

solute error to be assigned to these points is 30 percent. For the low energy points the measured total cross section is in essential agreement with the calculated cross section; however, in the region of the meson threshold the experimental cross section is higher by a factor of about 2.5. Assuming the angular distributions of references 2 and 3 and that used by Austern<sup>4</sup> in calculations of the isotropic contribution, an estimate can be made of the electric quadrupole cross section which is found to be about 1 percent of the electric dipole cross section in the energy region of this experiment. An estimate of the isotropic contribution is 40 percent of the electric dipole cross section. The errors in these estimates are obviously large, since they are limited by the counting statistics and the fact that observations were made at only three angles.

\* Supported by the joint program of the ONR and AEC.

<sup>1</sup> T. S. Benedict and W. M. Woodward, *Phys. Rev.* **83**, 1269 (1951).

<sup>2</sup> L. I. Schiff, *Phys. Rev.* **78**, 733 (1950).

<sup>3</sup> J. F. Marshall and E. Guth, *Phys. Rev.* **78**, 738 (1950).

<sup>4</sup> N. Austern, *Phys. Rev.* **85**, 283 (1952).

### Line Width of Paramagnetic Resonance and Exchange Interaction in Salts Containing Mn<sup>++</sup> and Fe<sup>+++</sup>

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(Received December 17, 1951)

IN column 3 of Table I, half-widths  $\Delta H_{\frac{1}{2}(\text{obs})}$  of paramagnetic microwave resonance absorption lines, at  $\lambda=3.01$  cm, are shown for nine kinds of polycrystalline salts containing Mn<sup>++</sup>

TABLE I. Half-widths of paramagnetic microwave resonance absorption lines.

Polycrystals	Crystal symmetry	$\Delta H_{\frac{1}{2}(\text{obs})}$ (oersteds)	$\Delta H_{\frac{1}{2}(\text{calc})}$ (oersteds)	$\theta$ (°K)	$z(\text{calc})$
FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub>	hexa.	580	1680	13 <sup>a</sup>	38
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	hexa.	180	2300	70 <sup>a,b</sup>	33
MnCl <sub>2</sub>	hexa.	1250	2950	-16 <sup>a</sup>	32
MnCl <sub>2</sub> ·2H <sub>2</sub> O	...	760	...	...	...
MnCl <sub>2</sub> ·4H <sub>2</sub> O	mono.	1340	1530	-3(≈0) <sup>c</sup>	...
MnSO <sub>4</sub>	mono.	655	3400	24 <sup>d</sup>	19
MnSO <sub>4</sub> ·H <sub>2</sub> O	mono.	305	2800	...	...
MnSO <sub>4</sub> ·4H <sub>2</sub> O	mono.	1140	1500	2(≈0) <sup>c,d</sup>	...
MnSO <sub>4</sub> ·5H <sub>2</sub> O	tric.	1250	1250	3(≈0) <sup>c</sup>	...

<sup>a</sup> See reference 3.

<sup>b</sup> See reference 4.

<sup>c</sup> See reference 5.

<sup>d</sup> See reference 6.

and Fe<sup>+++</sup>. Some of the results have already been reported.<sup>1</sup> When the  $g$  value is anisotropic, as in the case of cupric salts, the apparent width for a polycrystalline powder is increased. However, in powders of salts containing Mn<sup>++</sup> and Fe<sup>+++</sup>, there is no such effect since these ions are in  $S$  states and the  $g$  value is almost isotropic.

The theoretical half-width caused by dipolar coupling in a powdered cubic crystal has been calculated by Van Vleck<sup>2</sup> under the assumption that the shape function is Gaussian. The formula thus obtained is

$$\Delta H_{\frac{1}{2}(\text{calc})} \approx 2.35[(\Delta H^2)_{AV}]^{\frac{1}{2}} = 2.35g\beta\left\{\frac{3}{2}S(S+1)\sum_{k \neq j} k^{-6}\right\}^{\frac{1}{2}}. \quad (1)$$

As we have little knowledge of the detailed structure of crystals in the table, we have assumed tentatively, as a first approximation, that the arrangement of ions is simple cubic with lattice constant  $a$ . Half-widths calculated by this simplification of (1) are given in the fourth column of the table. In cases where the crystal structure is known from x-ray analysis, as for instance (NH<sub>4</sub>)Fe(SO<sub>4</sub>)<sub>2</sub>, the calculated width for the simple cubic arrangement of ions is generally narrower than that calculated allowing for the correct arrangement of ions in the crystals. However, the resulting change in the calculated half-width is by a factor ranging from about 1 to 1.4, so the difference in ionic arrangements has no significant influence on our rather qualitative discussion.

In some cases, the observed width is much smaller than the calculated one on account of the effect of exchange coupling. The fifth column shows the observed values<sup>3-6</sup> of  $\theta$  in the Curie-Weiss formula for the static susceptibility,  $\chi_s = c/(T+\theta)$ . The departures of  $\theta$  from zero are caused by the exchange coupling of electrons and the splitting of electronic levels by the crystalline field. The inference is clear that when  $\Delta H_{\frac{1}{2}(\text{calc})}/\Delta H_{\frac{1}{2}(\text{obs})}$  is large,  $\theta$  is large. This circumstance can be explained in order of magnitude in the following way.

According to Van Vleck's considerations,<sup>2</sup>  $\Delta\nu_{\frac{1}{2}}$  under exchange coupling is given by  $\Delta\nu_{\frac{1}{2}} \approx \tau_c \langle \Delta\nu^2 \rangle_{AV}$ , where  $\tau_c = h/2J$  and  $J$  is the exchange integral. We tentatively set

$$\Delta\nu_{\frac{1}{2}} = \tau_c \langle \Delta\nu^2 \rangle_{AV} = (h/2J) \langle \Delta\nu^2 \rangle_{AV}, \quad (2)$$

in which  $\Delta\nu_{\frac{1}{2}}$  is  $\Delta H_{\frac{1}{2}(\text{obs})} \cdot g\beta/h$ .

In our cases of Mn<sup>++</sup> and Fe<sup>+++</sup>, it is probable that the effect of splitting of electronic levels upon  $\theta$  is negligible and that  $\theta$  is caused only by exchange coupling.<sup>7</sup> In this case,  $\theta$  is connected with  $J$  by the relation<sup>8</sup>

$$3k\theta = 2JzS(S+1), \quad (3)$$

where  $k$  is the Boltzmann constant,  $S$  is the spin quantum number (in our case  $S=5/2$ ), and  $z$  is the number of nearest neighbors in the lattice.

We can try calculating values of  $z$  by using the formula

$$z(\text{calc}) = \frac{3k\theta(2.35)^2 \Delta H_{\frac{1}{2}(\text{obs})}}{(\Delta H_{\frac{1}{2}(\text{calc})})^2 g\beta S(S+1)},$$

which follows from Eqs. (1), (2), and (3). The resulting values of  $z$  are shown in the sixth column of the table. They show no large divergences from each other, but they are all several times larger than the values of  $z$  deduced from the crystal structures. Further elaborations of our rather qualitative considerations would be futile.

A more detailed report will appear in *J. Phys. Soc. Japan*. Our thanks are due Professor T. Mutô for his cordial discussions.

<sup>1</sup> Kumagai, Ono, Hayashi, Abe, Shimada, Shôno, and Ibamoto, *Phys. Rev.* **83**, 1077 (1951).

<sup>2</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

<sup>3</sup> T. Ishiwara, *Sci. Repts. Tohoku Univ.* **3**, 303 (1914).

<sup>4</sup> P. Théodoridés, *J. phys. et radium* **3**, 1 (1922).

<sup>5</sup> L. C. Jackson, *Proc. Roy. Soc. (London)* **A140**, 695 (1933).

<sup>6</sup> H. K. Onnes and E. Oosterhuis, *Leiden Comm.* **12**, 132e (1913).

<sup>7</sup> J. H. Van Vleck and W. C. Penny, *Phil. Mag.* **17**, 961 (1934).

<sup>8</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), p. 332.

### Adiabatic Study of the 128°C Transition in Barium Titanate

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(Received January 9, 1952)

THERE has been much discussion about the nature of the so-called Curie point transition in barium titanate. Some writers have classed it as second order,<sup>1</sup> while others have noticed discontinuities typical of a first-order transition.<sup>2,3</sup> A first-order transition would be characterized by a latent heat which in barium titanate has heretofore escaped direct detection. Blattner and Merz<sup>4</sup> observed a specific heat anomaly amounting to 47 cal/mole; however, this was spread over a range of about 15°C and cannot be cited as evidence that the transition is first order. A more convincing argument may be based on the change of temperature which we find takes place when the transition is induced adiabatically by applying an electric field.

For this analysis ceramic disks of barium titanate of the highest obtainable purity were used. These were attached to suitable connecting wires and thermocouple leads and suspended by these wires in a small oven in which air was circulated. Small changes in temperature were detected by a recording galvanometer in the thermocouple potentiometer circuit. The sensitivity of indication