melting point curve of Kennedy could easily join with the II-"liquid" curve in Fig. 6.

If it is indeed liquid, it is interesting to note that barium is then a liquid at temperatures and pressures where even helium should be solid.

The solid II phase is obviously denser than solid I (the transition is probably bcc-fcc). The liquid phase must be denser than solid II. It should be noted, however, that solid III is slightly denser than the liquid. The transition II-III must then take place with a large volume decrease. It may well involve the promotion of an electron from the 6*s* shell to a band arising from the atomic 5*d* state, in analogy to the transition observed in cesium by Bridgman.[3]

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Evidence for Covalent Bonding from Electron Spin Resonance Spectra of Some Rare-Earth Ions in Single Crystals of Calcium Oxide*

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Investigations of electron spin resonance (ESR) spectra of Yb^{3+} and Dy^{3+} in the cubic crystal field of calcium oxide show *g* factors which are smaller than the calculated *g* factors. It is shown that covalent bonding through the effect of the orbital reduction factor can explain these discrepancies. It is found that $(1-k)$ is about 0.04, much smaller than found in the iron group, but larger than that found for rare earth ions in the crystal field of CaF_2. From the ESR spectra of Dy^{3+} and Er^{3+} it is inferred that the fourth-order potential B_4 is at least 200 times larger than the sixth-order potential B_6.

RECENT investigations of rare-earth ions in the calcium oxide lattice have been confined to the *S*-state ions, Eu^{2+} and Gd^{3+}.[1–4] In both these cases, the spherically symmetrical *S*-state wave functions have given rise to intense cubic spectra, although much weaker noncubic spectra were observed in Gd^{3+}.[4] As CaO is the first lattice in which rare earths have been substituted into a site of octahedral symmetry, it is of great interest to extend the investigation to non-*S*-state ions, in which the relative strengths of the crystalline field potentials may be obtained more directly. In this note we discuss the results of experiments on single crystals of CaO containing Yb^{3+}, Dy^{3+}, and Er^{3+}.[5] It will be shown that covalent bonding must be taken into account to explain the experimentally measured *g* values for Yb^{3+} and Dy^{3+}.

Yb^{3+}, $4f^{13}$, $^2F_{7/2}$

This was the simplest system investigated, with an electronic configuration consisting of a single hole in the 4*f* shell. In the pure octahedral field of CaO, the Γ_6 level, with a theoretical *g* value of 2.667, should lie lowest for all values of the crystalline field potentials.[6]

At 20°K, an isotropic spectrum was observed with $g=2.585\pm0.003$, $A(171)=(578\pm5)$ G $=(698\pm6)\times10^{-4}$ cm^{-1}. The measurements were made over the frequency range 8.2 to 11.2 kMc/sec. No significant deviations of the *g* factor were found in this frequency interval. The linewidth (between points of half-maximum intensity) was approximately 12 G, enabling accurate measurement of the hfs of the odd isotope $^{171}Yb(I=\frac{1}{2})$ only.

A striking feature of these results is the 3% reduction of the experimental *g* value, when compared with the theoretical value for the Γ_6 level. This discrepancy provides strong evidence for the existence of covalent bonding in the rare-earth ions. Bleaney[7] has come to a similar conclusion in order to explain the smaller discrepancy in the *g* value found for the isoelectronic Tm^{2+} in CaF_2.[8,9] The experimental values can be explained by introducing the orbital reduction factor. In the case of octahedral symmetry the calculation is relatively simple because there is no admixture from the excited $J=\frac{5}{2}$ level since this level does not contain the Γ_6 representation. When the factor *k* is included, the *g* value of the Γ_6 level becomes $(7/3)g_J'$, where g_J' (the

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reduced value of the Landé g factor, g_J) is given by

$$g_J'=g_J-(1-k)\left[\frac{J(J+1)-S(S+1)+L(L+1)}{2J(J+1)}\right]$$
$$=8/7-(6/7)(1-k).$$

If experimental and theoretical values are now equated, we have $\Delta g=0.082\pm0.003=(7/3)(g_J-g_J')=2(1-k)$. Therefore,

$$(1-k)=0.041\pm0.001(5).$$

This value is considerably greater than that of 0.009 ±0.001 deduced for Tm^{2+} in[7] CaF_2 but smaller than the value of about 0.2 found for iron group elements in crystals of octahedral symmetry.[10] This is consistent with the general picture of greater covalency in the oxide systems than in the fluoride systems.

The hyperfine structure does not give sufficient information regarding covalent bonding since the contribution of unpaired s electrons is not known in the crystal of CaO. However, the relation $A_{\Gamma_7}/A_{\Gamma_6}\sim g_{\Gamma_7}/g_{\Gamma_6}$, where the A and g values are taken from the CaF_2 and the CaO data respectively, is found to be correct within a few percent.

Dy^{3+}, $4f^9$, $^6H_{15/2}$

If the crystalline field in the spin Hamiltonian be represented by $H=B_4(O_4^0+5O_4^4)+B_6(O_6^0-21O_6^4)$, then the graphs of Lea *et al.*[6] show that the Γ_6 level ($g=6.67$) lies lowest if $|B_4/B_6|\gg 190$, with B_4 of opposite sign to B_6. For other ratios the Γ_7 level ($g=7.55$) lies lowest in an octahedral field. The theoretical g value is calculated assuming no admixtures from other excited states.

At 20°K, a very broad isotropic line of half-width approximately 50 G was observed with $g=6.60\pm0.05$. Three sets of axial spectra with mutually perpendicular tetragonal axes were also observed with $g_{\parallel}=3.09\pm0.02$, and $g_{\perp}\sim15$. The line intensities of the latter spectra decreased rapidly as the steady magnetic field was rotated out of the parallel orientation. Because of the large linewidth, hyperfine structure was not observed.

The g value of the dominant isotropic line is close to that of the Γ_6 level. The low value indicates that there is present appreciable covalent bonding. Here, in view of the large experimental error, its magnitude may be estimated only approximately. If the effects of admixtures from excited states are neglected, we may calculate the orbital reduction factor as before, i.e.,

$$\Delta g=0.07\pm0.05=5(g_J-g'_J)=(10/3)(1-k)$$
$$(1-k)=0.02\pm0.01(5),$$

an answer which is of the same order of magnitude as that obtained for Yb^{3+}.

Er^{3+}, $4f^{11}$, $^4I_{15/2}$

The graphs of Lea *et al.*[6] indicate that the $\Gamma_8^{(1)}$ level lies lowest if $B_4/B_6\geq320$: otherwise, the Γ_7 level ($g=6.80$) is lowest.

At 20°K, several sets of spectra were observed, with intensities divided roughly equally between cubic and tetragonal sites. The single intense cubic line showed turning points along the principal crystal axes, and the measured g values in these directions were

$$g_{100}=4.84\pm0.01,$$
$$g_{110}=3.85\pm0.01,$$
$$g_{111}=3.50\pm0.01.$$

The measured linewidths were approximately 25 G. Three sets of axial spectra with mutually perpendicular tetragonal axes were observed with $g_{\parallel}=4.730\pm0.005$, $g_{\perp}=7.86\pm0.01$, and linewidth approximately 16 G. No changes were observed in the spectra at 4.2°K.

The cubic line appears to be almost certainly one member of the $\Gamma_8^{(1)}$ quartet. Rough agreement with the experimental g values may be obtained by setting $B_4/B_6\simeq350$ (or $x=0.6$ in Ref. 6). The principal g values for the $|S_z'=\pm\frac{3}{2}\rangle\rightarrow|S_z'=\pm\frac{1}{2}\rangle$ transitions are then $g_{100}=4.9$, $g_{110}=3.8(5)$, $g_{111}=3.5$. The theory would, however, require the presence of a line of similar intensity, corresponding to the $|\frac{1}{2}\rangle\rightarrow|-\frac{1}{2}\rangle$ transition, with principal g values $g_{100}=2.3$, $g_{110}=4.3$, $g_{111}=4.9$. Careful measurements have revealed the presence of a very broad weak line with $4<g_{110}<5$ and $g_{100}<1.5$. Before such an explanation can be considered valid it is necessary both to obtain better agreement between experimental and theoretical g values, and also to find a mechanism which would broaden the $|\pm\frac{1}{2}\rangle\leftrightarrow|-\frac{1}{2}\rangle$ transitions, but not the $|\pm\frac{3}{2}\rangle\leftrightarrow|\pm\frac{1}{2}\rangle$ transitions.

From the experiments discussed above, it is possible to form the following conclusions:

(a) That the substitution of trivalent rare-earth ions into sites of either cubic or tetragonal symmetry takes place.

(b) That the orbital reduction $(1-k)$ is of the order of a few percent for rare-earth ions in octahedral CaO and considerably larger than in CaF_2. The effect of covalent bonding, therefore, has to be taken into account in the evaluation of nuclear moments.

(c) That the fourth-order potential B_4 is at least about 200 times greater than the sixth-order potential B_6 and is of the opposite sign to that of B_6.

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[10] For a summary on the effect of covalent bonding on iron group elements, see W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960).