OBSERVATION OF DEPOPULATION OF THE PARAMAGNETIC RESONANCE OF TRIVALENT IRON IN CALCIUM TUNGSTATE

J. Kirton* and R. C. Newman†

Associated Electrical Industries, Limited Central Research Laboratory, Rugby, Warwickshire, England
(Received 7 June 1965)

In a recent paper, Kedzie, Lyons, and Kestigian[1] have described observations of paramagnetic resonance of trivalent iron in a strong crystal field in calcium tungstate ($CaWO_4$). The resonance was almost isotropic and had a g value of about 4.3 at both 9 and 25 Gc/sec and is thus similar to that observed by Castner et al.[2] from trivalent iron in some glasses. The latter authors have shown that a strong second-order rhombic crystal field will split the $^6S_{5/2}$ ground state of the Fe^{3+} free ion into three Kramers doublets, the center one of which has an isotropic g value of 4.3. However, Kedzie, Lyons, and Kestigian have shown that an isotropic $g = 4.3$ resonance can also arise from a ground state of Fe^{3+} if there is an accidental relationship between the second- and fourth-order components of a strong tetragonal crystal field. It is evident that an experiment to search for depopulation of the resonance should decide which model is correct for Fe^{3+} in calcium tungstate. Without giving experimental details Kedzie, Lyons, and Kestigian state that they failed to observe depopulation at 25 Gc/sec between 4.2 and 1.5°K, and they concluded that the tetragonal-field model was correct. We have carried out similar experiments over the same temperature range but at a frequency near 9 Gc/sec and have found evidence to the contrary. In this Letter we describe observations of depopulation of the $g = 4.3$ doublet and estimate its height above the ground state.

The two samples examined were cut from a boule which was pulled from a calcium-tungstate melt doped with a nominal 0.005 at.% of iron oxide (Fe_3O_4). As Kedzie and Kestigian[3] have pointed out, the small (0.5%) anisotropy of the g value leads to the observation of four lines when the dc magnetic field is oriented along a general direction relative to the crystal axes. To avoid misorientation problems, measurements were made on just one of four such lines. The sample temperature was taken to be the same as that of the brass cavity and was measured by means of a standardized carbon resistor. Great care was taken to avoid saturation effects, and the power incident on the sample was always less than 100 μW. The intensity measurements were made relative to a standard sample of phosphorus-doped silicon (3×10^{18} donors/cm^3) which was kindly provided by E. A. Gere who also supplied details of the temperature variation of the linewidth and spin concentration.[4] The results of independent experiments on two samples at five fixed temperatures are shown in the following table.

Temperature (°K)	No. of spins giving rise to one resonance line ($\times10^{14}/cm^3$) RUN 1	RUN 2	Difference between two runs (%)
4.17 ± 0.05	1.70	1.53	10
3.40 ± 0.05	1.55	1.35	13
2.85 ± 0.05	1.10	1.10	...
2.37 ± 0.05	0.79	0.89	14
2.00 ± 0.05	0.70	0.72	3

We conclude from these measurements that depopulation occurs and that the $g = 4.3$ resonance is, in fact, observed from an excited doublet. If it occurs from the center doublet of three equally spaced doublets, as in the model of Castner et al.,[2] we can calculate the expected temperature variation of intensity I_{34}. In a magnetic field the three doublets of Fe^{3+} will each be split, and the levels can be numbered 1 to 6 from the lowest level upwards. I_{34} will then be proportional to the population difference f_{34} between levels 3 and 4 where

$$f_{34} \propto \frac{e^{-E_{13}/kT} - e^{-E_{14}/kT}}{1 + e^{-E_{12}/kT} + e^{-E_{13}/kT} + e^{-E_{14}/kT} + e^{-E_{15}/kT} + e^{-E_{16}/kT}}. \quad (1)$$

Our observed temperature variation is predicted by Eq. (1) when $\Delta = \frac{1}{2}(E_{14}+E_{13}) = 4.8 \pm 0.5\ \text{cm}^{-1}$. A maximum in the intensity is predicted at a temperature of ~6°K for $h\nu = 0.3\ \text{cm}^{-1}$ (9 Gc/sec), and it is calculated that almost the same depopulation should still occur between 4 and 1.5°K with $h\nu = 0.83\ \text{cm}^{-1}$ (25 Gc/sec).

In view of the discrepancy between our results and those of Kedzie, Lyons, and Kestigian, the same experiment was kindly carried out independently by S. D. McLaughlan and A. F. Fray of the Royal Radar Establishment, Malvern, who examined the relative intensities of a Si-P marker and the $g = 4.3$ resonance in one of our samples using their 9-Gc/sec equipment at 10, 4.2, and 1.4°K. They confirmed that depopulation occurred between 4.2 and 1.4°K and found almost equal intensities at 4.2 and 10°K which is qualitatively consistent with the temperature variation predicted by Eq. (1) with $\Delta = 4.8\ \text{cm}^{-1}$.

We therefore suggest that the conclusions of Kedzie, Lyons, and Kestigian concerning the detailed nature of the site occupied by Fe^{3+} in $CaWO_4$ are questionable. We hope to publish a full account of observations on this resonance when our own investigations of the center are complete.

We wish to thank D. B. Gasson who grew the calcium-tungstate crystals and F. C. Thorpe for his experimental assistance.

*Present address: Royal Radar Establishment, Malvern, Worcestershire, England.

†Present address: J. J. Thomson Physical Laboratory, University of Reading, Reading, Berkshire, England.

[1]R. W. Kedzie, D. H. Lyons, and M. Kestigian, Phys. Rev. 138, A918 (1965).

[2]T. Castner, Jr., G. S. Newell, W. C. Holton, and C. P. Slichter, J. Chem. Phys. 32, 668 (1960).

[3]R. W. Kedzie and M. Kestigian, Appl. Phys. Letters 3, 86 (1963).

[4]E. A. Gere, unpublished memorandum.

MEASUREMENT OF THE ENERGY LOSS OF GERMANIUM ATOMS TO ELECTRONS IN GERMANIUM AT ENERGIES BELOW 100 keV*

C. Chasman, K. W. Jones, and R. A. Ristinen

Brookhaven National Laboratory, Upton, New York

(Received 9 July 1965)

Knowledge of the relative importance of the mechanisms by which moving atoms lose energy in solids is important in studies of radiation-damage effects and in interpretation and design of experiments in certain areas of nuclear physics. Energy losses at high particle velocities are dominated by the effects of collisions which transfer energy to electrons and at low velocities by the effects of collisions which transfer energy to an entire atom. The theory[1,2] for this energy division is especially straightforward if the particle has the same mass and atomic number as the environment in which it stops because then there are only heavy particles of one type. However, no measurements have previously been made to verify the theory for this particularly simple situation in an energy region where the energy losses to electronic and atomic collisions are comparable, although the calculations of Lindhard, Scharff, and Schiott[1] are in good agreement with measurements of particle ranges in various media. It is the purpose of this Letter to present the results of a direct determination of the energy loss to electron collisions of germanium atoms in a germanium environment.

In a previous investigation[3] of the spectra produced by neutron bombardment of a lithium-drifted germanium-radiation detector, it was found that internal-conversion electrons from the decay of the O^+ first-excited nuclear state