

Anisotropic Diffusion of Cadmium and Gold Tracers in Zinc Single Crystals*†

P. B. GHATE‡

Rensselaer Polytechnic Institute, Troy, New York

(Received 25 February 1963)

The anisotropic diffusion coefficients of the radioactive tracers cadmium (115m) and gold (198) in single crystals of high-purity zinc, in directions parallel and perpendicular to the hexagonal axis, were measured by the standard sectioning technique. Cadmium diffused at a rate faster than that of self-diffusion and with $D_{\perp} > D_{\parallel}$. Gold diffused at a rate slower than that of self-diffusion and with $D_{\parallel} > D_{\perp}$. The results of the measurements are as follows: For cadmium (115m), $D_{\parallel} = (0.11 \pm 0.01) \exp[-(20.54 \pm 0.09) \times 10^3/RT]$ cm²/sec, $D_{\perp} = (0.12 \pm 0.01) \exp[-(20.42 \pm 0.03) \times 10^3/RT]$ cm²/sec; for gold (198), $D_{\parallel} = (0.97 \pm 0.22) \times \exp[-(29.73 \pm 0.26) \times 10^3/RT]$ cm²/sec, $D_{\perp} = (0.29 \pm 0.12) \exp[-(29.72 \pm 0.45) \times 10^3/RT]$ cm²/sec. On the basis of the vacancy mechanism one can interpret the fast diffusion of cadmium in terms of an appreciable binding between the vacancy and the diffusing ion; conversely the slow diffusion of gold in terms of a repulsion between the vacancy and the diffusing ion.

INTRODUCTION

IN recent years, impurity diffusion in metals has received considerable attention. Since Lazarus¹ proposed his screening theory of impurity diffusion in metals, diffusion coefficients of various impurity atoms in monovalent metals such as copper, silver, and gold have been measured.²⁻¹¹ However, little has been reported on the impurity diffusion in noncubic metals. Zinc was chosen as the solvent metal for the investigation because the diffusion is expected to be anisotropic and because self-diffusion data¹² and the results¹³ of the diffusion of indium and silver tracers were readily available.

In the present work, cadmium¹⁴ and gold tracers have been diffused in zinc single crystals. Cadmium was chosen because like zinc, it is divalent. It would be interesting to compare the diffusion rates of the cadmium with those of the zinc tracer. Gold was chosen because it would enable one to compare the diffusion of

the monovalent impurities silver and gold in the same solvent metal zinc.

In a medium where the diffusion is anisotropic, it is possible to choose a system of coordinates where the diffusion tensor D is diagonal. For the concentration gradient in a particular direction with direction cosines $\gamma_1, \gamma_2,$ and γ_3 , the diffusion coefficient¹⁵ can be expressed in terms of the principal diffusion coefficients $D_{xx}, D_{yy},$ and D_{zz} as follows:

$$D(\gamma_1, \gamma_2, \gamma_3) = D_{xx}\gamma_1^2 + D_{yy}\gamma_2^2 + D_{zz}\gamma_3^2. \quad (1)$$

If the crystal has a threefold or higher symmetry axis, the diffusion tensor has a twofold degeneracy. If the z axis coincides with the axis of symmetry, then $D_{xx} = D_{yy}$. D can be expressed as

$$D(\theta) = D_{\perp} \sin^2\theta + D_{\parallel} \cos^2\theta, \quad (2)$$

where $D(\theta)$ is the diffusion coefficient for the direction making an angle θ with the symmetry axis and D_{\perp} and D_{\parallel} are the principal diffusion coefficients perpendicular and parallel to the symmetry axis.

In the present work, a flat surface is prepared normal to the axis of the cylindrical sample. A thin layer of the radioactive material is deposited on the surface and is allowed to diffuse into the sample at a particular temperature. Under these circumstances, the concentration of the diffusing material at a later time t , can be expressed as¹⁶

$$C(x, t) = \frac{C_0}{(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (3)$$

where C_0 is the initial surface concentration, x equals the distance from the originally plated surface measured along the axis of the cylindrical sample, and D equals the diffusion coefficient parallel to the cylindrical axis of the sample. If $\ln C$ is plotted against (penetration),²

* This article is based on a thesis submitted to the Physics Department at Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Work supported by the U. S. Atomic Energy Commission.

‡ Present address: Cornell University, Ithaca, New York.

¹ D. Lazarus, Phys. Rev. **23**, 973 (1954); and *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

² L. Slifkin, D. Lazarus, and C. T. Tomizuka, J. Appl. Phys. **23**, 1405 (1952).

³ E. Sonder, L. Slifkin, and C. T. Tomizuka, Phys. Rev. **93**, 970 (1954).

⁴ C. T. Tomizuka and L. Slifkin, Phys. Rev. **96**, 610 (1954).

⁵ C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1182 (1956).

⁶ C. T. Tomizuka (to be published).

⁷ A. Sawatzky and F. E. Jaumot, J. Metals **9**, 1207 (1954); Phys. Rev. **100**, 1627 (1955); J. Appl. Phys. **27**, 1186 (1956).

⁸ C. A. Mackliet, Phys. Rev. **109**, 1964 (1958).

⁹ T. Hirone and H. Yamamoto, J. Phys. Soc. Japan **16**, 455 (1961).

¹⁰ T. Hirone, S. Miura, and T. Suzuoka, J. Phys. Soc. Japan **16**, 2456 (1961).

¹¹ A. Gardner and L. Slifkin, Bull. Am. Phys. Soc. **7**, 234 (1962).

¹² G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta. Met. **1**, 513 (1953).

¹³ J. H. Rosolowski, Phys. Rev. **124**, 1828 (1961).

¹⁴ P. B. Ghate and H. B. Huntington, Bull. Am. Phys. Soc. **7**, 403 (1962).

¹⁵ J. F. Nye, *The Physical Properties of Crystals* (Clarendon Press, Oxford, England, 1957).

¹⁶ J. Crank, *Mathematics of Diffusion* (Clarendon Press, Oxford, England, 1956).

and a straight line is drawn through the resulting points, the slope gives $(-4Dt)^{-1}$. The diffusion coefficient is readily calculated from the slope.

EXPERIMENTAL PROCEDURE

(a) Sample Preparation

Single crystals of zinc were grown from 99.999% pure zinc as obtained from the New Jersey Zinc Company. The samples for diffusion experiments were prepared following the procedure described by Rosolowski.¹³

(b) Plating

The radioisotopes Cd^{115m} and Au^{198} were obtained from the Oak Ridge National Laboratory. The following plating solutions were used: (1) Cadmium plating solution¹⁷; 100 ml of distilled water, 10.8 g of NaCN, and 2.8 g of CdO. (2) Gold plating solution; 100 ml of distilled water, 1.9 g of KCN, 1.02 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, and 0.212 g of Na_2HPO_4 .

About 8 cc of the above plating solution was used in each case to which the radioactive solution received from Oak Ridge National Laboratory was added. The specific activities of the plating baths were about 0.2 mCi/ml for cadmium and 1.5 mCi/ml for gold, respectively. The sides of each sample were coated with red paint soluble in acetone. The plating was then done by dipping the sample into the plating solution. The thickness of the layer was estimated to be less than 1000 Å. After plating, the paint on the sides was removed.

(c) Diffusion Heating

For each diffusion anneal, two samples were used. The cylindrical axis of one of the samples was closely parallel to the symmetry axis and that of the other was

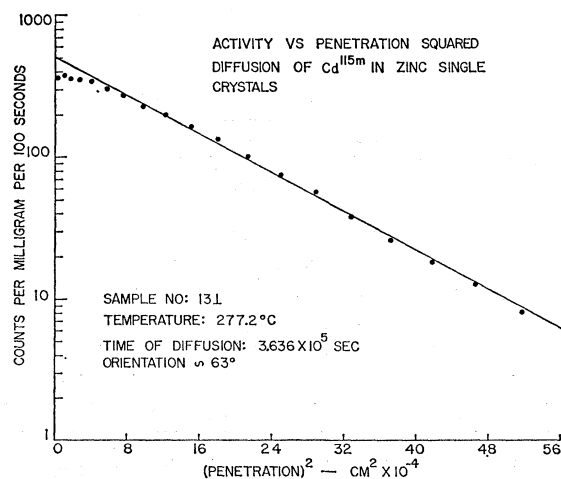


FIG. 1. Sample penetration plot for Cd^{115m} .

¹⁷ H. B. Huntington, N. C. Miller, and V. Nerses, *Acta Met.* 9, 749 (1961).

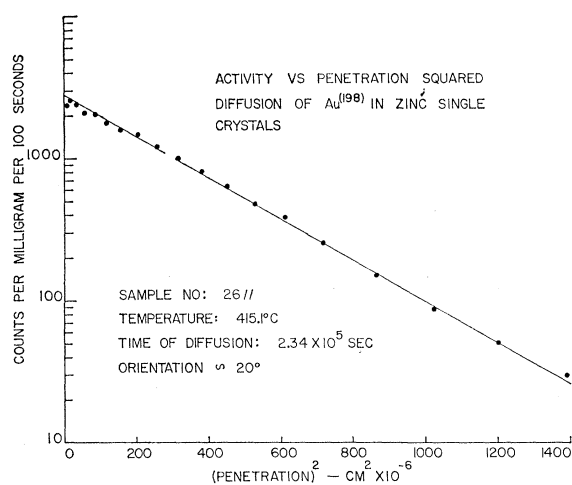


FIG. 2. Sample penetration plot for Au^{198} .

closely perpendicular to the symmetry axis. The samples, placed so that their plated surfaces faced each other and separated by a Pyrex disk, were sealed off under vacuum in Pyrex capsules. The furnaces used for the diffusion anneals maintained constant temperature to 0.2°C. The temperature of the furnace was monitored during an anneal with a chromel alumel thermocouple. At the end of each anneal, the temperature was measured with a platinum platinum-rhodium thermocouple (calibrated by the National Bureau of Standards) located close to, and at the same level in the furnace as the faces of the samples. The temperature was also measured by the monitoring chromel alumel thermocouple. This calibration was used to determine the mean temperature of the samples during the anneal from the readings taken with the monitoring thermocouple.

(d) Sectioning

After the diffusion anneal, the sample was mounted in a lathe and was aligned within 0.002 rad. The diameter of the sample was reduced 40 to 50 mils to eliminate the possible effects of surface diffusion. Sections of approximately 1.5 mils thick were then turned off and the chips were carefully collected. These chips were put into a previously weighed plastic-coated stainless steel planchet and weighed to determine the thickness of the section. They were then dissolved in a 12% HCl acid solution and the uniformly spread solution was then dried.

(e) Counting

The β activity of each section was measured with a thin end window G.M. Counter and a standard scaling circuit. Nearly 10 000 counts were accumulated for each section to reduce the statistical error in counting. The specific activity of each section was then determined and was taken to be that at the center of the section. Cor-

TABLE I. Diffusion of Cd^{115m} in zinc single crystals.

Temp in °C	(1000/T) (°K ⁻¹)	D in cm ² /sec	D _⊥ in cm ² /sec
416.0	1.451	3.58 × 10 ⁻⁸	3.89 × 10 ⁻⁸
405.2	1.474	2.68 × 10 ⁻⁸	3.12 × 10 ⁻⁸
369.1	1.557	1.15 × 10 ⁻⁸	1.30 × 10 ⁻⁸
322.9 ^a	1.678	(2.94 × 10 ⁻⁹)	(3.13 × 10 ⁻⁹)
277.2	1.817	7.68 × 10 ⁻¹⁰	9.09 × 10 ⁻¹⁰
224.6	2.009	1.10 × 10 ⁻¹⁰	1.26 × 10 ⁻¹⁰

^a The diffusion coefficients at this temperature were not included in the least-squares analysis. See text.

rections due to the background and counter dead time were taken into account. Cd^{115m} has a fairly long half-life (~43 days) as compared to the counting time (~8 h) for a particular specimen and, hence, no corrections were deemed necessary for the decay of the activity. Au¹⁹⁸ has a half-life of about 2.7 days and, hence, the measured activities of the sections were converted to activities at a standard reference time.

RESULTS

The thickness of each section was calculated using the area of the sample face, the density of zinc, and the mass of the section. The penetration distances were established from the formula

$$X_n = \sum_{r=1}^{n-1} \delta_r + \frac{\delta_n}{2},$$

where the δ_r is the thickness of the r th section. Two sample semilogarithmic plots of specific activity vs penetration squared (penetration profiles) are shown in Figs. 1 and 2. From the slope of the best straight line drawn through the points on plots such as these, the diffusion coefficients were calculated. Usually two samples with the orientations θ_1 and θ_2 were diffused at the same temperature. The diffusion coefficients $D_1(\theta_1)$ and $D_2(\theta_2)$ determined from the slopes of the penetration profiles were used to calculate $D_{||}$ and D_{\perp} at this temperature. The results of all the diffusion runs are compiled in Tables I and II for the cadmium and gold, respectively.

Several experimental considerations limited the accuracy of the measurements of the diffusion coefficients. The error in weighing of the section was negligible. The error due to the finite thickness of the sections and their

TABLE II. Diffusion of Au¹⁹⁸ in zinc single crystals.

Temp in °C	(1000/T) (°K ⁻¹)	D in cm ² /sec	D _⊥ in cm ² /sec
415.1	1.453	3.48 × 10 ⁻¹⁰	1.05 × 10 ⁻¹⁰
396.5	1.493	1.97 × 10 ⁻¹⁰	5.84 × 10 ⁻¹¹
379.9	1.531	1.04 × 10 ⁻¹⁰	3.43 × 10 ⁻¹¹
347.1	1.612	3.37 × 10 ⁻¹¹	9.58 × 10 ⁻¹²
315.2	1.700	8.54 × 10 ⁻¹²	...

misalignment from the direction of diffusion was estimated following the procedure suggested by Shirn *et al.*¹² and was found to be of the order of a percent or so. The thickness of each section was calculated using the density of zinc at room temperature. The correction due to the heat-up time was estimated following the method described by Makin *et al.*¹⁸ This was of the order of a percent for the high-temperature anneals and was negligible for the low-temperature ones. The error in the measurement of the activities for cadmium diffusion was less than a percent. In the case of gold diffusion, the measured activities were corrected for the decay of the activity during counting and hence the upper limit

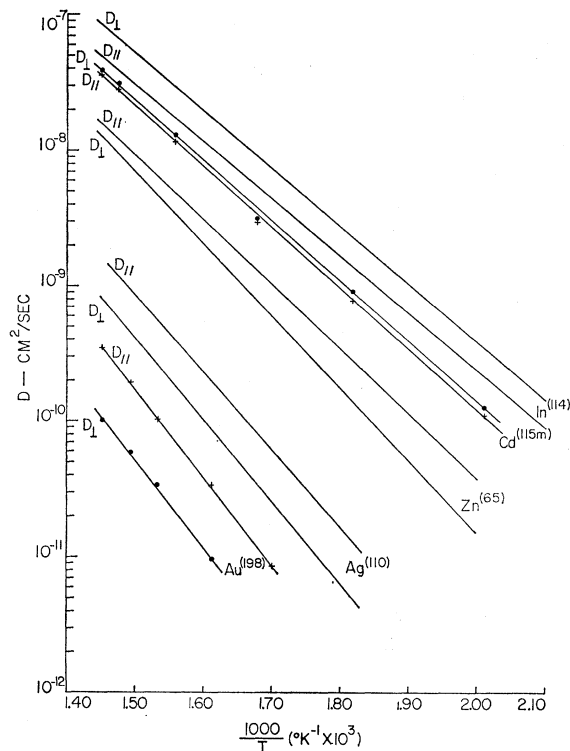


FIG. 3. Diffusion coefficient versus reciprocal temperature for Cd^{115m} and Au¹⁹⁸ tracers diffusing parallel and perpendicular to the hexagonal axis in zinc single crystals. Self-diffusion results of Shirn *et al.* and the diffusion data of Ag¹¹⁰ and In¹¹⁴ tracers of Rosolowski are shown for comparison.

of the error was estimated to be less than 2%. All errors being considered, the diffusion coefficients are accurate within 4% in the case of cadmium diffusion and 7% in the case of gold diffusion.

The logarithms of the diffusion constants ($D_{||}$ and D_{\perp} listed in Tables I and II) are plotted as a function of the reciprocal temperature in Fig. 3. The results of the self-diffusion and also those of the diffusion of indium and silver tracers have been included in the same figure for comparison.

¹⁸ S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) **B70**, 545 (1957).

Generally, the diffusion coefficient is taken to vary with temperature in a simple exponential manner

$$D = D_0 \exp(-Q/RT),$$

where D_0 =frequency factor, Q =activation energy, R =gas constant, T =absolute temperature. A plot of $\ln D$ vs $1/T$ enables one to calculate D_0 and Q from the intercept and the slope of the straight line drawn through the experimental points. A least-squares technique was used to determine the frequency factors and the activation energies for the parallel and perpendicular diffusion of cadmium and gold tracers and are listed in Table III. The frequency factors and the activation energies for the self-diffusion and the diffusion of indium and silver tracers have been included in the table for comparison.

In the case of cadmium diffusion, the diffusion coefficients at temperature 322.9°C were not included in the least-squares analysis as the values were found to lie beyond the 5σ limit. The cause of the discrepancy could not be traced.

DISCUSSION

Figure 3 shows that the cadmium tracer diffuses faster than the zinc tracer and slower than the indium tracer. The activation energies for the parallel and perpendicular diffusion of cadmium in zinc differ only by a tenth of a kcal/mole. The $\ln D$ vs $1000/T$ plots are almost parallel in the temperature range of the experiment. The anisotropy, namely, the ratio D_{11}/D_{\perp} , is about 0.9. Since cadmium and zinc are both divalent, one would normally expect the diffusion of cadmium in zinc to be similar to the self-diffusion in zinc. On the contrary, the general behavior of cadmium diffusion is similar to that of the indium diffusion in zinc. The faster rate of indium diffusion with $D_{\perp} > D_{11}$ is thought to be due to the strong electrostatic attraction between the vacancy and the diffusing ion. It is believed, therefore, that there may be an appreciable binding between the cadmium ion and a vacancy.

This may be qualitatively understood as follows. The first and second ionization potentials¹⁹ of zinc and cadmium are 9.39, 17.96, 8.99, and 16.90 eV, respectively. Although the energies needed to remove the outer electrons from the free atoms have no direct meaning for the solid state, one might infer that the density of valence electrons would be less around impurity ions to which the electrons were less strongly bound than to the ions of the matrix when in the free state. In a zinc matrix, each zinc atom gives two of its valence electrons and the zinc core has a charge $+2e$. If we construct a Wigner-Seitz cell around each zinc ion, the two electrons may be assumed to be encompassed into the cell. When a cadmium atom goes into the zinc

TABLE III. Frequency factors and activation energies for tracer diffusion in zinc-single crystals.

Isotope	Diffusion direction	D_0 (cm ² /sec)	Q (kcal/mole)	Reference
Cd ^{115m}		0.114±0.008	20.54±0.08	present work
Cd ^{115m}	⊥	0.117±0.003	20.42±0.03	
Au ¹⁹⁸		0.97 ±0.22	29.73±0.26	present work
Au ¹⁹⁸	⊥	0.29 ±0.12	29.72±0.45	
Zn ⁶⁵		0.13	21.8 ±0.2	12
Zn ⁶⁵	⊥	0.58	24.3 ±0.5	
In ¹¹⁴		0.062±0.008	19.1 ±0.1	13
In ¹¹⁴	⊥	0.14 ±0.02	19.6 ±0.1	
Ag ¹¹⁰		0.32 ±0.02	26.0 ±0.1	13
Ag ¹¹⁰	⊥	0.45 ±0.07	27.6 ±0.2	

lattice, it gives two of its valence electrons. Because the sum of the first two ionization potentials of cadmium is smaller than that of zinc, one may qualitatively expect the two electrons to be spread out over and above the cell. According to this speculative hypothesis, a cadmium ion will behave as an impurity with an excess charge $+Ze$ ($0 < Z < 1$). One may then expect a binding between a vacancy and the cadmium ion. This situation is somewhat similar to that of indium except that the excess charge Z is less than 1. Because of the electrostatic attraction between the cadmium ion and a vacancy, the diffusion rate of cadmium will be enhanced. It is energetically more favorable for a vacancy to be in the same basal plane as that of the cadmium ion and, hence, the diffusion in the perpendicular direction may be expected to be greater than that in the parallel direction.

It is observed that the gold tracer diffuses slower than the zinc tracer, in fact slower than silver tracer also (see Fig. 3). The activation energies for the parallel and perpendicular diffusion of gold in zinc are equal within the experimental error. The anisotropy, namely, the ratio D_{11}/D_{\perp} , is approximately 3.3 within $\pm 10\%$. The $\ln D$ vs $1000/T$ plots are almost parallel within the temperature range of the experiment.

It is interesting to note that gold also diffuses slower than silver in monovalent metals such as copper, silver, gold, and silver-gold alloys.^{6,5,7,11} A qualitative argument based on the ionization potentials of silver and gold would then explain why gold is a slow diffuser as compared to silver. Specifically, one would expect the excess charge of the gold ion to be smaller than that of the silver ion when both of these impurities are dissolved in a zinc matrix ($-1 \leq Z_{Au} < Z_{Ag} < 0$). A gold ion in a zinc matrix looks like a screened negative charge $Z_{Au}e$ and, hence, will repel a vacancy. If one assumes that the diffusion in zinc is taking place via the vacancy mechanism, slow diffusion of gold is in agreement with the predictions of Lazarus' theory. When a vacancy happens to be a nearest neighbor of the diffusing ion, energetically it is more favorable for a vacancy to occupy a site in an adjacent plane rather than a site in the same basal

¹⁹ G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944).

plane as that of the impurity. The probability that the diffusing ion will exchange sites with a vacancy in an adjacent plane is then larger than that of the impurity-vacancy exchange in the same basal plane. One may thus understand why the diffusion of gold in the parallel direction is faster than that in the perpendicular direction.

If the diffusion in the perpendicular direction were entirely due to the nonbasal jumps of the gold tracer, then one may expect $D_{11}/D_{\perp} \cong 5.2$ for zinc. The ratio of the diffusion coefficients D_{11}/D_{\perp} in the temperature range of the experiment is approximately 3.3 within

$\pm 10\%$. This suggests that both types of the jumps are probably contributing to the perpendicular diffusion.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Professor H. B. Huntington for his kind advice and many stimulating discussions and to A. P. Batra for his help in some of the measurements. I should also like to express my gratitude to the University of Bombay, India, for the award of the Sardar Bhimrao Ramrao Akbarnavis Scholarship and to the United States Educational Foundation in India for the Fulbright Travel Grant.

Spin Waves and Nuclear Magnetic Resonance Enhancement in NiF_2 Domain Walls*

DAVID I. PAUL

Department of Physics, University of California, Los Angeles, California

(Received 25 February 1963)

We have obtained the allowed magnetic resonance modes or spin waves in the canted antiferromagnet NiF_2 in the presence of a Bloch wall. Our formulation includes the anisotropy and exchange energies of the crystal together with characteristics of the wall such as its stiffness, mass, and viscosity. From the dispersion equations, we show that there exists a bound wall excitation branch having a lower excitation energy than the free spin wave excitation branch. Further, we have calculated the effective nuclear magnetic resonance field enhancement due to the bound wall excitation branch as a function of the parameters of the crystal and the Bloch wall and shown that our results are equivalent to those obtained experimentally. Finally, we compare this enhancement with that of a pure antiferromagnet—demonstrating that the canting is essential for this process.

I. INTRODUCTION

IN this paper, we investigate the effect of a Bloch wall on the spin wave excitation spectra in a canted antiferromagnet such as NiF_2 . In this type of substance, the canting arises from the spin-orbit coupling under the

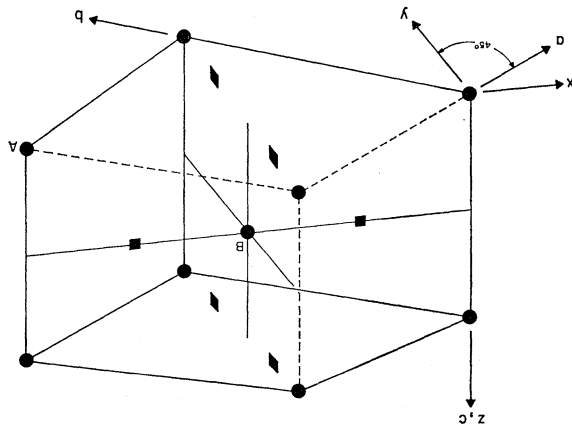


Fig. 1. Crystal structure of NiF_2 . The circles and the squares represent the nickel and the fluorine ions, respectively.

* This research was supported in part by the Office of Naval Research.

effect of the crystalline electric field. In Sec. V we obtain the allowed normal magnetic resonance modes and the dispersion equations for the bound wall excitations and the free spin wave excitations. The analogous ferromagnetic and antiferromagnetic cases have been considered by Boutron,¹ Winter,² and the author.³ In Sec. VI, we calculate the effective enhancement of the nuclear magnetic resonance signal caused by the bound wall excitations. This is similar to the enhancement factor obtained by Portis and Gossard⁴ for ferromagnetic substances and experimentally by Shulman⁵ for NiF_2 .

II. FORMULATION OF THE PROBLEM

The substance, NiF_2 , has a rutile-type crystal structure with both corner and body-center cation sites. We consider the magnetic corner cation sites as being on sublattice *A* with index *j* and the magnetic body-center sites as being on sublattice *B* with index *k* as shown in Fig. 1. The magnetic properties of NiF_2 have been con-

¹ Mlle. F. Boutron, *Compt. Rend.* **252**, 3955 (1961).

² J. M. Winter, *Phys. Rev.* **124**, 452 (1961).

³ D. I. Paul, *Phys. Rev.* **126**, 78 (1962).

⁴ A. Portis and A. Gossard, *Suppl. J. Appl. Phys.* **31**, 205S (1960).

⁵ R. G. Schulman, *Suppl. J. Appl. Phys.* **32**, 126S (1961).