The disagreement appears to be greater than our experimental error.

A direct comparison can be made of the values of $d \ln\gamma/d \ln V$ which are obtained, first, by direct calculation, and second, by the use of this requirement. Equation (1) can be rewritten in reduced form as

$$h^2 = 1 - 4\pi(\gamma T_c^2/V H_0^2)t^2 + \cdots. \qquad (8)$$

The requirements of simple similarity imply that the dimensionless quantity in the brackets must remain unchanged by variations in the pressure (or volume). This can be expressed as,

$$d \ln\gamma/d \ln V = 1 + 2d \ln H_0/d \ln V - 2d \ln T_c/d \ln V. \qquad (9)$$

The value of $d \ln\gamma/d \ln V$ which can be calculated from Eq. (9) and our experimental data $[2.4(\pm0.7)]$ is significantly higher than the directly calculated $[$Eq.

(2)$]$ value of $1.2(\pm0.4)$. If the data in Fig. 1 are fitted to Eq. (7) from $t^2 = 1$ to $t^2 = 0.3$ (where the rapid curvature begins), a value for $d \ln\gamma/d \ln V$ can be calculated from the extrapolation of this function to absolute zero which differs from the directly calculated value by a factor of three.

One can conclude from these experiments that the electronic behavior of tin is complex at low temperatures and is extremely sensitive to pressure effects. This is undoubtedly associated with the shape of the Fermi surface for tin, although direct correlations are not possible at present.[26] Certainly, as Kan et al. also suggest, further measurements of the electronic properties of high-purity single crystals of tin should be extremely profitable.

[26] A. V. Gold and M. G. Priestley, Phil. Mag. 5, 1089 (1960).

Paramagnetic Resonance Spectrum of Manganese in CdWO4

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(Received February 26, 1962)

The paramagnetic resonance spectrum of Mn^{2+} in $CdWO_4$ was measured at 34 kMc/sec at room temperature. The spectrum can be described by the spin Hamiltonian,

$$\mathcal{3C} = g\beta \mathbf{H} \cdot \mathbf{S} + D[S_z^2 + \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + A\mathbf{I} \cdot \mathbf{S},$$

with $g_z = 2.001$, $g_x = 2.003$, $g_y = 1.997$, $|D| = 5.153$ kMc/sec, $|E| = 1.395$ kMc/sec, $|A_z| = 0.246$ kMc/sec, $|A_x| = 0.242$ kMc/sec, $|A_y| = 0.259$ kMc/sec, $S = 5/2$, and $I = 5/2$.

INTRODUCTION

RECENTLY, considerable interest has been shown in the tungstates as host lattices for paramagnetic ions because of their possible application to quantum devices. Some of the paramagnetic resonance spectra that have been studied are Fe^{3+} in the monoclinic tungstates of Cd, Zn, and[1] Mg and Mn^{2+} and Gd^{3+} in the tetragonal $CaWO_4$.[2] In this paper we report our extension of this study to Mn^{2+} ($^6S_\frac{5}{2}$) in $CdWO_4$.

APPARATUS

The spectra were obtained with a radiation frequency of 34 kMc/sec. The spectrometer was a conventional bridge design with crystal detection. A VA97B klystron provided the radiation power and was stabilized to the cavity frequency by a circuit similar to that of George and Teaney.[3] The cylindrical (TE_{011}) cavity was made of lavite and silvered by thermal reduction of $AgNO_3$. With this technique it was possible to obtain a high Q ($\sim$3000) with a silvering thin enough to permit field modulation at 5 kc/sec for phase sensitive detection. The microwave frequency was measured with a wavemeter.

Magnetic fields in excess of 20 kOe were obtained with a 12-inch Varian electromagnet having $3\frac{1}{2}$-in. tapered polecaps and $1\frac{1}{4}$-in. air gap. The field was calibrated with an NMR probe[4] whose frequency was counted by a 10-Mc/sec decade counter. Since the narrow gap necessary to obtain the field required for the high field resonances did not permit the use of a Dewar, all measurements were made at room temperature.

OBSERVATIONS

The crystals of $CdWO_4$ were purchased from the Linde Company and had been grown by the Verneuil method. Spectrographic analysis indicated an impurity

[1] M. Peter, Phys. Rev. 113, 801 (1959). Also Peter, Van Uitert, and Mock, Second International Conference on Quantum Electronics, March 23–25, 1961. Berkeley, California (unpublished).
[2] C. F. Hempstead and K. D. Bowers, Phys. Rev. 118, 131 (1960).
[3] A. J. George and D. T. Teaney, Rev. Sci. Instr. 31, 997 (1960).
[4] J. R. Singer, Rev. Sci. Instr. 30, 92 (1959).

TABLE I. Best-fit parameters for Mn^{2+} in CdWO₄.

Parameter	Value
$|D|$	5.153±0.009 kMc/sec
$|E|$	1.395±0.003 kMc/sec
g_z	2.001±0.002
g_x	2.003±0.002
g_y	1.997±0.002
$|A_z|$	0.246±0.005 kMc/sec
$|A_x|$	0.242±0.005 kMc/sec
$|A_y|$	0.259±0.005 kMc/sec

concentration of 0.003 wt.% of Fe and less than 0.001 wt.% of Mn corresponding to 2×10^{18} and 7×10^{17} atoms/cc, respectively.

The crystal and magnetic symmetry of this class of compounds has been discussed by Peter[1] in the analyses of Fe^{3+} in the monoclinic tungstates. The diad (b) axis of the crystal fixes one of the magnetic axes and the other magnetic axes lie in the AC plane and rotated with respect to the crystalline axes. For Fe^{3+} in CdWO₄, Peter found the Z axis turned 43.6° from the A axis toward the C axis.

CdWO₄ has a pronounced cleavage in the AC plane. Since this plane contains the X and Z axes, following Peter's designation, it is convenient to at first rotate the magnetic field in this plane to determine the location of these axes. Upon doing this the spectrum for Mn was observed to have maxima in the directions of axes of the Fe spectrum. In these directions the spectrum consisted of five widely spaced groups of six lines each. The separations between successive groups were approximately 3600 Oe along the Z axis and 3200 Oe along the X axis. The linewidths were about 15 Oe for the $M=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transitions, 25 Oe for the $M=\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ transitions, and 35 Oe for the $M=\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ transitions. At intermediate angles lines corresponding to $\Delta M=\pm1$, $\Delta m=\pm1$ appear, particularly in the $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition where they are equal in intensity to the normal lines at less than 10° from the axes. Such a large intensity anomaly is to be expected as Friedman and Low[5] have shown the intensity of the forbidden lines varies as $(D/A)^2\sin^2\theta\cos^2\theta$ and in this crystal $D/A>20$.

The crystal was then mounted so that the magnetic field could be rotated in the XY and YZ planes. Again the spectrum reached extremes along the axes, however, along the Y axis the $\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ transitions were both at higher fields than the $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition. One of the $\pm\frac{1}{2}\leftrightarrow\frac{3}{2}$ transitions overlapped the $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transitions; the other overlapped one of the $\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ transitions. The fields at which resonance occurred were measured along each axis.

The results can be described in terms of the spin Hamiltonian,

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2+\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)+A\mathbf{I}\cdot\mathbf{S},$$

with $S=\frac{5}{2}$ and $I=\frac{5}{2}$. Since D and E are so large, second-order perturbation theory is not sufficiently accurate for calculating energy levels. We therefore solved the secular determinant numerically, adjusting the constants given in Table I for best fit.

Since the measurements were made at room temperature the sign of the constants could not be determined unambiguously. For the choice of X and Y axes, E must be of opposite sign to D. From the convergence of the hyperfine structure A_x, A_y, and A_z are of the same sign as D. Since normal hyperfine constants are negative, we infer that the sign of D is negative.

[5] E. Friedman and W. Low, Phys. Rev. 120, 408 (1959).