have plotted three curves, each corresponding to the computed values of  $\nu_E$  and  $K$  which are consistent with the measured  $H_{\text{res}}$  for that frequency. Within experimental error, the three curves intersect at one point which gives the values of  $\nu_E$  and  $K$  in  $\text{Re}^{187}$ . We have plotted similar curves for  $\text{Re}^{185}$ . The values of the zero-field splitting,  $6\nu_E$ , are given in Table I, as are the measured values of  $K$ , referred to published values of the rhenium magnetic moment measured in aqueous  $\text{NaReO}_4$ .<sup>9,10</sup> Within experimental error,  $K$  is the same for both isotopes. This Knight shift is of the expected order of magnitude for  $5d$  transition elements and has the same value as for tantalum and tungsten.<sup>11</sup> It is difficult to measure an anisotropy in the Knight shift because of the strong dependence of  $H_{\text{res}}$  on angle for  $\theta \neq 90^\circ$ . We have observed the resonance signal for  $30^\circ < \theta < 150^\circ$  and have seen no anisotropy. This puts an upper limit of 0.2% on the anisotropic Knight shift,  $K'$ .<sup>12</sup>

The ratio of the electric quadrupole moments

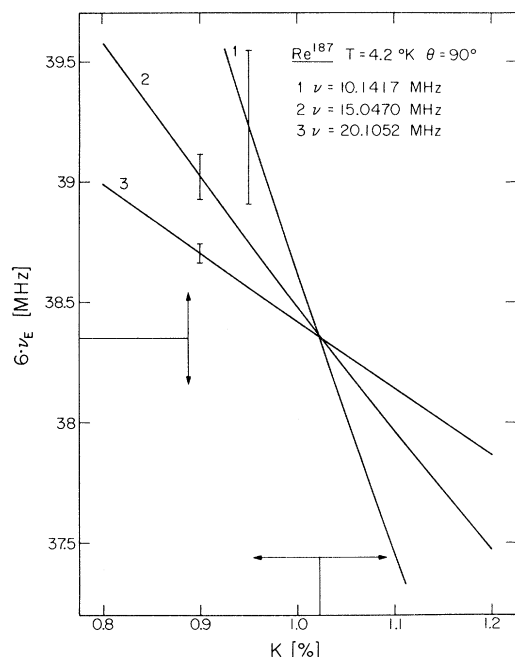


FIG. 3. Determination of  $K$  and  $\nu_E$  in  $\text{Re}^{187}$ . The error bars on each curve correspond to a random error of  $\pm 1$  G in the measured value of  $H_{\text{res}}$ . An additional systematic error of 1 G in each  $H_{\text{res}}$  gives the error bars shown for  $\nu_E$  and  $K$ .

of the two isotopes is given by the ratio  $\nu_E(\text{Re}^{185})/\nu_E(\text{Re}^{187})$ . Our measurements give a value of  $1.059 \pm 0.014$  which is in agreement with the value of  $1.056 \pm 0.005$  measured in  $\text{Re}_2(\text{CO})_{10}$ .<sup>13</sup> Specific-heat measurements determine a value of the zero-field splitting,  $6\nu_E$ , which is a weighted average of the values for  $\text{Re}^{185}$  and  $\text{Re}^{187}$ . From our results, we calculate the value of  $6\nu_E$  which would be measured by calorimetric methods to be  $39.2 \pm 0.3$  MHz for the naturally occurring mixture of the two isotopes. Measured specific-heat values are systematically higher, being 45 MHz<sup>3</sup> and 41 MHz<sup>4</sup> in two recently reported measurements. Das and Pomerantz<sup>14</sup> have calculated the lattice contribution to the zero-field splitting assuming an ionic charge of +2 and a Sternheimer antishielding factor of 100. Their calculated value is approximately one-third of the measured value. This indicates the importance of the local conduction-electron contribution.<sup>15</sup>

The mechanism for the coupling between the sound wave and the nuclear spins is not completely understood because it is difficult to measure accurately the transition probabilities as a function of the angle  $\theta$ . This is due to the limited skin depth (0.3 mm at 35 Hz) for the modulation field at 4.2°K. Because of geometric and mag-

Table I. Knight shift and zero-field splitting at  $T = 4.2^\circ\text{K}$  and  $\theta = 90^\circ$ .

	$K$ (%)	$6\nu_E$ (MHz)
$\text{Re}^{185}$	$1.01 \pm 0.08$	$40.6 \pm 0.35$
$\text{Re}^{187}$	$1.02 \pm 0.06$	$38.35 \pm 0.2$

netoresistive effects, the effective skin depth changes as  $\theta$  changes. Our results are in qualitative agreement with the transition probabilities calculated for electric quadrupole coupling. If  $\vec{H}_0$  rotates in the plane formed by the sound-wave propagation vector and the shear-wave polarization vector, the calculated transition probability is greatest when  $\theta = 90^\circ$  and vanishes for  $\theta = 0^\circ$ . The resonance signal has the correct qualitative behavior between  $90^\circ$  and  $30^\circ$ , and is unobservable for  $\theta < 30^\circ$ . If  $\vec{H}_0$  rotates in the plane perpendicular to the polarization vector, the predicted transition probability is zero for  $\theta = 90^\circ$ . In this orientation, we have observed a signal ten times smaller than in the other orientation. For shear waves, the transition probability for magnetic dipolar coupling vanishes at  $\theta = 90^\circ$ . Further work is in progress in order to understand the details of the interaction mechanism.

The peak-to-peak linewidth for the transition between the states  $|a\rangle$  and  $|b\rangle$  is equal to  $11 \pm 1$  G for  $\text{Re}^{187}$ . While an exact calculation of the second moment of the line due to dipolar broadening has not been done for the Hamiltonian of Eq. (1), the  $\text{Re}^{187}$  linewidth in the pure Zeeman case would be 4.7 G in a powder. We have also observed the transition between the states  $|b\rangle$  and  $|c\rangle$  (see Fig. 1) for  $\theta = 30^\circ$ . The peak-to-peak linewidth is equal to 85 G. For this transition,  $H_{\text{res}}$  is very sensitive to changes in the value of  $\nu_E$  and a spread of 25 kHz in  $\nu_E$  would explain the observed linewidth. This spread would give a linewidth of 3.5 G for the transition between  $|a\rangle$  and  $|b\rangle$ . Additional measurements and detailed calculations are necessary to determine if the dipolar broadening and the spread in  $\nu_E$  are the only sources of the measured linewidth.

We would like to thank Professor H. E. Bömel and Dr. E. H. Gregory for suggesting this experiment to us. We would also like to thank Dr. S. D. Rockwood for his help with the computer calculation of the energy levels.

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## DYNAMICS OF CONCENTRATION FLUCTUATIONS IN A BINARY MIXTURE IN THE HYDRODYNAMICAL AND NONHYDRODYNAMICAL REGIMES

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The experimental results obtained by optical-mixing spectroscopy on a critical binary mixture are compared with Kawasaki's theory.

By means of self-beating optical-mixing spectroscopy we have completed a series of detailed experiments on a binary mixture at critical concentration (53% cyclohexane, 47% aniline weight concentration) for different temperatures and scattering angles. Some of the results have already been reported elsewhere.<sup>1-4</sup> In these previous papers it was shown that the spectra of the scattered light are Lorentzian (except maybe in the immediate vicinity of the critical temperature where a slight deviation of the spectra from a Lorentzian shape was observed). It was in any case possible to obtain the half-width of the spectra as a function of  $(T-T_c)/T_c$  and of the scattering angle  $\theta$ .

Our results were interpreted in terms of three distinct regions according to the value of  $\xi K$ , where  $K$  is the scattering vector defined by  $|\vec{K}| = (4\pi/\lambda_0)n \sin \frac{1}{2}\theta$ , and where  $\xi$  is the long-range correlation length which is defined by the asymptotic form ( $r \rightarrow \infty$ ) of the modified Ornstein-Zernike formula,

$$g(r) = e^{-r/\xi} / r^{1-\eta/2}.$$

The three distinct regions are defined as follows:

(1)  $\xi K \ll 1$  (hydrodynamical region). In this re-

gion our results agree with the Landau-Placzek equation  $\Gamma = DK^2$  and we obtain

$$D \sim [(T-T_c)/T_c]^{0.61 \pm 0.07},$$

$D$  being the mass diffusion coefficient.

(2)  $\xi K$  small but not negligible compared with unity. In this region, which we may call the non-local hydrodynamical region, our results agree with the Fixman equation,

$$\Gamma = DK^2(1 + K^2 \xi'^2)^{1-\eta/2},$$

with  $\eta \simeq 0$ ; and by fitting our results to it, we obtain

$$\xi'^2 = \xi_0'^2 [(T-T_c)/T_c]^{-1.21 \pm 0.05},$$

where  $\xi_0' = 1.65 \pm 0.07$  Å. (The prime symbol is used to distinguish Fixman's from Kawasaki's definitions.)

(3) Finally,  $\xi K \geq 1$  (critical region). We have shown experimentally that the half-width of our spectra is well represented by the formula  $\Gamma = AK^3$ , where  $A$  is a coefficient whose value in the critical region was found to be  $A = 1.52 \times 10^{-13}$  cm<sup>3</sup> sec<sup>-1</sup>.<sup>5</sup> This result was in agreement with the theoretical predictions of Halperin and Hohenberg.<sup>6,7</sup>