effect would increase the absolute value of the density gradient of helium over that computed on the basis of Eq. (1).[5] 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.

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* This work is sponsored by a contract with the Meteorological Branch of the U. S. Army Signal Corps.

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An Empirical Formula for the Microwave Spectrum of Ammonia

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(Received February 13, 1951)

THE inversion splitting for a double minimum potential was obtained by Dennison and Uhlenbeck[1] using the W-K-B approximation. They found

$$\Delta = 2\hbar\nu\,\exp\left[(-2/\hbar)\int_0^{y_1}[2\mu(V-E)]^{\frac{1}{2}}dy\right]. \qquad (1)$$

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

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

than by the usual expression

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

TABLE I. Frequency of NH_3 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
2	2	23,722.63	−0.01	2	9	8	23,657.48	−0.08	2
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	9	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[2−4] 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

$$\begin{aligned}\nu = 23{,}785.88\,\exp[&-6.36996\times10^{-3}J(J+1)+8.88986\times10^{-3}K^2\\&+8.6922\times10^{-7}J^2(J+1)^2-1.7845\times10^{-6}J(J+1)K^2\\&+5.3075\times10^{-7}K^4]. \qquad (4)\end{aligned}$$

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,[3] such as Eq. (3), gives an average deviation of 26 Mc/sec, while a partially exponential equation[5] gives 46 Mc/sec. With a power series employing sixth-power terms in J and K and ten constants,[4] 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.[2] 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[6] have shown that the deviation to be expected theoretically is of the form

$$\Delta\nu = AF(J). \qquad (5)$$

They calculated $A=0.258\pm10$ 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.

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New Ferroelectric Tartrates

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(Received February 8, 1951)

ALTHOUGH several groups of ferroelectric crystals have been discovered in the thirty years since Valasek[1] 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,[2] no other tartrate being known to be ferroelectric by itself. In reviewing this subject we have recently noticed that Scholz's[3] measurements on $LiNH_4C_4H_4O_6\cdot H_2O$ 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.

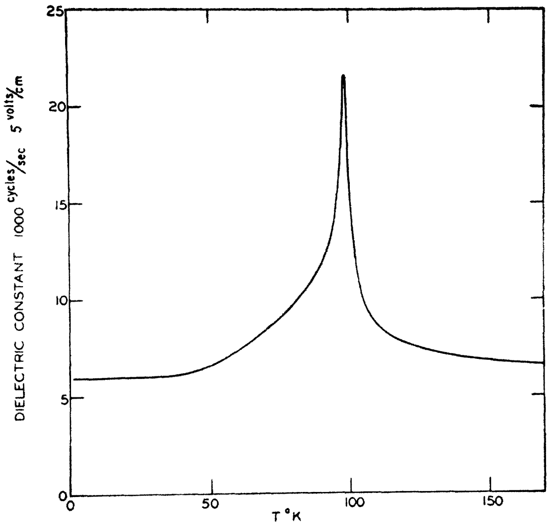

FIG. 1. Temperature variation of ϵ_b, $LiNH_4C_4H_4O_6\cdot H_2O$.

Figure 1 shows the temperature variation of ϵ_b, the dielectric constant, of a typical $LiNH_4C_4H_4O_6\cdot H_2O$ crystal plate with the electric field parallel to the *b* axis of the crystal. The sharp peak at 98.5°K marks an upper Curie point below which the crystal exhibits a well-defined ferroelectric hysteresis loop at high field strength (~10,000 volts/cm), with a spontaneous polarization 0.22×10^{-6} coulomb per cm^2 in the *b* direction at 78°K. Other striking features of Fig. 1 are, firstly, the low average value of the dielectric constant compared with average values for other ferroelectric crystals, including Rochelle salt; and, secondly, the absence of a lower Curie point, which may be inferred from the monotonic variation of ϵ_b from the upper Curie point down to 1.3°K, the lowest temperature of measurement.

The above discovery immediately raised the question as to whether a similar type of ferroelectric behavior might occur in other isomorphous crystals, or whether lithium ammonium tartrate would turn out to be another singular case. Although the only other isomorphous crystal studied by Scholz,[3] $LiKC_4H_4O_6\cdot H_2O$, gave no marked variation of piezo-moduli with temperature, this did not seem unreasonable in view of the difference between the K^+ and NH_4^+ ions. It appeared that ferroelectricity would be less disturbed in the replacement of NH_4^+ by the more nearly isosteric Rb^+ and Tl^+ ions; and, since no electrical data were available for either of the resulting crystals, we undertook a study of both.

Figure 2 shows the temperature variation of the dielectric constant, ϵ_a, of a crystal of $LiTlC_4H_4O_6\cdot H_2O$ with the electric field applied parallel to the *a* axis. With decreasing temperature, ϵ_a showed an unusually rapid rise between liquid hydrogen and liquid helium temperatures, but for a given field strength, it eventually passed through a very flat maximum and tended to a steady value as the absolute zero was approached. At liquid helium temperature, however, ϵ_a was extremely sensitive to small changes in field strength owing to the fact that below 10 (±1)°K the crystal exhibited a ferroelectric hysteresis loop, the coercive field strength being only 120 volts per cm for an applied field of 3000 volts per cm. In this field at 1.3°K, the crystal showed a reversible spontaneous polarization of about 0.14×10^{-6} coulomb per cm^2 (which is probably close to the saturation value), superimposed on an induced polarization of the same order of magnitude associated with the high initial dielectric constant. The existence of an upper Curie point at about 10°K was evident from the disappearance of hysteresis and field dependence of ϵ_a on heating through this temperature, and also from application of a Curie-Weiss formula to the steeply falling dielectric constant at higher temperatures. No lower Curie point was observed down to 1.3°K.

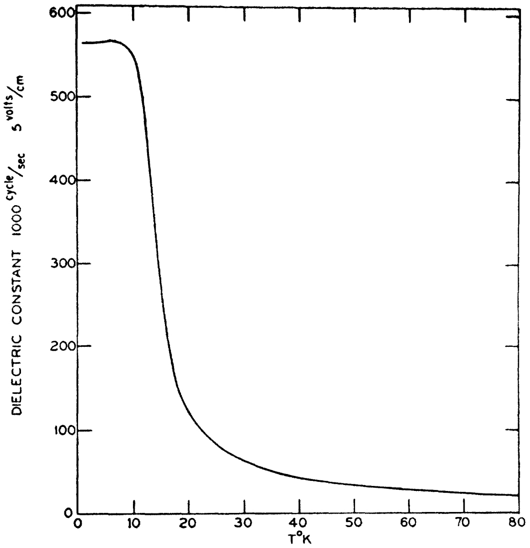

FIG. 2. Temperature variation of ϵ_a, $LiTlC_4H_4O_6\cdot H_2O$.

In comparing the new ferroelectric crystals with Rochelle salt, it has to be borne in mind that although the crystal symmetry is the same in each case, the axial ratios are quite different, while in addition, Rochelle salt has four molecules of water of crystallization compared with one molecule in both of the new crystals. In view of this fact, it is somewhat surprising that practically the same value of spontaneous polarization is observed for each crystal, which may indicate that the water molecules play a relatively unimportant role in the ferroelectric behavior. The low value of dielectric constant and unusual (*b*) direction of ferroelectric behavior in lithium ammonium tartrate is possibly the result of an interaction between ammonium ions of the type observed in $NH_4H_2PO_4$.[4] The new results strengthen the assumption that the lower Curie point in Rochelle salt is somewhat accidental. A comparison of the lithium thallium tartrate data with those for potassium tantalate[5] seems to indicate that sharp dielectric constant peaks do not occur near the absolute zero. Finally, we draw attention to the positive birefringence of all three known ferroelectric tartrates, a property which is rather uncommon among other orthorhombic tartrates.

A more detailed paper, with data on lithium rubidium tartrate, will be published later.

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Resistivity and Hall Constant of Semiconductors

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(Received January 26, 1951)

IN a recent letter Jones[1] has pointed out that the contributions to the resistivity of semiconductors caused by lattice scattering and by ionized impurity scattering are not simply additive. It is necessary to consider an energy average of these contributions; and, when this is done, new expressions for the Hall constant and the resistivity result.

There have been calculations paralleling those of Jones carried out at this laboratory, but in a more general representation. One considers mean free paths l_L, due to lattice scattering, l_{II}, due to