MASTER

QUADRUPOLE INTERACTIONS
IN MOLYBDENUM BASE DILUTE BINARY
VANADIUM AND NIOBIUM ALLOYS

BY

LIH-HSIN CHOU

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THESIS

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WE HEREBY RECOMMEND THAT THE THESIS BY

LIH-HSIN CHOU

ENTITLED QUADRUPOLE INTERACTIONS IN MOLYBDENUM BASE

DILUTE BINARY VANADIUM AND NIOBIUM ALLOYS

BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Theodore J. Rowland

Director of Thesis Research

C. A. West

Head of Department

Committee on Final Examination†

Chairman

† Required for doctor's degree but not for master's.

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. THEORY	3
III. EXPERIMENTAL PROCEDURE	
(A) Preparation of Samples	12
(B) Experimental Apparatus	15
(C) Measurement Procedure	
(C.1) Relative intensity comparison of ^{95}Mo with ^{31}P	17
(C.2) The effect of V and Nb additions on the intensity of ^{95}Mo	18
IV. EXPERIMENTAL RESULTS AND CALCULATIONS	20
V. DISCUSSION AND CONCLUSIONS	24
REFERENCES	40
Computer program for the BCC lattice sum $\sum_j r_{ij}^{-6}$ within a sphere of radius 65 (assume $a=1$)	41

LIST OF TABLES

Table	Page
I. Impurity analysis of Mo rod from Climelt, Inc.	33
II.a Annealing temperature and annealing time for pure Mo samples	34
II.b Annealing temperature and annealing time for Mo-V alloys	35
II.c Annealing temperature and annealing time for Mo-Nb alloys	36
III.a Experimental line width and corrected integrated intensity for three different pure Mo samples	37
III.b Experimental line width and corrected integrated intensity for Mo-V alloys	38
III.c Experimental line width and corrected integrated intensity for Mo-Nb alloys	39

LIST OF FIGURES

Figure	Page
1. Energy level diagrams and their spectra for the ^{95}Mo nucleus in a magnetic field H_0 , showing the change in the spacing of the energy levels caused by first order quadrupole interactions. The spacing shown corresponds to $\theta = 0$	26
2. Block diagram of the equipment used in the resonance intensity comparison between ^{31}P and ^{95}Mo metal powder.	27
3. Block diagram of the experimental equipment used in the resonance intensity measurements made on Mo and Mo alloys	28
4. Recordings of ^{95}Mo resonance in (a) Mo-0.996 at.% V, (b) Mo-2.494 at.% V, and (c) Mo-10.013 at.% V alloys.	29
5. Recordings of ^{95}Mo resonance in (a) Mo-0.999 at.% Nb, (b) Mo-2.744 at.% Nb, (c) Mo-4.998 at.% Nb, and (d) Mo-10.699 at.% Nb alloys.	31

I. INTRODUCTION

An early study[1] of hyperfine structure of atomic spectra revealed that a nucleus may possess an electric quadrupole moment as well as a magnetic dipole moment, the former having its origin in a nonspherically symmetric nuclear charge distribution.

There is one significant difference between magnetic dipole and electric quadrupole moment effects. The magnetic dipole moment interacts with a magnetic field. On the other hand, the nuclear electric quadrupole moment interacts with an electric field gradient (EFG). No appreciable gradient can be produced by direct external means; thus a significant gradient is always the result of internal electric fields. These internal electric fields are very sensitive to the details of the charge distribution around the nucleus. The electric quadrupole moments of nuclei are known to a very much lower precision than the magnetic dipole moment. It is often difficult to give a highly quantitative interpretation even though the nuclear quadrupole moment can serve as a very sensitive probe of the internal electric field in solids. These two paragraphs paraphrase Cohen and Reif[2].

Knight shifts of Nb in Nb-Mo alloys[3] have been studied. Above 40 at.% Mo the shift decreases linearly as Mo concentration increases and for Mo concentration less than 40 at.% the shift remains constant. Two alternative interpretations account for this; one is the d states on the Mo side are antibonding states and have negative hyperfine interaction; the other is that the change in shift might come from a change in the orbital

paramagnetism corresponding to the paramagnetic term in the chemical shift. The ^{95}Mo and ^{97}Mo nuclear spin-spin and spin-lattice relaxation rates in Mo metal[4] have also been studied, and the quadrupole moments of ^{95}Mo and ^{97}Mo calculated.

Previous work[5] on ^{51}V quadrupole effects in V-base, binary transition-metal alloys discussed the origin of the field gradient, and its dependence on distance from different solute atoms, as well as the effectiveness of various shielding and antishielding mechanisms. In this thesis we investigate some of the Mo quadrupole interactions for pure Mo metal, Mo base V alloys, and Mo base Nb alloys. Mo, Nb and V metals all have the BCC structure. The alloys we made were all substitutional type solid solutions.

II. THEORY

Consider a nucleus of atomic number Z whose total electric charge Ze is distributed over the nuclear volume with a density $\rho(\vec{r})$ at the point $\vec{r}$. Let $V(\vec{r})$ be the electrostatic potential arising from all charges other than those of the nucleus under consideration. The electrostatic interaction between the two charge distributions $\mathcal{H}_{int}$ is simply expressed as an integral over the nuclear volume

$$\mathcal{H}_{int} = \int \rho(\vec{r}) V(\vec{r}) d\vec{r} \quad (1)$$

We expand $V(\vec{r})$ in a Taylor series about the center of mass of the nucleus

$$V(\vec{r}) = V(0) + \sum_{\alpha} x_{\alpha} \left(\frac{\partial V}{\partial x_{\alpha}} \right)_0 + \frac{1}{2} \sum_{\alpha\beta} x_{\alpha} x_{\beta} \left(\frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \right)_0 + \dots, \quad (2)$$

where x_{α} ($\alpha=1,2,3$) stands for x , y , or z respectively.

We define

$$V_{\alpha} \equiv \left(-\frac{\partial V}{\partial x_{\alpha}} \right)_0 \quad \text{as the negative of electric field, and}$$

$$V_{\alpha\beta} \equiv \left(-\frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \right)_0 \quad \text{as the negative of EFG;} \quad (3)$$

we have

$$\begin{aligned} \mathcal{H}_{int} = & V(0) \int \rho(\vec{r}) d\vec{r} + \sum_{\alpha} V_{\alpha} \int \rho(\vec{r}) x_{\alpha} d\vec{r} \\ & + \frac{1}{2} \sum_{\alpha\beta} V_{\alpha\beta} \int \rho(\vec{r}) x_{\alpha} x_{\beta} d\vec{r} + \dots, \end{aligned} \quad (4)$$

thus

$$\mathcal{H}_{int} = ZeV(0) + \sum_{\alpha} V_{\alpha} P_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} V_{\alpha\beta} Q'_{\alpha\beta} + \dots, \quad (5)$$

where

$$\int \rho(\vec{r}) d\vec{r} \equiv Ze = \text{nuclear charge (monopole moment)}, \quad (6)$$

$$\int \rho(\vec{r}) x_{\alpha} d\vec{r} \equiv P_{\alpha} = \text{electric dipole moment}, \quad (7)$$

$$\int \rho(\vec{r}) x_{\alpha} x_{\beta} d\vec{r} \equiv Q'_{\alpha\beta} = \text{component of electric quadrupole moment tensor}. \quad (8)$$

In the following, even and odd terms are defined by whether n is even or odd in the corresponding 2^n -pole term.

The nucleus may be exposed to a magnetic field arising from within the solid or essentially resulting from an externally imposed magnetic field H . An interaction energy $\mathcal{H}_B$ will result from this interaction of the nuclear magnetic moment with the magnetic field $\vec{B}$ existing within the solid:

$$\mathcal{H}_B = -\gamma \hbar \vec{I} \cdot \vec{B} \quad (9)$$

where

$\vec{I}$ = nuclear spin vector

$\vec{B}$ = magnetic field (induction)

γ = gyromagnetic ratio divided by 2π

h = Planck's constant.

In the absence of $\mathcal{H}_{int}$ (and in the nonrelativistic theory) the wave function satisfies the eigenvalue equation, (where now we use the eigenket to represent the eigenfunction)

$$\mathcal{H}_B |I, m\rangle = W |I, m\rangle \quad (10)$$

$$I \cdot I |I, m\rangle = I(I+1) |I, m\rangle \quad (11)$$

$$I_z |I, m\rangle = m |I, m\rangle, \quad m = -I, -I+1, \dots, I-1, I \quad (12)$$

$$P |I, m\rangle = \pm |I, m\rangle \quad (13)$$

$$\langle I, m' | I, m \rangle = \delta_{m'm}$$

where $\delta_{m'm} = 0$ if $m' \neq m$, and $\delta_{m'm} = 1$ if $m' = m$. P is the parity operator, I is the spin operator, $|I, m\rangle$ is the eigenket of $\mathcal{H}_B$. $I \cdot I$, I_z and P operating on $|I, m\rangle$ describe a $(2I+1)$ -fold degenerate nuclear level which has energy W and $(\text{spin})^{\text{parity}}$ equal to $I^\pm$.

The quadrupole interaction energy is small compared to the energy of interaction with the external magnetic field (about 3MHz in the present work) as we will show later. We thus can treat the quadrupole interaction as a perturbation of the magnetic energy levels. From the more detailed discussion of Cohen and Reif[2] we know the contribution of the odd terms in Eq.(5) to the matrix element of $\langle I, m | \mathcal{H}_{\text{int}} | I, m \rangle$ is zero; also, the hexadecapole term is approximately 8 orders of magnitude smaller than the quadrupole term. The first term in Eq.(5) will just shift the energy by a constant amount; it is independent of nuclear size, shape, and orientation, and is thus of no interest to us. We need to consider only the quadrupole term; Eq.(5) then becomes

$$\mathcal{H}_{\text{int}} = \frac{1}{2} \sum_{\alpha\beta} Q'_{\alpha\beta} V_{\alpha\beta}. \quad (14)$$

Define

$$Q_{\alpha\beta} = 3Q'_{\alpha\beta} - \delta_{\alpha\beta} \sum_i Q'_{ii}. \quad (15)$$

In terms of $Q_{\alpha\beta}$ Eq.(14) becomes

$$\mathcal{H}_{\text{int}} = \frac{1}{6} \sum_{\alpha\beta} Q_{\alpha\beta} V_{\alpha\beta} + \frac{1}{6} \left(\sum_i Q'_{ii} \right) \left(\sum_{\alpha} V_{\alpha\alpha} \right). \quad (16)$$

The last term in Eq.(16) can be neglected for our purpose because it is independent of nuclear orientation. Eq.(15) can then be written

$$\mathcal{H}_{\text{int}} = \frac{1}{6} \sum_{\alpha\beta} Q_{\alpha\beta} V_{\alpha\beta}. \quad (17)$$

We can simplify the Hamiltonian (17) by relating all 5 components of $Q_{\alpha\beta}$ to a single one. From a semiclassical point of view this is possible because the charges in the nucleus precess very rapidly about the direction of the nuclear spin. The external charges thus interact only with the time average of the nuclear charge distribution which has radial symmetry about the nuclear spin, or x_3 , direction. By symmetry, in the principle axis system, the time-average quadrupole components are $Q_{\alpha\beta} = 0$ for $\alpha \neq \beta$, and $Q_{11} = Q_{22}$. Also $Q_{\alpha\beta}$ is a traceless irreducible tensor, $Q_{11} + Q_{22} + Q_{33} = 0$, so that $Q_{11} = Q_{22} = -\frac{1}{2}Q_{33}$. Hence all quadrupole components can be expressed in terms of Q_{33} referred to the spin (z) axis as the principle axis.

Let us define nuclear electric quadrupole moment Q as

$$eQ \equiv \langle I I | Q_{33} | I I \rangle. \quad (18)$$

We can see Q is the expectation value, measured in units of the proton charge e , of Q_{33} in the state in which the component of I along the z axis is a maximum. It reflects the departure of the symmetry of the distribution of the charge density from spherical. From Eq.(8), Eq.(15) and Eq.(18) we know

$$Q \equiv (1/e) \langle I | I | \int \rho(\vec{r}) (3x_3^2 - r^2) d\vec{r} | I | \rangle. \quad (19)$$

In case of $\rho(\vec{r})$ having spherical symmetry, we see that Q is zero. A prolate ellipsoidal (football shaped) nucleus has Q positive; an oblate ellipsoidal (discus shaped) nucleus has Q negative. In our case, for ^{95}Mo , Q is $(0.12 \pm 0.03) \times 10^{-24} \text{ cm}^2$.

The electric field gradient, given by Eq.(3), is equal to the negative value of the second derivative of the electrostatic potential at a point. By proper choice of the principal axes $x_{\alpha'}$ ($\alpha' = 1, 2, 3$) only the 3 components $V_{x'x'}$, $V_{y'y'}$, $V_{z'z'}$ do not vanish, also since the $V_{\alpha'\alpha'}$ are the result of charges external to the nucleus

$$\nabla^2 V = V_{x'x'} + V_{y'y'} + V_{z'z'} = 0. \quad (20)$$

In the present work, the field gradient will be treated as axially symmetric with respect to z' axis, i.e. $V_{x'x'} = V_{y'y'}$, and there is only one independent component $V_{z'z'}$. $V_{z'z'}$ is a scalar descriptive of the electric environment defined as [6]

$$V_{z'z'} = eq = \int \rho_e(\vec{r}) (3 \cos^2 \phi - 1) r^{-3} dV, \quad (21)$$

where the integral is taken over all charges external to the nucleus, $\rho_e(\vec{r})$ is the density of that charge, $\vec{r}$ is the vector joining the nucleus to the volume element dV , and ϕ is the angle between $\vec{r}$ and the symmetry axis of $V(\vec{r})$. The EFG in the original coordinate system is then given by

$$\frac{d^2 V}{dz^2} = \frac{1}{2} eq (3 \cos^2 \theta - 1), \quad (22)$$

where θ is the angle between the axis of axial symmetry (z') and the

external field H_0 (along the z direction).

If the charge distribution is spherically symmetric, or equally well if it has cubic symmetry, $V_{x'x'} = V_{y'y'} = V_{z'z'}$, so that by Eq.(20) each component $V_{ii} = 0$ and the quadrupole interaction vanishes. This fact is very important to many experiments concerned with quadrupole interactions in solids. If a nucleus is at a lattice position of cubic point symmetry, then the electric field gradient must vanish.

When an isolated nucleus of spin I and magnetic dipole moment μ is placed in an external magnetic field H_0 , the magnetic energy levels of the nucleus become $2I+1$ in number. Their relative population is given by the Boltzmann distribution function characteristic of the temperature; and each level is separated from the next by an energy $\Delta E = \mu H_0 / I = \gamma h H_0$. For Mo , where $I=5/2$, there are six equally spaced energy levels, as shown in Fig. 1, and therefore five transitions of equal energy are possible if $q=0$ at every nucleus. The frequency corresponding to these transitions is

$$\nu_0 = \Delta E / h = \gamma H_0. \quad (23)$$

The application of a rotating field H_1 , perpendicular to H_0 , induces transitions between the levels when its frequency is equal to the energy level spacing divided by h . In the case of an isolated nucleus, energy is absorbed or emitted at only one frequency and a plot of absorbed energy versus applied frequency is a sharp spike at $\nu = \nu_0 = \gamma H_0$. When examined in materials, several factors tend to broaden the absorption; the most commonly considered effect is dipolar broadening caused by the fields of the nuclear dipoles themselves. For Mo , with two isotopes of non-zero

spin, ^{95}Mo and ^{97}Mo , of abundances 15.72% and 9.46% respectively, the broadening for ^{95}Mo may be approximated by [7]

$$\Delta H = 2 \langle \Delta H^2 \rangle_1^{1/2}, \quad (24)$$

where

$$\langle \Delta H^2 \rangle_1^{1/2} = \left[\frac{3}{5} I_1 (I_1 + 1) \hbar^2 P_1 + \frac{4}{15} I_2 (I_2 + 1) \hbar^2 P_2 \right] \times \sum_j r_{0j}^{-6}, \quad (25)$$

and ΔH is twice the root mean square theoretical dipolar width, in field. P_1 , P_2 are the abundances; the subscripts 1 and 2 represent ^{95}Mo and ^{97}Mo nuclei respectively throughout. Mo metal has the BCC structure and a lattice constant $a = 3.1469 \text{ \AA}$. The lattice sum $\sum_j r_{0j}^{-6}$ was done for a BCC lattice lying within a sphere of radius $65a$. The result is that $2 \langle \Delta H^2 \rangle_1^{1/2} \approx 0.65 \text{ G}$. This is an approximation to the line width, calculated for ^{95}Mo , in terms of field.

An important consideration with regard to the shape of the absorption curve is the interaction between the nuclear electric quadrupole moment and the EFG at the nucleus. Using first order perturbation theory we find that this interaction shifts the energy of the m^{th} level to [8]

$$E_m = -\gamma \hbar m H_0 + \{eQ/[4I(2I-1)]\} [3m^2 - I(I+1)] (d^2V/dz^2). \quad (26)$$

In our case, the EFG is axially symmetric and d^2V/dz^2 is given by Eq.(22). We can find the transition frequency from m^{th} level to $m-1^{th}$ level $\nu_{m \rightarrow m-1}$ by solving $(E_{m-1} - E_m)/h$. Substituting Eq.(22) into Eq.(26) we find that

$$\nu_{m \rightarrow m-1} = \nu_0 - (2m - 1)(3\cos^2\theta - 1) \frac{3e^2qQ}{8I(2I-1)h}. \quad (27)$$

As shown in Fig. 1, ν_0 is the frequency for the unshifted resonance. From Eq.(27), we can see that the transition frequency is different for each transition. The unshifted $m=1/2 \rightarrow -1/2$ transition is called the central line, all other transitions ($5/2 \rightarrow 3/2$, $3/2 \rightarrow 1/2$, $-1/2 \rightarrow -3/2$, $-3/2 \rightarrow -5/2$) are called satellite lines. The frequencies of the satellite lines are θ dependent, while for $m=1/2 \rightarrow -1/2$ the second term in Eq.(27) vanishes, and the transition remains at ν_0 , the unperturbed "center" position. The satellite lines are symmetrically disposed about ν_0 in this first order perturbation approximation.

In powders, all angles θ are present so the energy absorbed by the satellite lines is not just at one particular frequency, but is over a range of frequencies corresponding to $0 \leq \theta \leq \pi$. This causes a broadening, although no shift, of the resonance. The energy absorbed at each frequency in this range is small and difficult to detect and some of the frequencies may be beyond our field scanning range and escape detection. Very low absorption amplitude cannot be distinguished from the baseline far from the central peak.

The splitting $\Delta\nu_m (= \nu_{m \rightarrow m-1} - \nu_0)$ introduced by the first order quadrupole interaction is independent of external field strength, and the relative intensity of the satellite corresponding to the $m \rightarrow m-1$ transition is given to a good approximation by $(I+m) \cdot (I-m+1)$. For $I=5/2$, we have five lines with relative intensities 5:8:9:8:5. In powder, the satellite lines spread over a range corresponding to all angles, and their integrated

intensities have the above ratios.

In our alloys the parameter e^2qQ/h is sufficiently large to produce an apparent reduction of the central line intensity by second order quadrupole interaction. Using second order perturbation theory, we find that the transition frequency for the central line of a nucleus in an axially symmetric field gradient q is [7]

$$\nu_{\frac{1}{2} \rightarrow -\frac{1}{2}} = \nu_0 + (A/h) (1 - 9\cos^2\theta) (1 - \cos^2\theta) \quad (28)$$

where $A = (9/64)\{(2I+3)/[4I^2(2I-1)]\}(e^2q^2Q^2/h\nu_0)$.

From this we see that the central line is also shifted and broadened (for powders) by a sufficiently large EFG (given Q). The size of the resonance frequency shift is inversely proportional to the external applied field H_0 , as can be seen from Eq.(28), since A is inversely proportional to ν_0 .

III. EXPERIMENTAL PROCEDURE

(A) Preparation of Samples

The samples used in the present work were Mo powder, and filings of pure Mo and Mo alloys. Filings were from a 99.97% pure Mo rod, an arc-melted button of the same Mo rod, Mo-Nb alloys with Nb concentration from one to ten atomic percent, and Mo-V alloys with V concentration from one to ten atomic percent, Tables II.a, II.b, and II.c list the samples used in this experiment.

The Mo base alloys were made from 1.59 cm diameter rod of vacuum arc-melted Mo received from Climelt, Inc. and kindly given to us by Prof. C. A. Wert. It is the same Mo rod used by Dr. George W. Nelson for the work described in his thesis "Static and Cyclic Creep Behavior of Polycrystalline Mo in Ultra-High Vacuum Environment." The impurity concentration of the as-received material using mass spectrograph and vacuum fusion analyses is shown in Table I. The solute metals Nb and V, were obtained from Materials Research Corporation and had nominal purity contents of 99.96% and 99.9% respectively. The material was designated as MRC's "Very Pure" grade. The alloys were prepared in 15 gram quantities, the weighed constituents being arc-melted in an inert (argon) atmosphere in each case. The arc-melted buttons were turned over in the hearth at least five times during their preparation in an attempt to improve their homogeneity. The arc furnace was of standard design; both the copper hearth and the tungsten upper electrode were water cooled. A getter button of Zr was used to remove residual oxygen and nitrogen from the commercially pure argon.

The arc-melted buttons and Mo bar were filed by a filing machine which simulated hand filing. The file we used in the filing machine was a Nicholson No.1 smooth hand file. The filings collected were passed between the poles of a strong magnet ($\geq 2\text{kG}$) to remove any ferromagnetic particles. The latter would tend to broaden the resonance. After removing any ferromagnetic particles, the filings were washed twice with carbon tetrachloride in order to remove any grease that may have come from the filing machine. The result was clean and loose filings for the subsequent preparatory steps to be described below.

In experiments with metallic filings, the depth of penetration, or skin depth, of the radiofrequency field must be considered. When the size of the metallic filings exceeds the skin depth of the material being investigated, absorption measurements do not exhibit the imaginary part of the nuclear susceptibility χ'' only, but a mixture of the real χ' and imaginary susceptibilities.

In order to limit the size of metal filings investigated in this experiment, the filings were passed through a 200 mesh (0.074 mm opening) sieve. After passing the particles through the sieve, we attempted to find the Mo resonance but failed to locate it. A likely source of this difficulty was thought to be the cold work introduced through the filing process. Early experiments on other metals[9,10] had shown the possible drastic effects of filing; we thus decided to anneal the filings. After annealing in argon at approximately 950°C for several hours, we succeeded in locating the resonance.

Professor T. J. Rowland assisted with the annealing process. Each sample of filings was put into a small Mo thimble which was then put into a

quartz capsule. The latter was then evacuated and flushed with argon at least three times; finally a residual argon pressure of about 200-250 mm was established and the capsule sealed. The purpose of this was to ensure an argon pressure of roughly one atmosphere at the annealing temperature (900°C - $1,000^{\circ}\text{C}$). The sealed capsules were put into a furnace and the samples annealed at about 900°C with some differences in temperatures and times. The detailed annealing temperature and annealing time for each alloy is listed in Table II.

After annealing and cooling to room temperature, the capsules were broken. A column length of filings $1/4$ " long was placed into a weighed glass vial; reweighing gave the mass of filings in the vial.

(B) Experimental Apparatus

Block diagrams of the apparatus employed in the detection and display of the resonance absorption are shown in Fig.2 and Fig.3. Figure 2 shows the apparatus used for the resonance measurement in which the integrated absorption intensity of ^{31}P in 85 wt.% orthophosphoric acid (H_3PO_4) doped with ferric chloride was compared with that of Mo powder. Figure 3 shows the apparatus used for the resonance measurements of all of the metal and alloy samples considered in this thesis. The two arrangements were approximately the same except that a different kind of scanning unit, lock-in amplifier, data storage device and method of tracing the resonance curve were employed.

In both cases, we used the Bloch crossed-coil probe. The external magnetic field H was produced by a Pacific Electric Motor Company current regulated power supply and an 18-inch (pole piece diameter) electromagnet with faces tapered to 12 inches in diameter; it had a gap of $3\frac{1}{4}$ inches. The field inhomogeneity was estimated to be less than 0.2 gauss over the volume of our sample. A standard model V-4210A Varian variable frequency transmitter-receiver unit provided the rf field, signal amplification, and detection. The Varian probe used contained the crossed transmitter and receiver coils, the balancing paddles, and the modulation coils. A Hewlett-Packard model 200ABR audio oscillator driving an audio power amplifier supplied current to the modulation coils in the probe body for field modulation. For the apparatus in Fig.2, we used a Model 4280A Field Precession Scanning Unit to sweep the external field, and an Electronics, Missiles and Communication, Inc., Model RJB lock-in amplifier. The output of the lock-in was recorded on an L&N Speedomax Type G chart recorder. For

the apparatus in Fig.3, we used a Hewlett-Packard Model 3310A function generator which generated a triangle wave (ramp voltage) to sweep the external field, and a PAR Model 129 two-phase/vector lock-in amplifier (phase-sensitive detector) which showed both vector components of the audio input signal with respect to a reference voltage of the same frequency. A Fabri-Tek (now Nicolet) Model 1070 signal averager was used to assist in averaging the noise. The signal averager has two inputs, the synchronization input which is from the function generator, and the signal input, which is the in-phase output of the lock-in amplifier. An x-y recorder was used to trace out the resonance curve which had been averaged by the signal averager.

(C) Measurement Procedure

(C.1) Relative intensity comparison of ^{95}Mo with ^{31}P .

In order to know the fraction of the total absorption that the ^{95}Mo satellite lines and central line contribute to the observed resonance curves in Mo powder and Mo filings, we chose to use a well known nucleus and environment as a reference standard. In the present work, we chose ^{31}P , as our standard nucleus. Phosphorus has only one isotope ^{31}P , i.e. its natural abundance is 100% and its spin $I=1/2$; it thus has a quadrupole moment $Q=0$, thus no quadrupole interactions. In this experiment, we took advantage of these two properties.

At 11°C , elemental white phosphorus has an electrical resistivity of 1×10^{17} microhm-cm, which gave us a clue that its spin-lattice relaxation time T_1 was probably very long; we verified this, and decided to use not elemental phosphorus, but instead a carefully weighed amount of 85% by weight orthophosphoric acid (H_3PO_4). To this we added a paramagnetic salt, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) to decrease T_1 . The higher the concentration of paramagnetic ions became [11], the broader the line width, since the width of the resonance line, in frequency, is roughly $1/T_1 \approx 1/T_2$ in this case. We experimented with several concentrations of ferric chloride in the H_3PO_4 (85 % by weight) until the line width of ^{31}P was approximately 0.8G. The measured line width of our Mo powder was approximately 0.84G.

We used the electronic apparatus shown in Fig.1 to make the measurements for both P in orthophosphoric acid, and ^{95}Mo in Mo powder at approximately the same frequency. For both cases, we used identical experimental conditions except for the lock-in gain. The audio frequency

was 40Hz, and the rf field was set at the value which appeared to give a saturation factor of one for the Mo metal resonance. Phosphorus in our doped H_3PO_4 under this rf field is far below saturation. The rate of change of the external field H_0 was 0.193 G/min for ^{95}Mo and 0.153 G/min for ^{31}P . The difference arises from the greatly different external field at which the resonance were observed. We put each vial into the center of the field, and then adjusted the rf homodyning signal so that only pure absorption was observed. A time constant of 30 sec was used in the lock-in amplifier output filter.

(C.2) The effect of V and Nb additions on the intensity of ^{95}Mo .

For the measurement of all the Mo and Mo alloy samples the apparatus shown in Fig.2 was used. ^{95}Mo has a measured spin-spin relaxation time $T_2 = 10$ msec; in order to get a good signal-to-noise ratio, we must employ an audio frequency ν_m , such that $1/\nu_m \gg T_2$. We used an audio modulation frequency of 20Hz, which gives $1/\nu_m = T_m = 50$ msec, five times larger than T_2 . For these experiments we used a Fabri-Tek signal averager; 1024 sweeps were made for each resonance curve, it took 24.1 sec per sweep, and at least 1.3 sec to pass through the resonance (from peak-to-peak of the derivative curve). From these considerations we decided to use a 0.3 sec time constant for the lock-in amplifier. The latter is essentially a narrow-band amplifier followed by a phase-sensitive detector with an over all band width of roughly the reciprocal of the output time constant. Before the vial is put into the center of the crossed coils, the filings are made loose (not packed down), so that the electromagnetic field will penetrate into the center of the mass of filings and all the ^{95}Mo nuclei

will contribute to the resonance absorption. In addition there are less conduction paths if the powder is loose; this leads to a higher Q for the receiver coil.

The radio frequency used for ^{31}P was 4MHz which will produce a P resonance at a main field of approximately 2.3kG. For ^{95}Mo the resonance frequency was 3.0692MHz, corresponding to a resonance field of approximately 11kG for ^{95}Mo .

IV. EXPERIMENTAL RESULTS AND CALCULATIONS

The measured value of the full line width (peak-to-peak of the recorded derivative) of ^{95}Mo in Mo powder is 0.84G. This is a little wider than the calculated value 0.65G, which is derived by considering the dipole-dipole interaction only.

In order to make comparison of ^{95}Mo in Mo powder with ^{31}P in 85 wt.% orthophosphoric acid (H_3PO_4) doped with ferric chloride, we require a theoretical expression allowing a comparison to be made between their observed absorption magnitudes. Our situation is not straight forward, as will be seen below.

At the same frequency, the NMR sensitivity for equal numbers of different nuclei is different; the relative sensitivity is available in NMR tables. In the present work, we use different numbers of nuclei and different resonance frequencies for the resonance measurements of ^{95}Mo and ^{31}P . More importantly we use two different conditions of saturation for the two systems. In calculating the ratio of the integrated intensity of ^{31}P to that of ^{95}Mo , we have to take these three factors into account. We then get two different values for the calculated ratio corresponding to two different assumptions: one is that all the central line and satellite lines contribute to the measured ^{95}Mo resonance peak, the other is that only the central line contributes to the observed ^{95}Mo resonance peak.

Experimentally each resonance curve which we record directly from the lock-in amplifier is the derivative of an absorption curve; from this we measure the peak-to-peak height J , and the peak-to-peak separation ΔH (full line width). Expressions have been developed[12] which compare the numbers

of resonating nuclei in two equal specimen volumes in terms of J' and ΔH for both saturated and unsaturated conditions of absorption lines with either the Gaussian or the Lorentzian line shape. We developed a variation of the calculation which took the resonating frequency and rf field (including saturation effects) into consideration because they are different for ^{95}Mo and ^{31}P in our case. We found that:

(i) Saturated case ($s \equiv \pi \gamma^2 H_1^2 T_1 g(0) = 1$)

$$N \approx \frac{c^* J' (\Delta H)^{3/2} T_1^{1/2}}{\omega_0^{3/2} \gamma^{1/2} I(I+1)}, \quad (29)$$

where $c^* = 3.28$ for a Lorentzian and 1.46 for a Gaussian line. T_1 is the spin-lattice relaxation time. (This is the condition under which the ^{95}Mo resonance is observed; its shape is approximately Gaussian.)

(ii) Unsaturated case ($s \ll 1$)

$$N \approx \frac{c^* J' (\Delta H)^2}{\omega_0^{3/2} \gamma I(I+1) H_1}, \quad (30)$$

where $c^* = 1.81$ for a Lorentzian and 0.516 for a Gaussian line; H_1 is one-half of the linear rf field magnitude. The ferric chloride caused this unsaturated condition to obtain in the phosphoric acid sample and also caused the Lorentzian line shape.

As mentioned above, in the present work, the ^{95}Mo resonance curve approximates a Gaussian shape (a frequent result of dipole-dipole broadening), and the ^{31}P resonance curve is Lorentzian in shape (due to lifetime broadening). We apply the same voltage across the rf coil in both

cases. For the same voltage across the tuned transmitter output tank circuit the rf field is inversely proportional to frequency. From the saturation condition ($s = \pi \gamma^2 H^2 T_1 g(0) = 1$) of ^{95}Mo , we can calculate the rf field H_1 at one frequency ($\sim 3\text{MHz}$) and then at another frequency (e.g. 4MHz , in our case for ^{31}P). Substituting the experimentally measured values of J' and ΔH into Eq.(29) and Eq.(30) for ^{95}Mo and ^{31}P respectively we can calculate the ratio of N_{31} (number of nuclei of ^{31}P) to N_{95} (number of nuclei of ^{95}Mo) and make a comparison with the theoretical value. The result is that the experimental value corresponds to the theoretical value of only the ^{95}Mo central line contribution to the measured ^{95}Mo resonance peak. The measured value is within 10% of the theoretical intensity of the central peak alone whereas it differs from the total ^{95}Mo intensity by a factor of roughly 4.

The satellite lines are not observable due to first order quadrupole broadening and so only $9/35 = 25.7\%$ of the intensity, corresponding to the $m = 1/2 \rightarrow -1/2$ transition, is observed.

The integrated intensities $J'(\Delta H)^{3/2}$ corrected for the number of ^{95}Mo nuclei in the various samples are listed in Tables III.a, III.b, and III.c. We can see that when the solute concentration is less than 5 at.%, the line width of the resonance increases as the solute concentration increases. The corrected integrated intensities of Mo powder(A) and Mo filings(A) are almost the same with a difference of less than 2%; that of Mo filings(C) is 12% smaller than the above two, but the difference is comparable to our estimated error for these measurements. When we annealed the Mo filings, we assumed that the annealing temperature and annealing time were high enough and long enough to remove the imperfections introduced by the filing process. In that case the energy absorbed by the ^{95}Mo nuclei should be the

same in any pure Mo, regardless of its origin. Our experiments prove this, at least with regard to the central line, and for annealing treatments near 1000°C. For the integrated intensity comparison of ^{95}Mo in Mo alloys, we chose Mo filings(A) as our comparison standard, because they were produced from an arc-melted button of the same starting material as all other alloys used in this experiment. This Mo was described in detail in Section (A) of Chapter III.

V. DISCUSSION AND CONCLUSIONS

The data reported in Tables III.b and III.c when viewed together with the line shape changes portrayed in Figs. 4 and 5 strongly suggest the explanation for the changes resulting from the addition of V or Nb to Mo. Similar, but different, behavior has been observed in Cu[10], Al[9], and V[5] alloys. In each of these metals, solutes produced striking effects on the solvent resonance amplitude. For Cu, central line broadening was the sole result of solute addition; for Al and V the observations could be described in large part in terms of first order perturbation of the satellite lines.

As we have shown, the ^{95}Mo resonance in pure Mo after filing and annealing near $1,000^\circ\text{C}$ consists entirely of the $m = 1/2 \rightarrow -1/2$ transition. Decreased absorption intensity and line broadening caused by solute addition can be understood as a direct result of second order perturbation of the $m = 1/2 \rightarrow -1/2$ transition. The magnitude of this perturbation can be estimated from the line shape, and especially the extent of the tails (low intensity absorption far from the center of the unperturbed resonance). We estimate that A/h for ^{95}Mo (cf. Eq(28)) is roughly 200 Hz for nuclei near either V or Nb in Mo. A calculation very similar to that carried out by von Meerwall and Rowland[5] using realistic central line shape functions would be required in order to analyze the data more quantitatively. The result would be a computer simulation of the observed lines. A detailed calculation could use probabilities formulated in the manner of Ref.[5] and a series of electric field gradients $q_1, q_2, \dots, q_i$.

associated with the 1st, 2nd,, ith nearest neighbor to a solute atom. The complete calculation is beyond the scope of this thesis. The body of data presented, together with the discussion above, establish the magnitude and the mechanism of the broadening observed in ^{95}Mo when V and Nb are present as minor alloying elements (0-10 at.%). These constitute the conclusions of the investigation presented herein.

$$\nu_0 = \gamma H_0$$

$$\Delta\nu = \frac{3e^2qQ}{40h} (3\cos^2\theta - 1) \underset{\theta \neq 0}{=} \frac{3e^2qQ}{20h}$$

Figure 1. Energy level diagrams and their spectra for the ^{95}Mo nucleus in a magnetic field H_0 showing the change in the spacing of the energy levels caused by first order quadrupole interactions. The spacing shown corresponds to $\theta = 0$.

Figure 2. Block diagram of the equipment used in the resonance intensity comparison between ^{31}P and ^{95}Mo metal powder.

Figure 3. Block diagram of the experimental equipment used in the resonance intensity measurements made on Mo and Mo alloys.

Figure 4. Recordings of ^{95}Mo resonance in (a) Mo-0.996 at.% V, (b) Mo-2.494 at.% V, and (c) Mo-10.013 at.% V alloys. The Recordings are positioned so as to have common zero.

Figure 5. Recordings of ^{95}Mo resonance in (a) Mo-0.999 at.% Nb, (b) Mo-2.744 at.% Nb, (c) Mo-4.998 at.% Nb, and (d) Mo-10.699 at.% Nb alloys. The recordings are positioned so as to have common zero.

Table I.

Impurity analysis of Mo rod from Climelt, Inc.

Element	Composition(ppm)
Carbon (C)	40
Oxygen (O)	9
Hydrogen (H)	7.2
Nitrogen (N)	10
Iron (Fe)	170
Niobium (Nb)	50
Tantalum (Ta)	>1,000
Tungsten (W)	>1,000

Table II.a

Annealing temperature and annealing time for pure Mo samples

Sample	Anneal. Temp. ($^{\circ}\text{C}$)	Anneal. Time (min)
Mo powder(A)	-----	-----
Mo filings(A)*	816	900
	1,000	300
	1,015	246
	900 ± 10	4,340
Mo filings(C)**	970 ± 10	4,320

* Mo filings(A) were filings from an arc-melted button of the same Mo as was used as the starting material for the Mo base alloys.

** Mo filings(C) were filings directly from the Mo rod used in making the alloys.

Table II.b

Annealing temperature and annealing time for Mo-V alloys

Sample*	Anneal. Temp. ($^{\circ}\text{C}$)	Anneal. Time (min)
Mo-0.996 at.% V	900	120
	970 ± 10	4,200
Mo-2.494 at.% V	900	65
	970 ± 10	4,255
Mo-5.054 at.% V	1,000	830
	1,015	275
Mo-9.879 at.% V	745	1,537
	1,015	208
	848	855
Mo-10.013 at.% V	880 ± 20	2,513
	908	1,812

* Sample compositions are believed known to 3 significant figures only; additional figures are used for sample identification purposes.

Table II.c

Annealing temperature and annealing time for Mo-Nb alloys

Sample*	Anneal. Temp. ($^{\circ}\text{C}$)	Anneal. Time (min)
Mo-0.999 at.% Nb	975 $\pm$ 7	4,320
Mo-2.744 at.% Nb	975 $\pm$ 7	4,320
Mo-4.998 at.% Nb	835	680
	1,120	295
	1,140	205
	975 $\pm$ 7	4,320
Mo-10.699 at.% Nb	835	750
	1,120	159
	1,140	132
	1,008	1,605

* Sample compositions are believed known to 3 significant figures only; additional figures are used for sample identification purposes.

Table III.a

Experimental line width and corrected integrated intensity
for three different pure Mo samples.

Sample	$\Delta H(G)$	$J'(\Delta H)^{3/2}*$
Mo powder(A)	0.84	16.260
Mo filings(A)	0.905	16.021
Mo filings(C)	0.880	14.307

* $J'(\Delta H)^{3/2}$ is in arbitrary units; J' is corrected for mass of Mo used.

Table III.b

Experimental line width and corrected integrated intensity
for Mo-V alloys.

Sample	$\Delta H(G)$	$J'(\Delta H)^{3/2}$	J/J_0 *
Mo filings(A)	0.905	16.021	1
Mo-0.996 at.% V	1.056	6.405	0.400
Mo-2.494 at.% V	1.76	5.988	0.374
Mo-5.054 at.% V	0.754(?)**	1.672	0.104
Mo-9.879 at.% V	0.873(?)**	(?)	(?)
Mo-10.013 at.% V	1.106(?)***	1.104(?)	0.069(?)

* $J \equiv J'(\Delta H)^{3/2}$; J_0 is the value $J'(\Delta H)^{3/2}$ for Mo filings(A).

** (?) signifies that the narrow line width is probably the result of severe coring during the arc-melting process.

*** (?) signifies a large uncertainty because of poor signal-to-noise ratio.

Table III.c

Experimental line width and corrected integrated intensity
for Mo-Nb alloys.

Sample	$\Delta H(G)$	$J'(\Delta H)^{3/4}$	J/J_0
Mo filings(A)	0.905	16.021	1
Mo-0.999 at.% Nb	0.956	6.086	0.380
Mo-2.744 at.% Nb	1.660	5.901	0.368
Mo-4.998 at.% Nb	2.716	5.835	0.364
Mo-10.699 at.% Nb	1.157(?)*	1.285(?)	0.080(?)

* (?) signifies a large uncertainty because of poor signal-to-noise ratio.

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Computer program for the BCC lattice sum $\sum_j V_{oj}^{-6}$ within
a sphere of radius .65 (assume a=1)

```

00100      REAL RA,B,X,Y,Z,RF,E,RP,RR
00200      B=.5
00300      RF=.
00400      E=1
00500      GO TO 90
00600      80      E=2
00700      90      Z=B
00800      50      X=B
00900      Y=B
01000      GO TO 20
01100      10      IF(X.EQ.0.)GO TO 110
01200      IF(Y.EQ.0.)GO TO 30
01300      Y=B
01400      X=X+1.
01500      20      R=X*X+Y*Y+Z*Z
01600      IF(R.GT.65.)GO TO 10
01800      RP=R*(-3)
01900      RF=RP+RF
02000      Y=Y+1.
02100      GO TO 20
02200      30      IF(Z.EQ.0.)GO TO 100
02300      IF(X.EQ.0.)GO TO 40
02400      Z=Z+1.
02500      GO TO 50
02600      40      GO TO (60,70)-E
02700      60      B=1.
02800      GO TO 80
02900      70      RA=B.*RF
03000      Z=0.
03100      RF=0.
03200      GO TO 50
03300      100     RA=RA+12.*RF
03400      X=0.
03500      RF=0.
03600      Y=B
03700      GO TO 20
03800      110     RA=RA+6.*RF
03900      TYPE 130,RA
04000      130     FORMAT (7/5X,E13.6)
04100      END

```

$$\sum_j V_{oj}^{-6} = RA \cdot b^{-6} \quad (b = \text{Lattice Parameter})$$