

Nuclear Magnetic Resonance Study of NbBe_x Compounds*

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Nuclear magnetic resonance techniques have been employed to study powder samples of the compounds NbBe₂, NbBe₃, Nb₂Be₁₇ and NbBe₁₂. Nuclear quadrupole coupling constants and Knight shifts were determined for the Nb sites in these compounds. The ⁹³Nb NMR from NbBe₂ is a single unsplit line with zero quadrupole coupling constant and a Knight shift of $0.70 \pm 0.03\%$. The ⁹³Nb NMR from a NbBe₃ sample shows the presence of three resonance lines having values of $e^2qQ/h = 0, 24.2 \pm 0.2, 30.1 \pm 0.3$ MHz and corresponding Knight shifts of $0.69 \pm 0.03, 0.72 \pm 0.03, 0.53 \pm 0.03\%$. One of these lines was identified as a NbBe₂ impurity. The ⁹³Nb NMR of Nb₂Be₁₇ exhibits a quadrupole coupling, $e^2qQ/h = 5.93 \pm 0.15$ MHz, and a Knight shift, $K_{axial} = 0.014\%$ and $K_{isotropic} = 0.34 \pm 0.02\%$. The ⁹³Nb resonance from NbBe₁₂ was split by a quadrupole interaction of $e^2qQ/h = 21.7 \pm 0.3$ MHz and a Knight shift of $0.55\% \pm 0.02\%$. The beryllium NMR was examined, yielding little information, since no measurable quadrupole interaction or Knight shift were present.

Introduction

The intermetallic compounds of the system NbBe_x are of interest since they possess high strength, strength retention at elevated temperatures, and thermal-shock resistance (1). These refractory compounds also have high melting points, low specific gravity, and show good oxidation resistance (2). The limiting-use temperature of beryllides appears to be about 3000°F.

The Nb nucleus is highly appropriate as a probe in studying bonding configuration and electron-nuclear interaction since it has a large nuclear electric quadrupole moment which can interact with electric field gradients. This quadrupole interaction causes a perturbation on the nuclear magnetic energy levels, resulting in splitting and broadening of the nuclear magnetic resonance (NMR) spectrum of Nb nuclei (3). An electric field gradient at the site of a nucleus of

half-integral spin *I* will produce pairs of satellite lines about ν_0 , the resonance frequency, for a nucleus in an external magnetic field H_0 . The separations between the pairs of ($m \leftrightarrow m-1$) and ($-(m-1) \leftrightarrow -m$) satellite transitions for a powder sample to first-order perturbation are given by

$$\Delta\nu = (m-1/2)3e^2qQ/2I(2I-1)h, \quad (1)$$

where *m* is the magnetic quantum number, *eq* is the component in the principle axis system of the electric field gradient tensor which is largest in magnitude, *Q* is the nuclear quadrupole moment, and e^2qQ/h is specified as the quadrupole coupling constant. In the case of the ⁹³Nb nucleus with a spin $I = 9/2$, four pairs of satellites would be expected, corresponding to the transitions ($\pm 9/2 \leftrightarrow \pm 7/2$), ($\pm 7/2 \leftrightarrow \pm 5/2$), ($\pm 5/2 \leftrightarrow \pm 3/2$), ($\pm 3/2 \leftrightarrow \pm 1/2$). The approximate relative intensity (4) of the $m \leftrightarrow m-1$ transition is given by $I(I+1) - m(m-1)$. If the quadrupole interaction is sufficiently large, the central ($1/2 \leftrightarrow -1/2$) transition will be altered, producing an asymmetrical NMR line which is characterized by a splitting of the central line given by (3)

$$\Delta\nu_{p-p_0} = \frac{25}{16} \left(\frac{e^2qQ}{h} \right)^2 \frac{[I(I+1) - 3/4] 1}{[2I(2I-1)]^2 \nu_0}. \quad (2)$$

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The above expression is obtained from a second-order perturbation calculation. In Eqs. (1) and (2) the asymmetry parameter (3) η for the field gradient has been taken as zero. From either expression [Eqs. (1) or (2)] it is possible to determine the quadrupole coupling constants for nuclei in their different lattice sites.

Conduction electrons, having magnetic moments, couple with the nuclear magnetic moments producing a shift of the NMR to higher frequency (5). The unshifted resonance which had occurred at the Larmor frequency ν_L now occurs at ν_0 , where

$$\nu_0 = \nu_L(1 + K_{iso}), \quad (3)$$

and K_{iso} is defined as the isotropic Knight shift. If the Knight shift of a second-order quadrupole-split central transition is measured, the center of (1/2 \leftrightarrow -1/2) transition is no longer midway between the peaks, but a distance A from the low field peak where $A = 9/25$ times the separation between the peaks.

Due to the lack of a quadrupole interaction or Knight shift, the NMR line shape of the ^9Be nucleus in the NbBe_x compounds yielded little information and hence is not discussed in this paper.

Experimental Methods

The compounds investigated were NbBe_2 , NbBe_3 , $\text{Nb}_2\text{Be}_{17}$, and NbBe_{12} in powdered form. They were graciously supplied by the Brush Beryllium Co., Cleveland, OH. A brief summary of X-ray analysis performed on these compounds prior to our experiments is presented in Table I (6-8).

The NMR spectra (the derivative of the absorption) of these compounds were obtained at room temperature using a Varian Associates

Model V-4210A spectrometer. In the determination of the Knight shifts the ^{79}Br NMR in KBr and the ^{93}Nb NMR in niobium metal powder were employed as magnetic field markers.

To determine the intensity of the observed NMR lines a double, numerical integration of the derivative curves was performed. Such integrations were normalized to the known number of nuclei present in the samples. The $\text{Nb}_2\text{Be}_{17}$ resonance was selected as an intensity reference since all of the individual satellite lines can be readily identified.

NbBe_2

The ^{93}Nb NMR resonance (Fig. 1) from NbBe_2 was obtained at frequencies ranging from 6 to 14 MHz. The resonance shows an absence of satellite lines, and the peak-to-peak separation of the derivative curve is independent of resonance frequency. An intensity measurement was performed on this resonance line, and the results indicated that all of the satellite transitions are present within the unsplit, single line. The width of this single line is 7.6 ± 0.5 G and is due primarily to the magnetic dipole-dipole interaction between the niobium nuclei and their neighbors. A calculation of the magnetic dipole line width considering a gaussian line shape and only contributions from the nearest neighbors (6) (12 Be atoms at 2.71 Å and the 4 Nb atoms at 2.83 Å) yields a value of 5 G. Even if all of the nuclei were considered in this calculation the

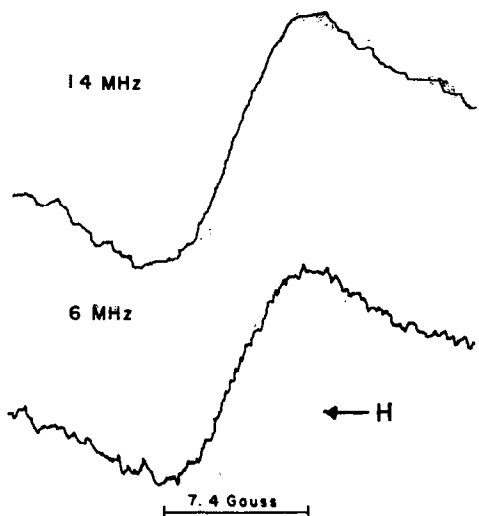


FIG. 1. First derivative of the ^{93}Nb resonance in NbBe_2 at 14 and 6 MHz.

TABLE I

CRYSTAL STRUCTURE^a OF NbBe_x SAMPLES

Beryllide	Structure	a_0 (Å)	c_0 (Å)	c_0/a_0
NbBe_2	fcc	6.535		
NbBe_3	Rhombohedral	7.495		
$\text{Nb}_2\text{Be}_{17}$	Rhombohedral	5.599		
NbBe_{12}	Tetragonal	7.356	4.258	0.577

^a Determined by X-ray analysis (6-8).

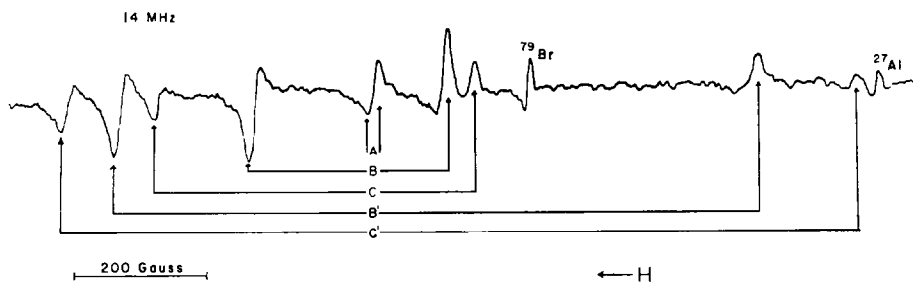


FIG. 2. First derivative of the ^{93}Nb resonance in NbBe_3 at 14 MHz. Lines marked A, B, and C are the central ($1/2 \leftrightarrow -1/2$) transitions. Lines marked B' and C' are first-order split ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions.

measured line width would exceed the calculated dipole line width. This additional line broadening can be reasonably attributed to a small amount of random, first-order quadrupole broadening produced perhaps by strain in this powdered sample. The frequency independence of the NMR line width, the absence of first-order satellite lines, and the intensity measurement, showing that all of the satellite transitions are contained in this single resonance, indicate that the quadrupole interaction is vanishingly small in NbBe_2 . The absence of a quadrupole interaction is consistent with the NbBe_2 having a fcc structure (6), since this symmetry results in a vanishing electric field gradient at the niobium sites.

The center of this resonance from NbBe_2 exhibits a Knight shift of $0.70 \pm 0.03\%$. This relatively large Knight shift is comparable to that of pure niobium metal (9) 0.82% . The similarity in the magnitude of the Knight shift suggests that the bonding in NbBe_2 is highly metallic.

NbBe_3

The NMR spectrum of the niobium nuclei in NbBe_3 was investigated under experimental conditions similar to those employed with the NbBe_2 sample. The resonance is presented in Fig. 2. Its complex spectrum was studied as a function of resonance frequency in order to categorize and identify the structures present in the sample. This analysis showed three niobium lattice positions which results in three separate families of lines. Line A in Fig. 2 is an unsplit central ($1/2 \leftrightarrow -1/2$) transition, while lines B and C are central transitions that are split by the electric quadrupole interaction. Since Nb should have only two distinct crystalline sites in this compound (6), one of the resonances is most

likely due to an impurity. Analysis of these resonances was carried out by plotting the peak-to-peak separation of the derivative of each resonance versus $1/\nu$, as shown in Fig. 3. The quadrupole coupling constants were computed using Eq. (2) and the slope of the lines A, B, and C in Fig. 3. The resulting coupling constants are presented in Table II. The centers of lines A, B, and C were found to exhibit Knight shifts. The

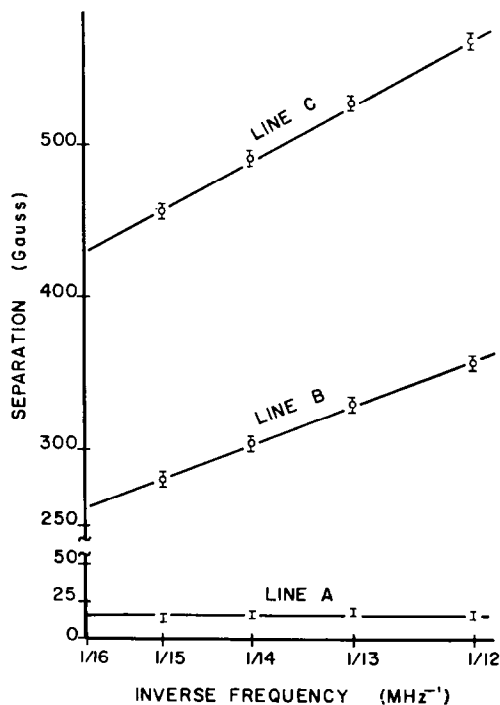


FIG. 3. Separation of the peaks of the derivative curve for the ($1/2 \leftrightarrow -1/2$) transition of lines A, B, and C from ^{93}Nb in NbBe_3 versus $1/\nu$.

TABLE II
QUADRUPOLE COUPLING CONSTANTS AND KNIGHT
SHIFTS OF $NbBe_3$

Line	e^2qQ/h (MHz)	Knight shift (%)
A ($NbBe_2$ contaminate)	0	0.68 ± 0.03
B	24.3 ± 0.5	0.72 ± 0.03
C	30.6 ± 0.7	0.53 ± 0.03
B'	24.2 ± 0.2	
C'	30.1 ± 0.3	

measured values of the Knight shifts are found in Table II.

Line A in Fig. 2 appears to be the result of $NbBe_2$ present in the $NbBe_3$ sample. This was substantiated by comparing the value of the quadrupole coupling constant, NMR line width, and the Knight shift of line A with the corresponding values for $NbBe_2$. The coupling constants are zero in both cases, and both Knight shifts are the same within the limits of error. In comparing the line widths, line A was found to have an apparent width of 16 G, which is larger than that of niobium in $NbBe_2$. This apparent width was partially due to the magnetic field modulation of 12 G which was required to observe the entire spectrum. Further investigation of this line, when examined at a slower scanning rate and less modulation, revealed a narrower width (~ 8 G) similar to that of $NbBe_2$. It was determined by an intensity measurement of the resonance curves, that only about 1.5% of the niobium nuclei present contributed to line A. The computed ratio of Nb nuclei contributing to the intensity of lines B and C agrees favorably with the two:one ratio predicted for the two different sites from X-ray analysis (6).

Nb_2Be_{17}

The NMR spectrum of the niobium nuclei in Nb_2Be_{17} exhibits a split central line ($1/2 \leftrightarrow -1/2$) and four pairs of satellites, corresponding to the ($\pm 3/2 \leftrightarrow \pm 1/2$), ($\pm 5/2 \leftrightarrow \pm 3/2$), ($\pm 7/2 \leftrightarrow \pm 5/2$) and ($\pm 9/2 \leftrightarrow \pm 7/2$) transitions. The three pairs (B, B'; C, C'; D, D') of satellite lines are displayed in Fig. 4. The central line in Fig. 4 is enlarged beyond the chart paper in order to show the satellites. The pair of transitions ($\pm 9/2 \leftrightarrow \pm 7/2$), which are very weak, are not shown.

The peak-to-peak separation of the split central transition was plotted as a function of the inverse of the resonance frequency (Fig. 5). Table III is presented to display the values of line widths and their associated uncertainties in measurement. A straight line cannot be fitted within the error bars to include both low- and high-frequency data. If only the low-frequency data points (6 to 2.5 MHz) are considered, then a straight line can be fitted. The slope of such a line yields a quadrupole coupling constant of 5.92 MHz with a residual

TABLE III

NMR LINE WIDTH OF ^{93}Nb IN Nb_2Be_{17} AT VARIOUS
FREQUENCIES

Frequency (MHz)	Line width (G)
14	14.2 ± 0.5
12	17.8 ± 0.3
10	22.1 ± 0.45
8	28.6 ± 0.5
6	39.6 ± 0.5
4	60 ± 1
3	82 ± 2
2.5	97 ± 2

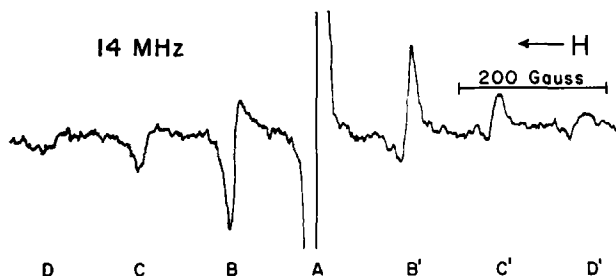


FIG. 4. First derivative of the ^{93}Nb resonance in Nb_2Be_{17} at 14 MHz. Line A is the ($1/2 \leftrightarrow -1/2$) transition. Lines B and B', C and C', D and D' are the ($\pm 3/2 \leftrightarrow \pm 1/2$), ($\pm 5/2 \leftrightarrow \pm 3/2$), ($\pm 7/2 \leftrightarrow \pm 5/2$) transitions, respectively.

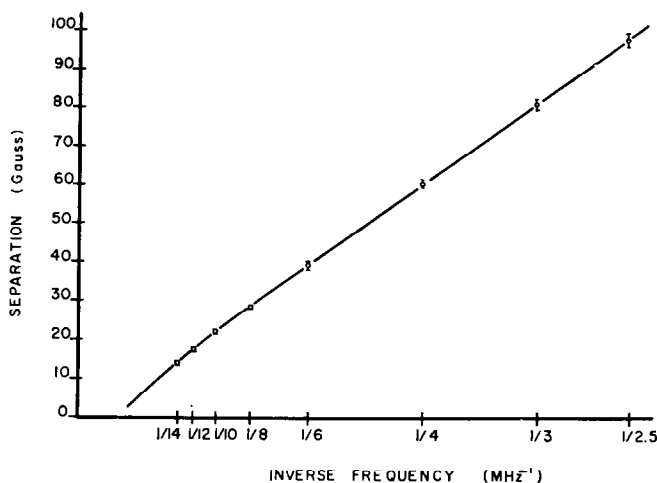


FIG. 5. Separation of the peaks of the derivative curve for the $(1/2 \leftrightarrow -1/2)$ transition of ^{93}Nb in $\text{Nb}_2\text{Be}_{17}$ versus $1/\nu$. (—) A plot of Eq. (7).

line width of approximately zero gauss at infinite frequency. However, if the higher frequency data (8 to 14 MHz) are fitted to a straight line, its slope is greater than that of the lower frequency data and the intercept of the line when extrapolated to infinite frequency is an unrealistic -4.3 G. Another interaction must be taken into consideration to explain this distortion.

Bloembergen and Rowland (10) have discussed in detail the first-order effects of an anisotropic shift tensor on the NMR line shape of a conductor in the absence of electric quadrupole effects. In the case of an axially symmetric shift tensor all $2I+1$ Zeeman levels are shifted by an equal amount, resulting in a single resonance line for the case of a single crystal (10). The resonance frequency is given by

$$\nu = \nu_L(1 + K_{\text{iso}})[1 + K_{\text{ax}}(3 \cos^2 \theta - 1)/(1 + K_{\text{iso}})], \quad (4)$$

where θ is the angle between the Z axis of the principle axes system of the shift tensor and the direction of the applied external magnetic field.

If an anisotropic Knight shift interaction is present in a powdered sample having a second-order quadrupole interaction, then it is possible to determine the separation, $\Delta\nu = \nu_{\text{H1}} - \nu_{\text{L0}}$, of the singularities in the probability distribution which would also determine the first-derivative peak-to-peak separation for the central $1/2 \leftrightarrow -1/2$ transition. The assumption was made that the axially symmetric magnetic shift tensor has its principle axis coincident with that of an

axially symmetric electric field gradient tensor. The separation between peaks $\Delta\nu$ can be written, as derived by Jones, Graham and Barnes (11), as

$$\Delta\nu = 25b/9\nu_0 - 5a\nu_0/3 + a^2\nu_0^3/4b, \quad (5)$$

where $b = \nu_Q^2[I(I+1) - 3/4]/16$, $a = K_{\text{ax}}/(1 + K_{\text{iso}})$, and $\nu_Q = 3e^2qQ/2I(2I-1)h$. This expression takes into account the presence of anisotropic Knight shift by replacing ν_L with ν_0 [see Eq. (3)]. The first term in Eq. (5) is due to the second-order quadrupole interaction [see Eq. (2)]. The second term is the contribution from the anisotropic Knight shift. The third term depends upon a^2 and can be neglected because of the smallness of a . If there is a finite dipolar line width σ present, then the separation can be written (11)

$$\Delta\nu = 25b/9\nu_0 - 5a\nu_0/3 + (1/2)\sigma. \quad (6)$$

A least-squares calculation was performed fitting Eq. (6) without the dipolar contribution, since the low-frequency data, if extrapolated, indicated zero dipolar broadening within the limits of this experiment. The resulting equation is

$$\Delta\nu = 0.255/\nu_0 - 0.000238\nu_0. \quad (7)$$

In Fig. 5 a curve is drawn to show the fit of Eq. (7) to the data. Utilizing Eq. (7) the quadrupole coupling constant and the axial component of the shift tensor were computed to be $e^2qQ/h = 5.93 \pm 0.15$ MHz and $K_{\text{ax}} = 0.014\%$. In addition to these parameters K_{iso} can be

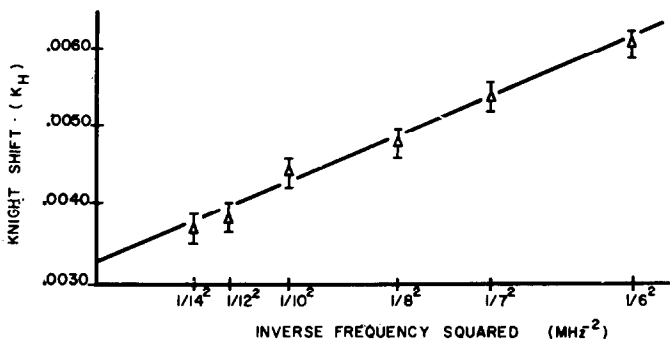


FIG. 6. K_H versus $1/\nu^2$ for $\text{Nb}_2\text{Be}_{17}$.

determined by plotting the relative shift of the low-field derivative peak K_H (11), where

$$K_H = (\nu_{H1} - \nu_L)/\nu_L = K_{\text{iso}} - a + b/\nu_L^2, \quad (8)$$

as a function of the inverse of resonance frequency squared. The difference between ν_L and the actual resonance frequency in the denominator is insignificant in this particular calculation. The plot of K_H vs $1/\nu^2$ is shown in Fig. 6. A least-squares fit yields the following equation:

$$K_H = 0.0032 + 0.1064/\nu^2. \quad (9)$$

The infinite frequency intercept determines $K_{\text{iso}} = 0.33\% \pm 0.02\%$, using the value of "a" obtained from Eq. (6). The value of K_{iso} obtained by neglecting the shift due to the effects of K_{ax} and defining the center of the resonance as in Eq. (3), $K_{\text{iso}} = 0.34 \pm 0.02\%$, which coincides with the previous value within the uncertainties of the measurement. This relatively small Knight shift as compared with the previously examined beryllides indicates that less metallic type behavior and possibly fewer *s*-state electrons in the conduction band.

The separation between the ($\pm 3/2 \leftrightarrow \pm 1/2$) satellite transitions was measured to be 254 ± 3 G and constant in the frequency range from 4 to 14 MHz. The individual satellite lines possess a broadened width due to the effects of over-modulation. The extra width can be subtracted off using the method given by Adams, Williams and Hewitt (12). The quadrupole coupling constant was then calculated using Eq. (7) and the adjusted widths. A coupling constant of $e^2qQ/h = 5.8 \pm 0.2$ MHz was obtained. This value is in agreement with that value obtained from the analysis of the central transition.

NbBe_{12}

The NbBe_{12} compound has the highest atomic ratio of beryllium to niobium of the series. The NMR of niobium nuclei observed at room temperature was extremely weak due to the low abundance of ^{93}Nb nuclei. Consequently, high gain and high modulation amplitude were necessary to resolve the signal. The NMR from this sample was investigated in the frequency range from 10 to 15 MHz. Spectra contained a split central transition. The ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions could just be detected since they were extremely weak. A plot of the peak-to-peak separation of the central transition was made as a function of the inverse resonance frequency. The straight-line fit indicates the resonance line is split by the second-order quadrupole perturbation. An electric quadrupole coupling constant of 21.7 ± 0.3 MHz was determined. This relatively large interaction is caused by strong electric field gradients and is the consequence of the tetragonal crystal structure (8) of NbBe_{12} .

A Knight shift of $0.55 \pm 0.02\%$ was observed in this sample.

Conclusion

Compounds of NbBe_x were identified and categorized by their NMR spectra. The relative amounts of niobium in the various phases as well as any uncombined niobium nuclei may be identified by the process of a double integration of the resonance curve. Quadrupole splittings and Knight shifts have been determined and are strikingly different for each compound. The quadrupole coupling constants are in agreement with the X-ray structural data. The Knight shifts observed in these compounds vary over the range

of 0.72 to 0.34% with the largest Knight shifts occurring in the two compounds containing the larger ratio of Nb to Be. From an examination of the Knight shift data, it is evident that the Knight shifts are structurally dependent and not related simply to the Nb/Be ratio.

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