

PARAMAGNETIC RESONANCE OF Cu^{2+} AND Ti^{3+} IONS IN BORAX BEADS

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Summary

Paramagnetic resonance absorption has been observed in borax beads containing Cu^{2+} and Ti^{3+} ions. In these cases broad lines were observed near $g = 2$, but hyperfine structure was also apparent in the case of the Cu^{2+} ions, making it possible to estimate average values of the spin Hamiltonian parameters. Analysis of the results indicated that the Cu^{2+} and Ti^{3+} ions occurred in octahedral complexes with very strong axial deformations.

I. INTRODUCTION

The use of coloured glasses for the investigation of structural elements in glasses is very convenient because not only are they amenable to study by optical spectroscopy but also to investigation by means of electron paramagnetic resonance.

Recently papers have been published describing paramagnetic resonance absorption in silicate glasses containing Cu^{2+} (Sands 1955) and Ti^{3+} (Yafaev and Yablokov 1962). In the present paper an analysis is made of the paramagnetic resonance absorption due to similar centres in borate glasses.

Specimens of sodium borate glass containing impurity ions were made in accordance with the method used in the well-known borax bead test. The Cu^{2+} doped samples were obtained by fusing the beads with CuO in the outer (oxidizing) part of the bunsen flame, while the Ti^{3+} ions were obtained in beads by heating them in the strongly reducing conditions in the centre of the flame. The beads were then investigated by means of the superheterodyne paramagnetic resonance spectrometer described by Cavenett (1964).

II. THEORY OF THE Cu^{2+} AND Ti^{3+} SPECTRA

In the classical theory of glasses due to Zachariasen (1932) the oxides in glassy substances were divided into network formers and network modifiers. The network modifiers were held to be uni-, bi-, and trivalent metal ions located in the interstices of the chain network formed by the covalent coordination of the network formers to three or four oxygen atoms.

However, Douglas (1958) has pointed out that although the "network-former-modifier hypothesis can be regarded as a convenient first approximation to be used in relating the physical properties of silicate-type glasses to their chemical compositions . . . , as a second approximation the nature of the chemical bonding of a given atom in a glass must be considered". "In some cases this may be conveniently described in terms of coordination number and ionic field strength."

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Recent optical work by Bamford (1962) has been taken as indicating that as a transition metal M is introduced into a series of $\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3$ glasses with a very high B_2O_3 content, the number of oxygens surrounding the M^{n+} ion is dictated by the B_2O_3 network, but with more soda present, as in borax, the network is broken up and the M^{n+} can then dictate its surroundings, "giving probably a true octahedral $[\text{MO}_6]^{n+}$ complex ion".

However, it should be borne in mind that a true octahedral field would only partially remove the orbital degeneracy of the free ion ground terms in Cu^{2+} and Ti^{3+} , (splitting the fivefold orbital degeneracy of the 2D ground term into a doublet Γ_3 and a triplet Γ_5). Hence in a crystal lattice one would expect Jahn-Teller distortions from true octahedral symmetry, removing entirely the remaining orbital degeneracies of the ground terms (van Vleck 1939; Öpik and Pryce 1957). Thus, as van Vleck (1940) indicated, we might expect a trigonal distortion of an octahedral complex of Ti^{3+} , and Polder (1942) has shown the likelihood of tetragonal distortions in octahedrally coordinated Cu^{2+} . However, in a glass, where long-range disorder is the essence, a similar effect might be caused by distant neighbours.

Hence in both Cu^{2+} and Ti^{3+} doped beads we would expect the individual ions to have low-lying Kramers spin doublets, having axially symmetric paramagnetic resonance spectra. The symmetry axes of the complex ions, and hence of their spectra, would of course be randomly orientated in the glass beads. Accordingly, the appropriate spin Hamiltonians are the space-averaged forms of

$$\mathcal{H}^i = g_{\parallel}^i \beta H_z S_z + g_{\perp}^i \beta (H_x S_x + H_y S_y) + A^i S_z I_z + B^i (S_x I_x + S_y I_y),$$

where S is the effective electronic spin, I is the nuclear spin, and z is the direction of the axial component of the electric field at a given site i .

Sands (1955) has derived formulae which show that if all the sites are similar, apart from their orientation with respect to the magnetic field, this leads to a single line near $g = 2$, whose width and asymmetry depend on the anisotropy of the g factor and whose structure depends on the nuclear hyperfine parameters. Differences between the sites would introduce a dispersion of the spin Hamiltonian parameters and so tend to smear out the observed line.

III. MEASUREMENTS OF THE Cu^{2+} AND Ti^{3+} SPECTRA

All the Cu^{2+} ions had a nuclear spin equal to $3/2$, which, together with the strongly anisotropic spin Hamiltonian parameters, gave a broad asymmetric line with eight distinct peaks. This made it easy to see that the spin Hamiltonian parameters were grouped around the following average values:

$$\begin{aligned} g_{\parallel} &= 2.330 \pm 0.010, \\ g_{\perp} &= 2.040 \pm 0.003, \\ A &= 146(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\ B &= 33(\pm 1) \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

There were no observable temperature variations of these average values between 77 and 300°K.

The Ti^{3+} ions had no observable nuclear spin interactions and consequently it was difficult to obtain estimates of the average values of $g_{\parallel}$ and $g_{\perp}$ (although the asymmetry of the lines suggested that $g_{\perp}$ was greater than $g_{\parallel}$). Hence the lines are described here in terms of an effective g value ($g_{\text{eff.}}$), which denotes the point where the derivative of the absorption line was zero, and the width (ΔH) between the points of maximum and minimum slope. The results obtained at 300°K for a sample whose composition by synthesis was $20\text{Na}_2\text{O} \cdot 40\text{B}_2\text{O}_3 \cdot 5\text{TiO}_2$ were as follows:

$$g_{\text{eff.}} = 1.944 \pm 0.008,$$

$$\Delta H = 67 \pm 4 \text{ Oe.}$$

At 77°K rather different results were obtained, namely,

$$g_{\text{eff.}} = 1.873 \pm 0.008,$$

$$\Delta H = 122 \pm 10 \text{ Oe.}$$

IV. DISCUSSION OF THE Cu^{2+} AND Ti^{3+} SPECTRA

In his discussion of the energy levels of Cu^{2+} in borax glass, Bamford (1962) attributed the visible absorption band near $12\,500 \text{ cm}^{-1}$ to the splitting by the octahedral field of the complex ion of the 2D ground state into a low-lying doublet Γ_3 and a higher triplet Γ_5 . However, this imputation seems arguable (Orgel 1959) and here we follow Polder (1942) in attributing this band to transitions between the orbital singlets F_3 and F_1 produced by a tetragonal distortion acting on the low-lying Γ_3 doublet. The same distortion splits the higher level Γ_5 into two levels labelled F_4 and F_5 . Polder's theory indicates that the g values are given by:

$$g_{\parallel} = 2 \left\{ 1 - \frac{4\lambda}{F_4 - F_3} \right\},$$

and

$$g_{\perp} = 2 \left\{ 1 - \frac{\lambda}{F_5 - F_3} \right\},$$

where λ is the spin orbit coupling constant.

If we take the free ion value of λ and substitute the values of $g_{\parallel}$ and $g_{\perp}$ found previously into the above equations, then we have $F_5 - F_3 = 44\,000 \pm 4000 \text{ cm}^{-1}$ and $F_4 - F_3 = 21\,000 \pm 1000 \text{ cm}^{-1}$. This latter value may prove interesting in the light of the transition near $22\,000 \text{ cm}^{-1}$ observed by Bamford (1962) for which he was unable to offer any explanation. These values also indicate that the terms describing the tetragonal splitting are not small compared with the cubic terms.

In the Ti^{3+} doped beads the asymmetric line shape would also suggest that it was due to the superposition of axially symmetric spectra from many sites randomly orientated with respect to the direction of the magnetic field. But in this case the g values are close to 2, and $g_{\perp}$ is greater than $g_{\parallel}$. Hence according to van Vleck (1940) and Rei (1962) there must be a very strong trigonal field splitting the threefold degeneracy of the Γ_5 ground state of Ti^{3+} given by a true octahedral complex.

Following the discussion given by Yafaev and Yablokov (1962) for Ti^{3+} in silicate glass, we suppose that some Ti^{3+} sites in borax glass with smaller trigonal splittings (and consequently smaller relaxation times and g values) give sharp absorption lines only at low temperatures. This then explains the broadening of the observed lines towards high fields as the temperature is lowered.

We note that, as in the case of Cu^{2+} ions, the paramagnetic resonance absorption of Ti^{3+} ions in borax glass suggests that they occur in octahedral complexes with very strong axial distortions.

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