



FIG. 2. Observed separations of  ${}^3D_1$  level.

possibly also due to perturbing effects from the  $5p4f$  configuration. While the quadrupole effect is definitely recognizable, it does not seem feasible

to attempt a determination of the quadrupole moment from the observed deviations.

As a check on the measurements reported here the ratios of the magnetic moments for the two isotopes can be determined from the total separations of the hyperfine structures. This gives  $\mu_{121}/\mu_{123}=1.316$  and is in close agreement with the value 1.32 which is obtained from the separations of the  $5s6s^3S_1$  level of Sb IV studied by Crawford and Bateson.<sup>4</sup>

Finally it is of interest to see whether the observed line shows any isotope shift. This can be done by determining the center of gravity of the observed structures taking the statistical weight of each hyperfine state  $(2F+1)$ . As shown in Fig. 2 the centers of gravity for  $\text{Sb}^{121}$  and  $\text{Sb}^{123}$  are almost coincident. The c.g. for  $\text{Sb}^{121}$  lies  $0.001 \text{ cm}^{-1}$  above that for  $\text{Sb}^{123}$  indicating that the isotope shift in this transition is negligible.

### Note on the Effect of Pressure on the Curie Point of Iron-Nickel Alloys

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By applying Clapeyron's equation, an estimate is made of the increase of the Curie point of nickel with pressure, which comes out of the order of magnitude of  $5 \times 10^{-5}$  degree per atmosphere. For iron-nickel alloys, the increase of Curie point with pressure would become less as more iron is added, becoming zero with something like 70 percent of nickel, and for the alloys containing more iron the Curie

point would decrease with pressure. These magnitudes are such that it seems most unlikely that pressures existing in the iron-nickel core of the earth would raise the Curie point of the material enough so that it could be ferromagnetic at the temperatures existing inside the earth. This makes any ferromagnetic explanation of the magnetism of the earth most implausible.

IT is a matter of considerable geophysical interest to know the effect of pressure on the Curie point of iron-nickel alloys such as may constitute the core of the earth. It is ordinarily supposed that the permanent magnetism of the earth cannot be explained as being of ferromagnetic origin, because at the high temperatures assumed in the interior, of the order of several thousand degrees absolute, the alloys would be far above their Curie points, and would not be ferromagnetic. On the other hand, there are presumably very high pressures, of the order of  $10^6$  atmospheres, in the interior of the earth, and

if such a pressure should raise the Curie point enough, the interior of the earth might still be ferromagnetic. It thus becomes important to know whether pressure would be expected to raise or to lower the Curie point, and if it raises it, to know whether it could be by some such amount as  $5000/10^6 = 5 \times 10^{-3}$  degree per atmosphere (taking the temperature to be  $5000^\circ$ ), which would suffice to make the interior of the earth ferromagnetic. Not many experiments are available to settle this point, on account of the difficulty of combining high pressure and high temperature technique. It becomes important

therefore to see how much information can be given by theory. Shockley<sup>1</sup> has qualitatively discussed the anomaly in the thermal expansion of iron-nickel alloys at the Curie point, and the method of discussion which he uses has been extended by Bozorth<sup>2</sup> to the question of the effect of pressure on the Curie point. Bozorth concludes that pressure does in fact increase the Curie point of nickel, but decreases that of iron, and for alloys of intermediate composition has an intermediate effect, so that there is a certain concentration, with perhaps of the order of magnitude of 70 percent of nickel, for which the Curie point is independent of pressure. Bozorth makes no estimate of the magnitude of the change of Curie point, and it is the purpose of the present note to make such an estimate. The result is that the effect is too small to be of geophysical importance. A rough estimate of the effect of pressure on the Curie point of nickel would be an increase of  $5 \times 10^{-5}$  degree per atmosphere, only about one percent of that required to make the core of the earth ferromagnetic, and it is hard to see how the calculations could be in error by more than a factor of ten, to be generous. Thus our conclusion is that it remains extremely unlikely that the material of the interior of the earth is in a ferromagnetic state.

The method which we shall use is based on Clapeyron's equation. The Curie point is of course a phase change of the second order, to which Clapeyron's equation is not applicable. Nevertheless we commit no serious error if we consider only two limiting states of the metal, the completely magnetized and the completely unmagnetized states, and consider the phase change of the first order which would occur between them if states of intermediate magnetization did not exist. Actually, instead of a sharp transition between these two phases, we have a continuous transition, which becomes complete at the Curie point  $\theta$ . If there were only the two limiting phases, there would be a sharp transition at the temperature  $\theta'$  at which their free energies were the same. It is not hard to show that this temperature  $\theta'$  would be less than  $\theta$ , about  $0.7\theta$  in some simple cases. We are now justified in supposing that the effect of pressure

on the transition temperature  $\theta'$  will be similar to that on the Curie temperature  $\theta$ . It is simple to compute, however, for the assumptions of Clapeyron's equation apply to it. This equation may be written

$$d\theta'/dP = \Delta V/\Delta S, \quad (1)$$

where  $\Delta V$  is the volume difference between the magnetized and unmagnetized phases,  $\Delta S$  the entropy difference between the phases, equal in the case of a phase change of the first order to the latent heat of transition divided by the absolute temperature. To estimate the variation of the temperature  $\theta'$  with pressure, then, we need the increases of volume and entropy in going from the magnetized to the unmagnetized phases.

Experimentally, there is no sharp transition, so that there is no directly measurable change of volume and latent heat. Instead, the transition is spread through a range of temperatures, and there are anomalies in the thermal expansion and specific heat throughout these regions, coming to a peak at the Curie point. The quantities which we wish in Eq. (1) are the integrated anomalies in thermal expansion and specific heat, giving estimated values of the total changes in volume and entropy between the two phases. Shockley<sup>1</sup> and Bozorth<sup>2</sup> have both given curves for thermal expansion as a function of temperature, for a series of iron-nickel alloys. From these curves it is seen that pure nickel has an increase of thermal expansion below the Curie point, falling to zero suddenly at the Curie point, meaning that the unmagnetized, high temperature phase has a larger volume than the magnetized phase, so that by Eq. (1)  $d\theta'/dP$  is positive, and increase of pressure increases the Curie point. The other alloys shown by Shockley and Bozorth, however, beginning with 66.8 percent nickel, have decreases of thermal expansion, indicating a reduced volume for the unmagnetized phase, and a negative value of  $d\theta'/dP$ . A rough estimate from the figure indicates that the change of sign might come at about 70 or 75 percent nickel.

Using Shockley and Bozorth's curves, one can make a rough estimate of  $\Delta V$ , for pure nickel. Very crudely, we may suppose the anomaly to be a triangle, extending through about  $300^\circ$  (from about  $75^\circ\text{C}$  to  $375^\circ\text{C}$ ), and of height at the Curie point of  $1 \times 10^{-6}$ . Thus, since the area of a

<sup>1</sup> W. Shockley, *Bell Sys. Tech. J.* **18**, 645 (1939).

<sup>2</sup> R. M. Bozorth, *Bell Sys. Tech. J.* **19**, 1 (1940).

triangle is half the base times the altitude, the fractional increase in length from magnetized to unmagnetized state would be  $300 \times 1 \times 10^{-6} / 2 = 1.5 \times 10^{-4}$ , and the fractional increase in volume three times this, or  $4.5 \times 10^{-4}$ . Next we must estimate the change in entropy. This could be done from observations on specific heat. It is perhaps simpler, however, to use a direct theoretical estimate, since it is known that theory gives an adequate interpretation of the entropy anomaly. The estimate is slightly different depending on whether we use the Weiss-Heisenberg model or the electron band model, but since we are looking for only approximate values, we may use the Weiss model for simplicity. An elementary magnet with angular momentum  $lh/2\pi$  will have  $(2l+1)$  orientations, so that the entropy per magnet will be  $k \ln(2l+1)$ , or will be  $Nk \ln(2l+1)$  for  $N$  magnets. This will represent the entropy of the unmagnetized, random state; the magnetized state will have zero entropy of orientation. For nickel, we may take as far as order of magnitude is concerned  $l = \frac{1}{2}$ , giving two orientations (corresponding to one spin per atom), so that we have  $\Delta S = Nk \ln 2$ , for  $N$  atoms. If we now take  $N$  to be the number of atoms in unit volume, we may take  $\Delta V$  to be  $4.5 \times 10^{-4}$  cc, making all calculations for unit volume. For nickel, the density is 8.6, and the atomic weight 58.7. Thus the number of atoms per unit volume is  $6.03 \times 10^{23} \times 8.6 / 58.7 = 0.88 \times 10^{23}$ . Hence we have  $\Delta S = 0.88 \times 10^{23} \times 1.38 \times 10^{-16} \times 0.6931 = 0.84 \times 10^7$ . Finally, then, using Eq. (1),

$$\frac{d\theta'}{dP} = \frac{4.5 \times 10^{-4}}{0.84 \times 10^7} = 5 \times 10^{-11} \text{ degrees per unit pressure} \quad (2)$$

$$= 5 \times 10^{-5} \text{ degree per atmosphere.}$$

This is the estimate mentioned in the first paragraph. It is noteworthy that the one accurately measured value of change of Curie point with pressure, for a Ni-Cu alloy,<sup>3</sup> was  $6 \times 10^{-5}$  degree per atmosphere, just of this order of magnitude. The smallness of the effect of pressure on the Curie point is a direct result of the small volume difference between magnetized and unmagnetized states, a much smaller difference than found in the usual polymorphic transition, resulting in a

<sup>3</sup> A. Michels, A. Jaspers, J. de Boer and J. Stryland, *Physica* **4**, 1007 (1937).

correspondingly small effect of pressure. It is hard to see how this estimate can be very greatly in error. If one allows a factor of two in  $\Delta V$  and  $\Delta S$ , and assumes that our replacement of the phase change of the second order by one of the first order introduces an additional factor of two, and makes the unlikely assumption that all these errors work in the same direction, one could conceivably get an effect eight or ten times as large as (2), though there is no reason for expecting it. But it seems quite out of the question to understand an error by a factor of a hundred, as we should need to explain the magnetism of the earth. Furthermore, we must remember that the calculations are made for pure nickel, and that iron-nickel alloys will show a smaller, or even negative, effect.

An even stronger reason for suspecting that the effect of pressure on the Curie point is not large comes from the general point of view underlying the theory, as described for instance by Shockley and Bozorth. One can draw a curve of Curie point as a function of the ratio of the lattice spacing to the average radius of the  $d$  shell of electrons. This curve has its maximum about at cobalt, or alternatively about at a 70-percent Ni-Fe alloy, in which the iron atoms, with  $d$  shells larger than cobalt, and the nickel atoms with smaller  $d$  shells, seem to give about the same average effect. Pure nickel corresponds to a larger ratio than cobalt, pure iron to a smaller ratio. Compression decreases the lattice spacing, bringing nickel closer to the maximum of the curve and increasing its Curie point. But the most that pressure can do, according to the picture, is to change the lattice spacing enough to bring the material to the maximum of the curve, or to give it about the same Curie point as pure cobalt, or as a 70-percent Ni-Fe alloy. In other words, the only effect of pressure on the Curie points of real substances would be expected to be to change them so that they resemble other real substances. But there are no known substances with Curie points much above the 1400° Abs. which we find for cobalt. Thus it is most unlikely that pressure will raise the Curie point of any substance much above this value, so that it is most improbable that any material could be ferromagnetic in the interior of the earth, if it is as hot as usually supposed.