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EFFECTS OF UNIAXIAL STRESS ON THE OPTICAL SPECTRUM OF $DyVO_4$

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Abstract – Optical absorption spectroscopy is used to investigate the low lying energy levels of $DyVO_4$ under uniaxial stress and magnetic fields at temperatures above and below the co-operative Jahn–Teller transition. The results agree with the molecular field theory of the previous paper using the parameter $\sigma_0 = 64 \pm 4$ kg/mm^2 (which represents the stress of $e_{aa} - e_{bb}$ type required to split the ground state energy levels by 27 cm^{-1} at high temperatures). The behaviour of dilute Dy^{3+} in YVO_4 is studied and predicted from the theory. Deviations from the molecular field theory are found and discussed. Comparison of the results with known elastic constants of $DyVO_4$ indicates that strain coupling dominates the optic mode coupling.

1. INTRODUCTION

IN THIS paper we present an experimental study of the low lying energy levels of trivalent Dy in $DyVO_4$ observed by optical spectroscopy. The results are compared to the theory derived in the accompanying paper [1] which we refer to as I. There are very few studies in the literature on the effects of uniaxial stress on trivalent rare earth energy levels in insulators, e.g. [2, 3]. Trivalent rare earth ions are known to interact very weakly with their environment and therefore the levels are expected to shift very little under stress. In this study, for example, we report results on dilute Dy^{3+} in YVO_4 which appear to be typical. Isolated energy levels move less than 1 cm^{-1} in stresses up to 70 kg/mm^2, whereas a near accidental degeneracy can be split apart to ~ 15 cm^{-1} at the same stresses. Such effects are certainly measurable by optical spectroscopy but are of no particular interest in themselves; they represent the combined effects of elastic constants, internal spring constants and crystal field matrix elements, which cannot be separated in general.

Uniaxial stress experiments in materials which exhibit Jahn–Teller distortions are far more interesting, for such experiments can differentiate between the possible physical mechanisms which could cause the distortions. In most previously studied cases, the distortion temperature is so high that the stress-induced shifts in the energy levels are small compared to the Jahn–Teller stabilization energies, and therefore stress has little effect on the system. By contrast, the recently discovered Jahn–Teller effects in a series of isomorphous crystals, $DyVO_4$ [4], $TbVO_4$ [5, 6], $DyAsO_4$ [7, 8], and $TmAsO_4$ [9], occur in the range of tens of degrees Kelvin, almost an order of magnitude lower than any previously observed co-operative Jahn–Teller effect. For $DyVO_4$ and $TbVO_4$ we have found that stress can interact with and strongly

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influence the Jahn–Teller distortion and the resulting optical line shifts are among the largest ever observed in rare earth insulators.

This paper is divided as follows: in Section 2, we describe experimental techniques; in Section 3, the experimental results; in Section 4 fits of these results to the theory of the previous paper and a summary of our conclusions. A list of the different kinds of experiments reported in this paper is given in Table 1.

2. EXPERIMENTAL TECHNIQUES

Uniaxial stress experiments on single crystals of $DyVO_4$ were performed at a variety of temperatures by immersing the crystals in liquid helium, hydrogen, or nitrogen. The experiments at 77 K in liquid nitrogen made it possible to study $DyVO_4$ in a temperature range where the effects of crystallographic or magnetic ordering were negligible. The experiments from 20·4 to 14·1 K in pumped liquid hydrogen were convenient for studying the especially interesting range just above the distortion temperature of 14·0 K. Experiments at 4·2 to 1·4 K in pumped liquid helium made it possible to investigate the crystal in its fully Jahn–Teller ordered state, both above and below its magnetic Neel temperature of 3·0 K. $TbVO_4$, which undergoes a Jahn–Teller transition at 33 K, is much less convenient to study in its corresponding temperature ranges.

The Jahn–Teller active distortion of $DyVO_4$ is $(e_{aa}-e_{bb})$, where a and b are axes perpendicular to the tetragonal c-axis and happen to be parallel to natural growth faces of the material; b is indistinguishable from a in the absence of distortion. $DyVO_4$ tends to grow in needles along the c-axis, and to prepare the crystals for optical absorption experiments under uniaxial stress, they were cut in slices perpendicular to the c-axis and polished. A uniaxial stress was applied along the a-axis, and a magnetic field could be applied along the b-axis, while light was propagated along the c-axis, as shown in Fig. 1. The natural growth faces along a and b are very even and permit a reasonably homogeneous stress of up to 70 kg/mm² to be applied without cracking the crystals.

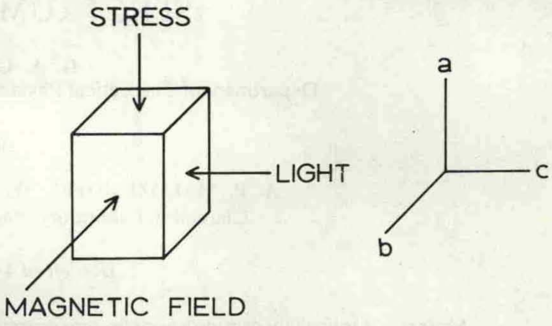

Fig. 1. Typical arrangement of stress and magnetic field for optical absorption experiments on pseudospin flop in $DyVO_4$.

By contrast, $TbVO_4$ distorts with e_{ab} strain; to couple to such a strain, a uniaxial stress would have to be applied at 45° to the natural growth faces. Therefore it is necessary to cut these crystals both in the c-direction and in the basal plane. The difficulty of obtaining truly flat surfaces and hence a homogeneous stress in the crystal is the main reason that we have chosen to study $DyVO_4$ rather than $TbVO_4$.

The stress was applied by means of a piston device developed for these experiments and illustrated in Fig. 2. It has the particular advantages of fitting directly in existing immersion cryostats so that temperature control is easy and a large magnetic field can simultaneously be applied, and also of permitting accurate low stresses to be applied to the crystal without elaborate counterweight arrangements. A moving piston, pulled upwards by an inner stainless steel wire, pressed the sample from below against the fixed piston. Bellows with compressed air of variable pressure are set on top of the cryostat to provide the necessary force for the pistons. Forces due to bellows distortion can be reduced to less than 100 g by adjusting the bellows to the zero position for any given air pressure. Friction in the packed grease seal and in the pistons is less than 20 g in the low