Strain-Induced Splitting of the ^2E State of V^{2+} in MgO

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The 11498-cm^{-1} fluorescent line of V^{2+} in MgO is split and shifted by uniaxial stress. As has previously been observed for Cr^{3+} in MgO, the splitting is in very good agreement with a simple point charge model using the Hartree-Fock wave function of the free ion. This is taken to show that the agreement for Cr^{3+} is not purely coincidental.

INTRODUCTION

IN a crystal field of cubic symmetry, some of the energy levels of an ion of the d^3 configuration are orbitally degenerate. This degeneracy is, in general, lifted by a field of lower symmetry. Schawlow *et al.*[1] (hereafter referred to as I), studied the strain-induced splitting of the sharp fluorescence line of Cr^{3+} in MgO, which is due to the $^2E \rightarrow {}^4A_2$ transition. The ^2E state is split by a fraction of a cm^{-1} by a uniaxial stress of 20 kg/mm^2; the $^4A_2$ ground state is split only in third order by an amount too small to measure optically. In I the splitting by stress in the [100], [111], and [110] directions (corresponding, respectively, to tetragonal distortion, trigonal distortion, and a combination of the two) was found to be in excellent quantitative agreement with the predictions of a point charge model in which Coulomb interactions only are considered. In view of the doubt which has been cast on the validity of this model,[2] this is a very surprising result. A further surprising feature of the results in I is that good agreement is obtained by using the Hartree-Fock wave function of the free Cr^{3+} ion, whereas a more expanded wave function is required in the closely related case of Cr^{3+} and other ions in Al$_2$O$_3$.[3,4] The question therefore arises whether the agreement is coincidental, dependent as it is on the choice of wave function.

It has recently been shown[4,5] that the energy level scheme of the V^{2+} ion in MgO and Al$_2$O$_3$ is qualitatively similar to that of the isoelectronic Cr^{3+}. The d wave function of the free V^{2+} ion is about 20% larger in radial extension than that of Cr^{3+}.[6] If the agreement of theory and experiment in the case of Cr^{3+} were coincidental, due to cancelling errors in the choice of model and the choice of wave function, the same choices should not give agreement in the case of V^{2+}.

For this reason the measurements of I have been repeated on MgO:V^{2+}. The results agree even better with the theory than do those for Cr^{3+}. However, the difficulty noted in I, that the cubic field parameter Dq

is given quite wrongly by the theory, remains, as does the difficulty of explaining the trigonal field parameters in Al$_2$O$_3$. It appears, however, that the case of V^{2+} and Cr^{3+} in strained MgO does provide a genuine (and rare) example of the applicability of a point charge model in which wave functions are calculated *a priori* and not fitted to experiment.

EXPERIMENTAL DETAILS

The fluorescence of V^{2+} in MgO has already been described.[4] Specimens a few mm long and of about 5 mm^2 cross section were cut with their long axes parallel to [100], [111], and [110] directions from a piece of MgO containing about 0.01% V^{2+}. In the absence of a stress this material shows a single fluorescent line at 11 498 cm^{-1}, 0.3 cm^{-1} wide at 77°K. A stress of up to 22 kg/mm^2, parallel to the specimen axis, was applied in an apparatus similar to that described in I. The fluorescence was observed with a Jarrell-Ash 1.8-m scanning spectrometer.

Under stress the line splits into two components. Figure 1 shows the positions of the fluorescent peaks as a function of stress in the [100], [111], and [110] directions. Table I shows the observed splittings, the mean shifts, and the polarizations of the components. The theoretical splittings are calculated in the next section. Agreement between experiment and theory is almost perfect.

DISCUSSION

The splittings of a $t_2^3\,{}^2E$ state by uniaxial stresses applied, respectively, along the [100], [111], and [110] directions are given by[1]

$$\Delta_{100} = \frac{-2P}{C_{11}-C_{12}}\left[b^2\left\{\frac{3.41\langle r^2\rangle}{R^3}+\frac{1.78\langle r^4\rangle}{R^5}\right\}\right.$$
$$\left.+bc\left\{\frac{6.82\langle r^2\rangle}{R^3}-\frac{4.22\langle r^2\rangle}{R^5}\right\}\right],$$

$$\Delta_{111} = \frac{-P}{3C_{44}}\frac{\zeta}{W(t_2^3\,{}^2T_2)-W(t_2^3\,{}^2E)}\left[\frac{6.82\langle r^2\rangle}{R^3}-\frac{7.80\langle r^4\rangle}{R^5}\right],$$

$$\Delta_{110} = \left(\tfrac{1}{4}\Delta^2{}_{100}+\tfrac{1}{3}\Delta^2{}_{111}\right)^{1/2}.$$

Here Δ_{100}, Δ_{111}, and Δ_{110} are the splittings in atomic

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[4] M. D. Sturge, Phys. Rev. 130, 639 (1963).
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[6] R. E. Watson, Massachusetts Institute of Technology, Solid State and Molecular Theory Group, Technical Report No. 12, 1959 (unpublished).

TABLE I. Strain-induced splittings of the ^2E state in MgO: V^{2+}.

Stress direction	Splitting $\times 10^{10}$ (cm^{-1}|dyn|cm^2) Obs	Calc	Polarization[a] Obs	Calc	Shift $\times 10^{10}$ (cm^{-1}|dyn|cm^2) Obs
[100]	10.3 ±0.2	10.5	σ 1.7	3	2.55±0.1
			π 0.3	0	
[111]	1.34±0.1	1.6	σ 0.5	0.6	2.5 ±0.1
			π 2.0	3	
[110]	5.75±0.2	5.35	σ^b 0.25	0.01	2.9 ±0.2
			π 2.0	3.6	

[a] The number represents the intensity ratio of the lower to the upper component in given polarization. As the transition is magnetic dipole, σ means $H \perp$stress and π, $H \|$stress.
[b] $H \| [001]$.

units (a.u.), b and c are configuration mixing coefficients defined in I, C_{ij} are the stiffness constants of the host lattice, ζ is the spin-orbit splitting of the central ion, $W(\Gamma)$ is the energy of the state Γ, R is the metal-oxygen distance in a.u. and $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are averages over the central ion wave function. In I, R is assumed to be the Mg-O spacing (3.97 a.u.) and $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are calculated from Watson's Hartree-Fock wave functions for the free Cr^{3+} ion. We follow the same procedure for V^{2+}. The configuration mixing coefficients b and c are calculated with the aid of Sugano and Peter's[7] program for the energy levels of a d^3 ion, using the parameters determined in Ref. 4. We find $b=0.14$ and $c=0.089$, not significantly different from the values for Cr^{3+}. Watson's wave function for V^{2+} give $\langle r^2 \rangle / R^2 = 0.130$, $\langle r^4 \rangle / R^4 = 0.038$, corresponding to an ion about 20% larger than Cr^{3+}. From Ref. 4 we have $\zeta \doteq 120$ cm^{-1} and $W(t_2^3 \, ^2T_2) - W(t_2^3 \, ^2E) = 5200$ cm^{-1}. The calculated splittings are listed in Table I. The uncertainties in the theoretical values (due to uncertainties in the parameters used) are at least as great as the experimental errors.

The shift in the mean position of the line is due to the isotropic component of the strain, which is $P/(C_{11}+2C_{12})$ for uniaxial stress, regardless of direction. The shift for V^{2+} in MgO is slightly less than that for Cr^{3+}. Minomura and Drickamer[8] have measured the positions of the principal absorption bands of MgO: Cr^{3+} as function of hydrostatic pressure (for which the strain is $3P/(C_{11}+2C_{12})$) and find $d(Dq)/dp=1.8$ cm^{-1}/kbar, $dB/dp \doteq -0.17$ cm^{-1}/kbar. Numerical diagonalization of Tanabe and Sugano's matrices[9] gives (for $B=650$, $C/B=4$, $Dq=1600$)

$$\frac{\partial}{\partial(Dq)}W(^2E)=0.4, \quad \frac{\partial}{\partial B}W(^2E)=17.5,$$

whence we find, for uniaxial stress,

$$\frac{d}{dp}W(^2E) = -7 \times 10^{-10} \text{ cm}^{-1}|\text{dyn}|\text{cm}^2.$$

[7] S. Sugano and M. Peter, Phys. Rev. 122, 381 (1961).
[8] S. Minomura and H. G. Drickamer, J. Chem. Phys. 35, 903 (1961).
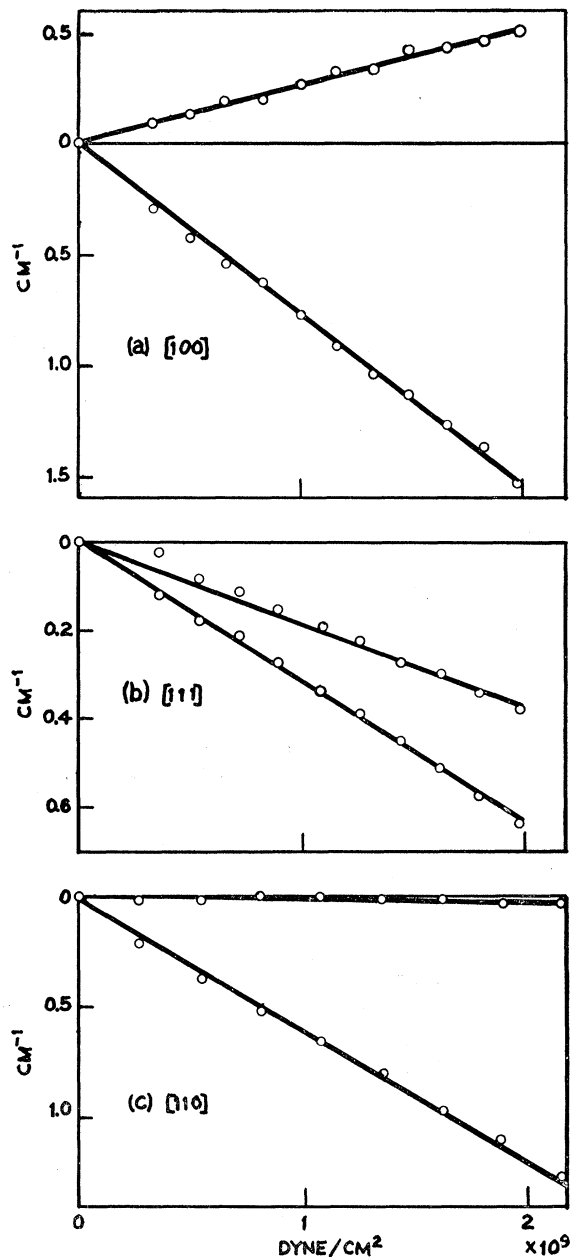[9] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753 (1954).

FIG. 1. Position of fluorescent peaks of MgO: V^{2+} (measured from the position at zero stress) as a function of stress. (a) Stress parallel to [100] direction. (b) Stress parallel to [111] direction (note change in vertical scale). (c) Stress parallel to [110] direction.

This is more than twice the observed shift for Cr^{3+}.[1] The discrepancy may be due to C/B changing with pressure [$W(^2E)$ is more sensitive to C than to B]. It seems more likely, however, that Minomura and Drickamer's value of dB/dp is incorrect (it is calculated from the very small change in separation of the broad $^4T_2$ and $^4T_1$ bands). Assuming the contribution of $d(Dq)/dp(+2.5 \times 10^{-10}$ cm$^{-1}|$dyn$|$cm$^2)$ to be correct,

the observed shift for Cr^{3+} (-2.8×10^{-10}) gives dB/dp $=-0.09$ cm^{-1}/kbar (for hydrostatic pressure), i.e., $l/B\ dB/dl\doteq+0.75$ (l is a unit cell dimension). The figure for V^{2+} is presumably about the same.

CONCLUSIONS

The experimental splittings agree so well with theory that one is tempted to conclude that the point charge model is valid for V^{2+} and Cr^{3+} ions in MgO, and that the Hartree-Fock wave function of the free ion is a good approximation to the wave function in the crystal. However, as pointed out in I, the model (using this wave function) gives quite the wrong value for the cubic field parameter Dq. Presumably this discrepancy is due to covalency effects,[2] which for some reason are not important, or cancel out, in the noncubic crystal field induced by strain. Furthermore, in the closely related case of $(3d)^3$ ions in Al_2O_3, the model gives the wrong sign for the trigonal field parameter.[3,4] This has been explained by McClure[3] as being due to a shift of the ion along the C_3 axis, but even so he has to assume a wave function substantially more extended than that of the free ion.[10] Either Al_2O_3 is so much more covalent than MgO that the wave functions of a $(3d)^3$ ion are quite different in the two lattices, or the geometrical arrangement of ions in Al_2O_3 is substantially modified by the presence of the impurity. The similarity of the spectra in the two lattices inclines one to believe the latter alternative.

[10] However large a shift along the C_3 axis one permits, it appears to be impossible to obtain a trigonal field parameter of the correct sign using free ion wave functions (at any rate from the nearest neighbor potential).

Temperature Dependence of the Debye Temperatures for the Thermodynamic Functions of Alkali Halide Crystals*

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The temperature dependence at constant volume of the experimental Debye temperatures for the entropy, the thermal energy, and the heat capacity at constant volume of potassium chloride, bromide and iodide, and of sodium iodide is analyzed over a wide range of temperature $(30°K \lesssim T \lesssim 270°K)$ taking into account anharmonic effects. The inclusion of the leading anharmonic contribution into the quasiharmonic expansions of the Debye temperatures for the three thermodynamic functions allows one to reproduce over the entire temperature range the curves for the entropy, which are the most accurate, and also those for the thermal energy. The curves for the heat capacity are reproduced at the lower temperatures, and their proper course is indicated at the higher temperatures, where they are affected by sizeable uncertainties. The different form of the temperature dependence of the Debye temperatures for the three functions in the quasiharmonic temperature range, and the different magnitude of the effect of the anharmonic contributions on the Debye temperatures for the three functions at high temperature, are clearly illustrated. Refined values are obtained in each salt for the geometric mean of the vibrational frequencies and for the first few moments of the vibrational spectrum. The good agreement between the values of the moments derived from the three functions confirms the good validity of the quasiharmonic description of the thermal free energy at the lower temperatures. Values are obtained for the anharmonic contributions to the thermodynamic functions at high temperature.

1. INTRODUCTION

THE temperature dependence of a thermodynamic function of an insulator at constant pressure is commonly described by an appropriate Debye temperature, which is, in general, temperature-dependent. A preliminary report of this work has been given in Ref. 1. For a cubic insulator the observed temperature dependence of a Debye temperature at constant pressure can be easily converted into the dependence at constant volume by correcting for the effect of thermal expansion. The temperature dependence of a Debye temperature at constant volume is in turn a quantity on which one can make some general theoretical predictions.[2] The expansion of the quasiharmonic expression for a thermodynamic function in inverse powers of the

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