we have

$$P = \{3c(\cos\theta - \cos\theta_1)[(1 - 3c\cos\theta$$
$$+ 6c^2\cos\theta - \cdots) + (1 - 2c\cos\theta + \cdots)\gamma/2]$$
$$- (1 - c\cos\theta + c^2\cos^2\theta - \cdots)\gamma/2)\}U/\gamma^2$$
$$= \{(3c\cos\theta + 9c^2/2 + \gamma/2 - 2\gamma c^2\cdots)$$
$$\times [(1 + c\cos\theta)^{-3} + (1 + c\cos\theta)^{-2}\gamma/2]$$
$$- (1 + c\cos\theta)^{-1}\gamma/2\}U/\gamma^2, \quad (5')$$

$\cos\theta_1$ having been determined by the condition $\langle P\rangle_{\text{Av}} = 0$. After substituting this in $(\partial u/\partial z)_{z=k} = (\frac{1}{2} - 1/k)U + Pk(1 - 5k/6)$ from (3'), and again

using $\langle\cos^2\theta\rangle_{\text{Av}} = \frac{1}{2}$, we obtain for the viscous torque on the stationary outer cylinder about its center,

$$M' = -2\pi\eta(a + g)^2\langle(\partial u/\partial z)_{z=k}\rangle_{\text{Av}}/a$$
$$= [2\pi\eta U(a + g)^2/g]$$
$$\times [1 - g/2a - c^2 + 9gc^2/4a + \cdots].$$

With $c = 0$ and $g = b - a$ this reduces to Eq. (1) of the preceding paper.[1] The error to be expected because of a nonvanishing c is thus slightly decreased by taking the curvature into account.

Magnetic Studies of Solid Solutions

I. Methods of Observations and Preliminary Results on the Precipitation of Iron from Copper

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This paper represents the first step in an extended program whose aim is the investigation of solid solutions with special reference to the structures that may be formed by heat treatment and plastic deformation. It is hoped to include eventually observations in high fields (100,000 gauss) and at low temperatures. The present work deals with observations up to 40,000 gauss and temperatures ranging from 20 to 1000°C. The manner of observation and reliability of the results is described in some detail. A series of observations on alloys of copper containing up to 0.7 percent iron are reported. Up to about 4 percent of iron can be put into solution in copper at high temperatures, but the solubility decreases to an exceedingly small value at room temperature. Our observations indicate that iron atoms in solution in copper retain a permanent magnetic moment of approximately 3.5 Bohr magnetons, and obey a Curie-Weiss law at high temperatures, the Curie temperature of an alloy containing 0.7 percent iron by weight being 150°K. The solution seems to be sluggish and can be greatly supercooled. The manner of precipitation from solution appears to be fairly complex, and the results are being tentatively interpreted as follows: First there is a rearrangement of the atoms in the solution followed by the precipitation of a nonmagnetic phase which can be converted into a ferromagnetic phase by cold work. This ferromagnetic phase can be made to grow thermally, but apparently does not form readily of its own accord.

I N a paper appearing concurrently in the *Review of Scientific Instruments* a newly equipped magnetic laboratory at The Massachusetts Institute of Technology is described in some detail. One of the projects for which this installation was designed is the investigation of the structures of alloys. Relatively little is known of the magnetic properties of matter except in the form of pure elements and compounds, or in solutions in thermodynamic equilibrium. Under certain circumstances magnetic properties may be exceedingly sensitive indicators of structure because they depend to a great extent on the interactions of neighboring atoms, and may be used to detect very small amounts of a particular

phase. There is also a very attractive field in low temperature research that has hardly been touched, and what observations have been made indicate that, especially in the high fields which we can produce, effects exist which may help us to understand some of the complexities of alloy structures. For these reasons we have decided to start a magnetic investigation of alloys, especially in the conditions of metastable equilibrium in which they manifest their most valuable properties.

The work of Tammann and his collaborators[1] indicated an interesting starting point. They used

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[1] G. Tammann and W. Oelsen, Zeits. f. anorg. Chemie V, **186**, 267 (1930).

magnetic methods with great success to determine the solubility limits of ferromagnetic metals in a series of solutions. More recently Gordon and Cohen[2] have investigated the aging of copper-iron and copper-cobalt alloys. They did not have available a sufficiently strong magnet to make a clear distinction between strong paramagnetism and weak ferromagnetism possible, but their results indicated so many interesting possibilities that we determined to follow it up with our more adequate equipment.

Methods of Measurement

The data which it is desired to obtain consist of a magnetization curve in which the intensity of magnetization of a sample is plotted as a function of magnetic field in fields ranging from zero to as large values as can be obtained. These curves should moreover be obtainable at any temperature. Magnetization curves for typical diamagnetic or paramagnetic substances are straight lines whose slope is called the susceptibility. Very few actual metals however, behave in this way, but show saturation effects which are commonly attributed to ferromagnetic impurities. In order to correct for these it is necessary to apply sufficiently strong fields to saturate any ferromagnetic components that are present, and to measure the slope of the magnetization curve in even stronger fields. The magnetization curve of a piece of ferromagnetic material depends, among other things, on its shape, and unless the ferromagnetic inclusions in a para- or diamagnetic sample are in the form of long needles pointing in the direction of magnetization, fields at least of the order of 10–20,000 gauss will be required to magnetize them to within a few percent of their saturation value. Strong magnetic fields should therefore be used, especially for samples containing appreciable amounts of ferromagnetism.

The magnet available for this work is described as magnet No. 1 in the above-mentioned publication appearing in the *Review of Scientific Instruments*. This is more or less of a legacy from our preliminary experiments on magnet design, and is not very greatly superior to a large iron core magnet. Its chief advantage lies in the fact

[2] This work is to be presented in the Trans. American Society for Metals, Age-Hardening Symposium.

that one can produce fields of any intensity up to 40,000 gauss without hysteresis effects, in that one can produce these fields in an adequate space, and especially in that the lateral stability of even a strongly magnetic sample is satisfactory. We have had little difficulty due to samples sticking to the inner walls of the solenoid.

The most satisfactory and most used method of measuring magnetization, especially in weakly magnetic materials, is to hang a sample near a magnet and measure the force exerted on it. This magnetic pull may best be interpreted in terms of magnetizations in two special cases. In the first the sample is in the form of a long cylinder with its lower end in the most intense part of the field and its upper end out of the field. This is called the Gouy method. The force on the sample in dynes is given by the expression

$$F = A \int_0^{H_m} I dH, \qquad (1)$$

where A is the cross-sectional area of the sample in sq. cm, I is the intensity of magnetization per unit volume, and H_m is the field strength at the center of the magnet. From Eq. (1) it is possible to calculate the intensity of magnetization at any field strength by differentiation.

$$I = \frac{1}{A} \frac{\partial F}{\partial H_m}. \qquad (2)$$

The process of differentiation, however, magnifies the observational errors and introduces new ones. It is therefore desirable to interpret the observations in the following way if one is concerned only with the saturation value of a ferromagnetic component and the susceptibility of a para- or diamagnetic component. In this case the intensity of magnetization has the form

$$I = I_s + kH \qquad (3)$$

for values of H greater than H_c, the critical field necessary to saturate the ferromagnetic component. I_s is this saturation intensity measured per unit volume of the alloy, and k is the volume susceptibility. Substituting this expression into Eq. (1) one gets

$$F = A \int_0^{H_c} I dH + A I_s (H - H_c)$$
$$+ \tfrac{1}{2} A k (H^2 - H_c^2). \qquad (4)$$
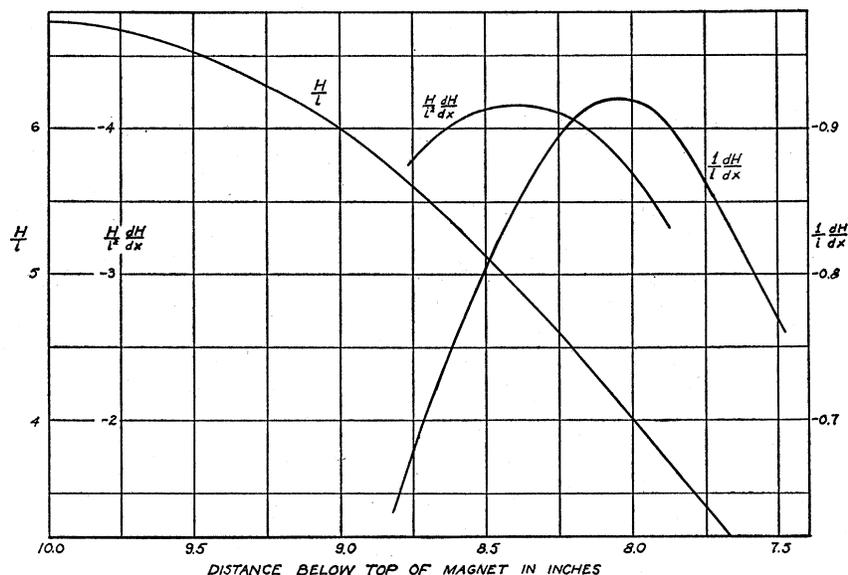
FIG. 1. Distribution of field along the axis of the magnetizing coil.

The behavior of the material in low fields may be completely eliminated by the following device.* Let H_0 be any particular value of the field greater than H_c, and let F_0 be the corresponding value of the magnetic force. We may then write

$$\frac{F-F_0}{H-H_0}=A I_s+A k\frac{H+H_0}{2}. \qquad (5)$$

The expression on the left plotted as a function of H is then a straight line from whose slope and position one may calculate I_s and k, provided only that H is greater than H_c. The advantage of the Gouy method lies in the fact that the position of the specimen in the magnet need not be accurately known if the field at the center of the magnet is homogeneous. The disadvantage lies in the fact that the specimen must be homogeneous, and must of course be at a uniform temperature. Both of these items are difficult to achieve if the specimen is as long as it must be in our magnet; namely, one foot.

The second method is called the Curie method, and consists of hanging a small sample of any shape at a point near the magnet where both the field and its gradient are known. The force acting on the sample is then given by the expression

$$F=m\sigma \partial H/\partial x, \qquad (6)$$

* This is more satisfactory than the usual procedure of plotting F/H^2 as a function of $1/H$ and extrapolating the resulting curve to infinite H to find k.

from which one can calculate the magnetization at any field strength directly. Here m is the mass of the sample and σ is the intensity of magnetization per unit mass. The great advantage of this method lies in the fact that one can make measurements on almost any kind of sample. The disadvantage is that one must know the position of the sample in the magnet accurately and that one cannot use the full field strength of the magnet. In our magnet these points turned out not to be serious. The magnetization of any sample may be expressed by a formula of the form

$$\sigma=a+bH \qquad (7)$$

in a sufficiently small range of fields, a and b being constants. The force exerted on the sample will therefore be given by

$$F=ma\partial H/\partial x+mbH\partial H/\partial x. \qquad (8)$$

The force therefore depends only on the quantities $\partial H/\partial x$ and $H\partial H/\partial x$ at the point where the sample is hung, and it is not necessary to know H itself accurately for the interpretation of the observation as the quantities a and b define the magnetization curve in the vicinity of the field strength used, and may be determined by observation at two field strengths near enough together so that a and b may be treated as constants. If in sufficiently large fields the magnetization curve becomes a straight line, as in

Eq. (3) for instance, the quantities a and b are truly constants, being the saturation intensity per unit mass σ_s, and the mass susceptibility χ, respectively.

The distribution of field in our magnet is shown in Fig. 1. The quantities plotted are independent of the magnet current i. By choosing a point $8\frac{1}{4}''$ below the top of the magnet to hang the specimens to be measured, conditions are such that an error of $\pm\frac{1}{32}''$ in locating the specimen will not result in an error of more than one percent in either $\partial H/\partial x$ or $H\partial H/\partial x$. Actually it is possible to locate the sample much more precisely than this, but this accuracy is ample for the present investigation. The values adopted for the constants of the magnet at this point are

$$H = 4.58\ i$$
$$\partial H/\partial x = -0.895\ i$$
$$H\partial H/\partial x = -4.10\ i^2. \qquad (9)$$

The absolute value of these constants has been determined only to within about 5 percent since we are chiefly interested in relative values. Both

methods have been used in the following investigation, and the Curie method found the more satisfactory except for the measurement of pure elements at room temperature.

The forces exerted on the specimens were measured with a chemical balance. This was found very convenient as it was necessary to vary the sensitivity in the course of the measurements because the balance tends to become unstable when the magnetic force is large, and this
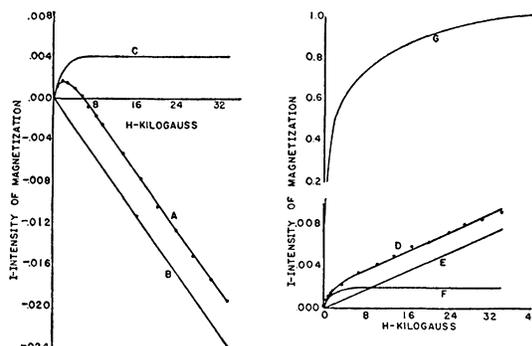
FIG. 3. Typical magnetization curves obtained on Cu-Fe alloys.

could easily be done by adding weights to the pointer. The magnet is provided with a platinum wound quartz furnace which can heat the sample to be measured to 1000°C. The design of the furnace is shown in Fig. 2. The sample S hangs in the hot zone, and its position can be located by means of a quartz stop A. Any desired atmosphere can be maintained by first flushing the furnace and then preventing air from diffusing in by passing a small amount of the desired gas in at the side arm B and out through the small opening in the glass plate C. Samples are held in a sling of molybdenum foil $0.001''$ thick hanging by means of a fine wire from one arm of the balance. A slight correction has always to be made for the force exerted on the sample-holder and balance.

Typical magnetization curves are shown in Fig. 3. Curve A was obtained on a sample of commercial copper. It may be interpreted as the sum of two curves B and C. B is the curve of a typically diamagnetic substance with a volume susceptibility of -0.714×10^{-6}. C is very similar to the magnetization curve to be expected of a small amount of ferromagnetic material in the form of more or less spherical particles. If this

FIG. 2. Diagram of magnet furnace.
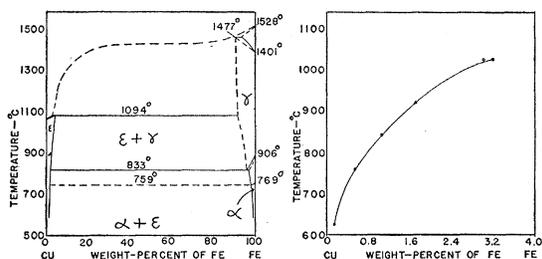
FIG. 4. The copper-iron phase diagram.

FIG. 6. Magnetic susceptibility and saturation intensity per unit volume of a powder compact containing 0.22 percent Fe during cooling.

material were iron, whose saturation intensity is about 1700, it would represent only 0.0002 percent of the sample. We shall here confine ourselves to the observation of the saturation intensity of the ferromagnetic component, and leave to some future date the interpretation of the initial portion of the magnetization curve of these ferromagnetic inclusions. Curve D was obtained on a sample of copper containing 0.1 percent of iron by weight. It may be interpreted as the sum of two curves E and F resulting from a paramagnetic and a ferromagnetic component in the alloy. Evidently some of the iron in this sample is in solution, thus making the diamagnetic copper paramagnetic, and a part of the iron is in its usual ferromagnetic form. Curve G was obtained on a sample of copper containing 0.7 percent of iron. This sample contains so

FIG. 7. Magnetic susceptibility and saturation intensity per unit volume of a cast specimen containing 0.09 percent Fe in solution during cooling.

much ferromagnetic material in a form difficult to magnetize that even in a field of 40,000 gauss we are not near enough to saturation to separate the paramagnetism from the last part of the approach to ferromagnetic saturation. Even larger fields would be required to do this, and we must remain content with a rough estimate of the amount of ferromagnetism in such samples.

OBSERVATIONS

The phase diagram for copper-iron alloys as given by Hansen[3] is shown in Fig. 4. According to this, copper rich alloys should exist in the form of solid solutions at elevated temperatures, and should precipitate out ferromagnetic iron at low temperatures. Our first concern was to determine whether it was satisfactory to prepare samples by the simple methods of powder metallurgy, or whether it was desirable to cast them in con-

FIG. 5. Volume and mass susceptibility of Cu-Fe alloys after annealing at 950°C for 16 hr. in H_2 and quenching in water.

[3] M. Hansen, *Der Aufbau der Zweistofflegierungen* (Springer, Berlin, 1936).
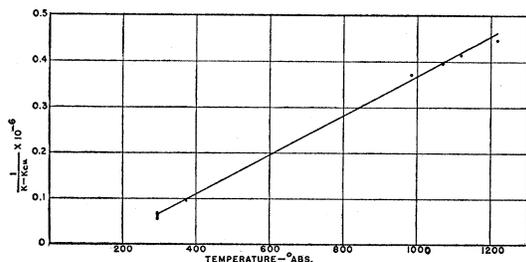
FIG. 8. Magnetic susceptibility per unit volume of a cast specimen containing 0.7 percent iron in solution.

trolled atmospheres. Alloys having compositions in the range 0–1 percent iron were prepared by both methods. The powder compacts were kindly supplied by John Wulff. Magnetic measurements on the latter after compression without the application of heat showed an amount of ferromagnetic material present in satisfactory agreement with the known composition. Samples of both types were then annealed at about 950°C in hydrogen for 16 hours and quenched in water. After this treatment all but a slight trace of ferromagnetism had disappeared, and the samples had the susceptibilities shown in Fig. 5. The points indicated by dots were obtained on Gouy specimens, those indicated by crosses were obtained on Curie specimens, and those indicated by circles were obtained on the powder compacts as Curie specimens. The latter showed consistently low values, indicating incomplete solution. A cast sample and a powder compact were then taken to a high temperature and measurements made during slow cooling. The results are shown in Figs. 6 and 7.

I_s is the saturation intensity per unit volume of the alloy, k is the volume susceptibility of the alloy, and K_{Cu} is the volume susceptibility of the copper used in making it. Our measurements indicate that this varies from -0.73×10^{-6} at room temperature to -0.61×10^{-6} at 1000°C.[4] If the iron in solution obeys a modified Curie law one might expect the total susceptibility of the quenched alloys to have the form

$$K = K_{Cu} + \frac{C}{T - \theta},$$

so that $(K - K_{Cu})^{-1}$ should be a linear function of the temperature if the above law is obeyed.

[4] This result is in close agreement with the measurements of K. Honda, Ann. d. Physik **32**, 1056 (1910).

The reappearance of a marked amount of ferromagnetism in the powder compact confirms the assumption of incomplete solution after the original heat treatment. Probably the copper penetrated the iron particles during the 16-hour heating at 950°C sufficiently to destroy their ferromagnetism, and diffused out of these particles again to a certain extent during the subsequent slow cooling. In the cast specimen, however, in which there was supposedly complete mixing during the solution treatment, no appreciable changes occurred during the subsequent slow cooling. The sluggishness of these alloys led us to give up the use of powder compacts, and to make our observations on cast specimens only. The above results indicate, however, that magnetic measurements may be of some value in powder metallurgy, and that powder compacts may be particularly adapted to producing special types of structures in alloys.

The next point on the program was to determine the behavior of the alloys in the form of solid solutions. From Fig. 5 it would appear that the susceptibility at room temperature is not directly proportional to the concentration. The behavior at high temperatures of the alloy containing 0.7 percent of iron is shown in Fig. 8. A Curie-Weiss law is at least approximately obeyed, with a Curie temperature in the neighborhood of 150°K. The number of Bohr magnetons per atom was calculated from the data in Figs. 7 and 8, and the values found are 3.4 and 3.6, respectively. This indicates the magnetic moment of the iron atoms in this range of compositions is independent of concentration, and that the departure from linearity in the susceptibility

TABLE I. Mass susceptibility χ and saturation intensity per unit mass of alloy measured at room temperature, in samples containing 0.7 percent Fe by weight.

SAMPLE		$\chi \times 10^6$	σ_s
A2E	Quenched	1.82	0.0005
	Cold Worked 12%	1.84	0.0002
A2F	Quenched	1.78	0.0005
	Annealed at 525°C		
	for 20 min.	~0.9	
	Cold Worked 12%	0.94	0.0001
A2G	Quenched	1.96	0.0005
	Annealed at 525°C		
	for 2 hr.	0.609	0.001
	Annealed from 685–		
	440°C for 6 hr.	0.237	0.006
	Cold Worked 12%	0.3	0.38
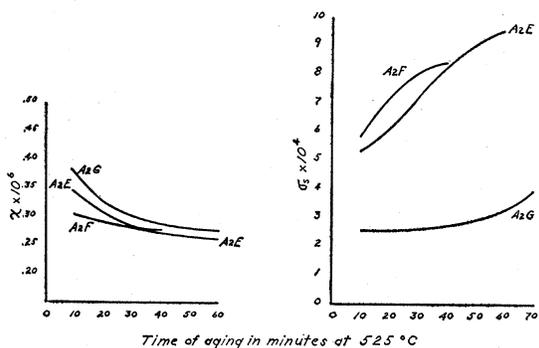
FIG. 9. Susceptibility and saturation intensity per unit mass of various samples during aging.

vs. temperature curves in Fig. 5 is due to interactions giving rise to a Curie temperature. The magneton number found above is rather lower than that found in salts (5 to 6 Bohr magnetons) or for iron in solution in gold (about 4.5 Bohr magnetons).[5]

A series of experiments was next undertaken to study the manner of precipitation from solution in a set of alloys containing approximately 0.7 percent of iron. The solubility limit for this composition is 800°C according to Fig. 4. The results of these experiments are summarized in Table I.

In the quenched samples the iron is retained in solution. Aging these supersaturated solutions below the solubility limit decreases the susceptibility, but does not cause ferromagnetism to appear. Cold working the alloy in the quenched or partly aged condition does not affect the magnetic properties, but cold working a more fully aged sample produces ferromagnetic inclusions.

An experiment was also performed to see whether recrystallization during aging altered the manner of precipitation. Samples A2E and A2F were measured at 525°C after the cold working operation, as was sample A2G immediately after the quench. The results are shown in Fig. 9. No observations during the first ten minutes are recorded as the samples were not completely up to temperature until after that time. A slightly greater amount of ferromagnetism appears in the cold worked samples A2E and *F* which are assumed to be recrystallizing but outside of this all the samples aged in a very similar manner. The aging of sample A2G was

continued for two hours, during which time the susceptibility decreased to 0.25×10^{-6}, but the amount of ferromagnetism showed no appreciable further change. There is apparently little tendency for the iron which presumably is precipitating out of this solution to appear in its ferromagnetic form. If, however, appreciable amounts of ferromagnetic iron are present in a partly aged sample, further aging will make this amount of ferromagnetism increase. A partly aged and cold worked sample having a saturation intensity per unit mass at room temperature of 0.23 was aged for $27\frac{1}{2}$ hours at 520°C. After this treatment the above quantity had increased to 0.45.

An attempt was made to find the temperatures at which precipitation first occurs, and at which the ferromagnetic and nonmagnetic precipitates dissolve. These experiments could not be carried through because it was found that the alloys could be supercooled about 100°C, and because the nearness of the Curie point to the solubility limit of the alloy we were working with made the interpretation of the results doubtful. Further attempts to make these measurements on alloys of different compositions are now under way.

CONCLUSIONS

The chief conclusion to be drawn from the above report is that the equipment now available and functioning is adequate for making measurements of considerable interest to both physicists and metallurgists. The preliminary observations made in the course of testing the equipment and establishing the methods of measurement indicate that the process of precipitation from solid solution in the copper-iron alloys investigated is a complex one in which equilibrium can be reached apparently only by the use of both cold work and aging at high temperatures. The results indicate that there may be at least two intermediate stages in the process. During the first, the solution is somehow disturbed, possibly by the appearance of fluctuations in concentration. In this stage the paramagnetic susceptibility is greatly reduced, but plastic deformation does not affect the structure. Further aging does not greatly affect the magnetic properties, but a feebly magnetic precipitate is probably forming, as is shown by the fact that in this stage cold work produces ferromagnetism, probably by

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[5] See E. C. Stoner, *Magnetism and Matter* (Methuen and Company, London, 1934), page 312; and J. W. Shih, Phys. Rev. **38**, 2051 (1931).

altering the lattice structure of the precipitate. The precipitate may possibly be face-centered cubic gamma-iron containing copper, or iron atoms in great concentration on the lattice points of the copper lattice.

The Rotation-Vibration Energies of Tetrahedrally Symmetric Pentatomic Molecules. II

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A general discussion of a method which may be used to obtain the first-order Coriolis splitting of the harmonic and combination states of ν_3 and ν_4 is presented. The method is applied to obtain these splittings of $2\nu_3$, $2\nu_4$ and $\nu_3+\nu_4$ and to derive the stabilized wave functions for these states. With these functions the selection rules and the elements of the matrix of the second-order Hamiltonian $H^{(2)'}$ have been calculated for these states.

I. INTRODUCTION

IN Part I of this paper[1] we have given the quantum-mechanical Hamiltonian for the investigation of the vibration-rotation energies of the XY_4 type molecules, including all terms which may contribute to the energy to second order of approximation. In addition to the harmonic oscillator and rigid spherical top terms of the zeroth order, the Hamiltonian includes cubic and quartic anharmonic terms, centrifugal expansion terms, all possible types of Coriolis and other interactions between rotation and oscillation. The Hamiltonian was transformed by a contact transformation into $H^{(0)}+\lambda H^{(1)'}+\lambda^2 H^{(2)'}$ so that to second approximation only the Coriolis interaction terms between rotation and the threefold degenerate oscillations ν_3 and ν_4 are contained in $H^{(1)'}$. This facilitates the calculation of the energies to second approximation which otherwise would be very difficult because of the high degree of degeneracy of the zeroth-order energies. In Part I we have calculated and set down the elements of the matrix H accurate to second order of approximation for the states $V_1\nu_1$, ν_2, $V_1\nu_1+\nu_3$, $V_1\nu_1+\nu_4$, $\nu_2+\nu_3$ and $\nu_2+\nu_4$.

Part II deals with the energies of the states $2\nu_3$ (or $2\nu_4$) and $\nu_3+\nu_4$, which are, respectively,

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[1] W. H. Shaffer, H. H. Nielsen and L. H. Thomas, Phys. Rev. **56**, 895 (1939).

six- and ninefold degenerate because of the degeneracy of ν_3 and ν_4. The manner in which this degeneracy is removed by the first-order Coriolis terms $H^{(1)'}$ is discussed and calculations are made on the selection rules and the second-order energies.

II. THE FIRST-ORDER CORIOLIS INTERACTION ENERGIES

We shall discuss first a general method of treating the first-order Coriolis interaction terms $H^{(1)'}$ which can be written in the form:

$$H^{(1)'} = -(\zeta_3/A_0)(\mathbf{J}_3 \cdot \mathbf{J}) - (\zeta_4/A_0)(\mathbf{J}_4 \cdot \mathbf{J}), \quad (1)$$

where $\mathbf{J}_3$ and $\mathbf{J}_4$ are the internal angular momenta associated with ν_3 and ν_4, respectively, and $\mathbf{J}$ is the total angular momentum of the molecule. It is readily shown from a study in spherical polar coordinates of the threefold degenerate modes ν_3 and ν_4 as isotropic three-dimensional oscillators that the quantum number J_3 may assume the values V_3, V_3-2, V_3-4, $\cdots 0$ or 1 (and J_4 the values V_4, V_4-2, etc.) where V_3 and V_4 are the vibrational quantum numbers associated with ν_3 and ν_4, respectively. The total internal angular momentum of the molecule is thus:

$$\mathbf{J}_2 = \mathbf{J}_3 + \mathbf{J}_4, \quad (2)$$

where $\mathbf{J}_2$ may evidently take the values:

$$J_2 = J_3 + J_4, \quad J_3 + J_4 - 1, \quad \cdots |J_3 - J_4|. \quad (3)$$