observed for nickel. The low anisotropy energy has been regarded as the reason for the failure to observe the domains. Bozorth and Walker<sup>3</sup> reported recently a pattern on a crystal of a cobalt-nickel alloy (40 percent Ni; 60 percent Co). This alloy was chosen because it has a higher anisotropy energy than nickel but the same direction of easiest magnetization.

Previous considerations of the effects of grain boundaries on ferromagnetic properties<sup>4</sup> led to the prediction that a domain structure should be observable in nickel bicrystals of suitable orientations. This has been confirmed by using ferromagnetic powder technique.<sup>5</sup> The experiments showed simple domain structures on the electropolished crystal surface. A typical pattern, obtained in the absence of an external field, is shown in Fig. 2,



FIG. 2. Powder pattern on the surface of the bicrystal. AB is the grain boundary.

in which AB is the grain boundary. Patterns formed in external magnetic fields were also studied. All observed patterns are consistent with domain structures to be expected in nickel. They contain basic domains and "tree pattern" with the walls of the basic domains as "trunks." In the immediate neighborhood of the grain boundary, however, the boundary itself forms the "trunk." Effects of the grain boundary can be observed on all patterns.

The study of ferromagnetic domain structures in their relationship to grain boundaries may provide additional information about the properties and structure of crystal boundaries.

<sup>1</sup> B. Chalmers, Proc. Roy. Soc. (London) A175, 100 (1940).
<sup>2</sup> K. V. Gow and B. Chalmers, to be published.
<sup>3</sup> R. M. Bozorth and T. G. Walker, Phys. Rev. 79, 888 (1950).
<sup>4</sup> U. M. Martius, Can. J. Phys. 1 (1951).
<sup>5</sup> Williams, Bozorth, and Shockley, Phys. Rev. 75, 155 (1949).

## Does Diffusive Separation Exist in the Atmosphere below 55 Kilometers?\*

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I N a recent letter,<sup>1</sup> McQueen infers that above 40 km diffusive separation increases the proportion of N14N14 molecules as compared to the N<sup>14</sup>N<sup>15</sup> molecules. This inference rests on mass spectrographic analyses of six air samples obtained by rockets under an U. S. Army Signal Corps contract with the University of Michigan. For purposes of discussion (and also inasmuch as there are errors in the dates and altitudes of several of the samples), McQueen's table of results is reproduced here with the correct dates and with certain results obtained at the University of Durham and at the University of Michigan, which will be discussed in a later paragraph.

Suppose that in a particular layer of the atmosphere there is no mixing at all. Then, for any constituent of molecular weight M, the height distribution in terms of the number of molecules, n, per unit volume is given by

$$n = n_0 e^{-h/H},\tag{1}$$

where  $n_0 =$  number of molecules per unit volume at the base of the layer, h = height above the base of the layer, and, if it is assumed that the temperature T is essentially constant throughout the layer, H = RT/Mg where R is the molar gas constant. Now consider the relative concentration,  $\rho = n'/n$ , of two gases of molecular weights M and M'. From Eq. (1)

$$\rho = \rho_0 e^{-(h/H' - h/H)} = \rho_0 e^{-h/H_1}, \tag{2}$$

where  $H_1 = RT/(M' - M)g$  and  $\rho_0$  is the ratio at the base of the layer. The percent change, P, in  $\rho$  relative to  $\rho_0$  is, from Eq. (2),

$$P = -100(1 - e^{-h/H_1}). \tag{3}$$

McQueen's results imply that there is no diffusive separation up to about 47 km but that there is about a 3 percent separation at about 55 km, implying a cessation or reduction of mixing over the 8.4 km between mean levels of the two groups of samples. (The time interval between the two groups is only a few months, and in this region diffusion is too slow for any appreciable change in P between the two levels to occur during this interval.) If it is assumed that no mixing occurs over the 8.4-km range and if Tis taken as 280°K,<sup>2,3</sup> then for the N14N14/N14N15 ratio, for which M'-M=-1, Eq. (3) gives P=3.5 percent so that McQueen's results are not inconsistent in this respect. On the other hand, for the He/(N<sub>2</sub>+A) ratio (M'=4, M=28), Eq. (3) gives P=134percent under the same conditions; and for Ne/A, P = 107 percent.

Other portions of the samples analyzed by McQueen have also been analyzed by the charcoal absorption method at the University of Durham by Paneth and co-workers4 for He, Ne, A, and  $N_2$ , and by the present writers for He, Ne, and  $(N_2+A_1)$  In these samples and in six others, the relative concentrations of the gases did not vary more than several percent from the corresponding values at the surface of the earth. At this time, analyses by the charcoal method have been made for only three of the six samples reported by McQueen (results on the three other samples will be reported later); results from these three samples are given in Table I in terms of percentage deviation of the relative helium (to nitrogen plus argon) concentration in the sample from the corresponding concentration at the surface of the earth, and in terms of the percentage deviation of the neon to argon ratio from the corresponding surface value.

The small concentration of helium in the earth's atmosphere implies escape of helium from upper atmospheric levels. This

TABLE I.\* Comparison of McQueen's results (reference 1) with those of Paneth and co-workers (reference 4) and with those obtained at the University of Michigan. The percent deviation is from the corresponding ratios at the earth's surface—i.e., the quantity P in Eq. (3). The mean deviations are given.

	Height	Date	Separation (%) N <sup>14</sup> N <sup>14</sup> N <sup>14</sup> N <sup>14</sup> N <sup>14</sup> McQueen (reference 1)	Separation Paneth and (referent He/(N <sub>2</sub> +A)	on (%) co-workers nce 4) Ne/A	Separation (%) He/(N <sub>2</sub> +A) (Univ. of Mich.)
(19B) (15C) (5B) (25B)	54.7-58.3 53.6-57.7 49.0-59.8 50.4-53.3	7-21-496-2-497-26-4812-6-49	$3.9\pm0.4$ $2.7\pm0.2$ $2.7\pm0.5$ $0.4\pm0.3$	0.3±0.3	-1.3±0.8	3p 0c
(20B) (28B)	45.0-47.8 41.4-44.9	9-20-49 12- 6-49	$0.8\pm0.3$ less than 0.3			$-0.3\pm0.3^{d}$

program, and it is estimated that the mean deviation is not greater than 3 percent. • This is the average of two runs which were made early in the analysis program, and it is estimated that the mean deviation is not greater than 3 percent. <sup>d</sup> This is the average of four runs.

effect would increase the absolute value of the density gradient of helium over that computed on the basis of Eq. (1).<sup>5</sup> However, the neon to argon ratio is not subject to this effect, since it is believed that these gases do not escape from the atmosphere.

Hence, it seems that mixing must prevail at least up to about 60 km and that McQueen's results must be interpreted in some other way than by diffusive separation in the atmosphere.

Details of the sampling procedure, etc., used by the writers will be published elsewhere. We are indebted to Professor Sydney Chapman for discussions in connection with our results.

\* This work is sponsored by a contract with the Meteorological Branch of the U. S. Army Signal Corps.
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<sup>2</sup> Havens, Koll, and Lagow, "Pressures and temperatures in the earth's upper atmosphere," Naval Research Laboratory Report, March, 1950.
<sup>3</sup> Bartman, Liu, and Schaefer, "An aerodynamic method of measuring ambient temperature of air at high altitudes," Engineering Research Institute, University of Michigan Report (U. S. Army Signal Corps Contract), July, 1950.

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<sup>8</sup> S. K. Mitra, *The Upper Atmosphere* (Royal Asiatic Society of Bengal, Calcutta, 1947), p. 21.

## An Empirical Formula for the Microwave Spectrum of Ammonia

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HE inversion splitting for a double minimum potential was obtained by Dennison and Uhlenbeck<sup>1</sup> using the W-K-B approximation. They found

$$\Delta = 2\hbar\nu \exp\left[\left(-2/\hbar\right) \int_{0}^{y_{1}} \left[2\mu(V-E)\right]^{\frac{1}{2}} dy\right] \cdot$$
(1)

If this expression is a good approximation for the region, the microwave inversion spectrum might be more accurately represented by a formula

$$\nu = \nu_0 \exp[AJ(J+1) + BK^2 + CJ^2(J+1)^2 + DJ(J+1)K^2 + EK^4] (2)$$

than by the usual expression

 $\nu = \nu_0 + A'J(J+1) + B'K^2 + C'J^2(J+1)^2 + D'J(J+1)K^2 + E'K^4.$  (3)

TABLE I. Frequency of NH<sub>2</sub> lines.

J	K	Freq.	Error	Ref.	J	K	Freq.	Error	Ref.
1	1	23.694.49	0	2	9	9	27.478.00	-0.08	3
$\overline{2}$	$\overline{2}$	23.722.63	-0.01	2	ģ	8	23.657.48	-0.08	ž
2	1	23.098.79	-0.07	2	9	7	20.735.44	+0.01	2
3	3	23.870.13	(-0.21)	2	9	6	18.499.5	-0.62	4
3	2	22.834.17	-0.05	2	ģ	5	16.798.3	-2.04	4
3	1	22.234.53	0	2	10	10	28.604.73	-0.18	3
4	4	24,139,41	+0.07	2	10	9	24,205,29	-0.10	2
4	3	22.688.29	(+1.76)	2	10	8	20.852.51	-0.04	2
4	2	21,703.36	+0.03	2	10	7	18,285.6	-1.08	4
4	1	21,134.29	+0.04	2	11	11	29,914.66	+0.12	3
5	5	24,532.98	+0.07	2	11	10	24,881.90	-0.01	2
5	4	22.653.00	-0.01	2	11	9	21.070.70	-0.01	2
5	3	21.985.27	(-7.03)	2	11	8	18,162.6	-1.59	4
5	2	20.371.46	`+0.11	2	12	12	31,424.97	+0.51	3
5	1	19.838.4	+0.14	4	12	11	25.695.23	+0.36	2
6	6	25.056.02	+0.05	2	12	10	21.391.55	+0.19	3
6	5	22,732.43	+0.02	2	12	9	18,127.2	-2.36	4
6	4	20,994,61	+0.09	2	13	13	33,156.95	+1.22	3
6	3	19,757.57	(+21.18)	2	13	12	26,655.00	+1.27	3
6	2	18,884.9	+0.14	4	13	11	21,818,1	+0.93	4
6	1	18,391.6	-0.15	4	13	10	18,178.0	-2.82	4
7	7	25,715.17	-0.01	2	14	14	35,134.44	+3.38	3
7	6	22,924.94	-0.01	2	14	13	27,772.52	+2.79	3
7	5	20,804.83	+0.10	2	14	11	18,313.9	-3.16	4
7	4	19,218.52	0	2	15	15	37,385.18	+6.74	3
7	3	18,017.6	(-52.39)	4	15	14	29,061.14	+5.05	3
7	2	17,291.6	-0.82	4	15	12	18,535.1	-3.26	4
7	1	16,841.3	-0.95	4	16	16	39,941.54	+12.61	3
8	8	26,518.91	-0.13	3	16	14	23,777.4	+6.52	4
8	7	23,232.24	-0.04	2	16	13	18,842.9	-2.64	4
8	6	20,719.21	+0.06	2	17	15	24,680.1	+12.27	4
8	5	18,808.7	-0.09	4					
8	4	17,378.1	-1.18	4					

Formula (2) was fitted to 64 lines, as published<sup>2-4</sup> to date. The six constants were obtained graphically using the differences of the logarithms of the frequencies, and were not adjusted to obtain a better fit for high J values. The equation obtained is

$$\nu = 23,785.88 \exp[-6.36996 \times 10^{-3}J(J+1) + 8.88986 \times 10^{-3}K^{2} + 8.6922 \times 10^{-7}J^{2}(J+1)^{2} - 1.7845 \times 10^{-6}J(J+1)K^{2} + 5.3075 \times 10^{-7}K^{4}]. \quad (4)$$

The experimental frequencies are listed in Table I, together with the errors obtained by subtracting the calculated from the experimental frequencies.

The rms error (omitting K=3 lines) in fitting Eq. (4) to 60 lines is 2.9 Mc/sec and the average error 1.3 Mc/sec. The best fit so far obtained with a power series,<sup>3</sup> such as Eq. (3), gives an average deviation of 26 Mc/sec, while a partially exponential equation<sup>5</sup> gives 46 Mc/sec. With a power series employing sixthpower terms in J and K and ten constants,<sup>4</sup> the average deviation is 7 Mc/sec, compared to 1.3 Mc/sec obtained with six constants above. The accuracy of Eq. (4) is best demonstrated by using only lines measured by Good and Coles.<sup>2</sup> Leaving out J = 12, K = 11, the rms error is then 0.05 Mc/sec.

The anomalous deviations of the 3,3; 4,3; 5,3; 6,3; 7,3 lines are -0.21; +1.76; -7.03; +21.18; -52.39 Mc/sec, respectively. Nielsen and Dennison<sup>6</sup> have shown that the deviation to be expected theoretically is of the form

$$\Delta \nu = AF(J). \tag{5}$$

They calculated  $A = 0.258 \pm 10$  percent from molecular constants, and F(J) = -1, 7, -28, 84, -210, for J = 3 to 7, inclusive. If A = 0.252, the deviations given by Eq. (5) are -0.25, +1.76, -7.06, +21.18, -52.9, for J=3 to 7, respectively.

The agreement obtained indicates that the functional form of Eq. (4) is correct. Further, the second-order coefficients are about  $10^{-4}$  of the first-order terms, a more reasonable value than  $10^{-2}$ of the first-order in the power series expressions. The third-order terms necessary for a more accurate fit of high J values were not calculated accurately but are reduced by a further factor of  $10^{-4}$ . Examination of the deviations calculated with Eq. (4) indicates that some of the frequencies given in reference 4 may be in error by about 1 Mc/sec.

<sup>1</sup> Dennison and Uhlenbeck, Phys. Rev. 41, 313 (1932).
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<sup>3</sup> Simmons and Gordy, Phys. Rev. 73, 713 (1948).
<sup>4</sup> Sharbaugh, Madison, and Bragg, Phys. Rev. 76, 1529 (1949).
<sup>5</sup> Strandberg, Kyhl, Wentink, and Hillger, Phys. Rev. 71, 326 (1947).
<sup>6</sup> Nielsen and Dennison, Phys. Rev. 72, 1101 (1947).

**New Ferroelectric Tartrates** 

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LTHOUGH several groups of ferroelectric crystals have been A discovered in the thirty years since Valasek<sup>1</sup> first observed the phenomenon of ferroelectricity in Rochelle salt, the latter substance has so far occupied a special position among ferroelectric materials because of two distinctive features of its behavior: first, the existence of both a lower and an upper Curie point, and second, the fact that the only known ferroelectric crystals isomorphous with Rochelle salt were mixtures of this substance with other tartrates,<sup>2</sup> no other tartrate being known to be ferroelectric by itself. In reviewing this subject we have recently noticed that Scholz's measurements on LiNH4C4H4O6 H2O at temperatures above 125°K show a steep rise in certain piezoelectric moduli for this crystal with decreasing temperature, a reasonable extrapolation indicating that the piezo-moduli become infinitely large in the neighborhood of 100°K. This behavior led us to expect the occurrence of ferroelectricity in lithium ammonium tartrate at low temperatures, a hypothesis which has now been confirmed by experiment.