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The Crystal and Magnetic Structures of Ca_2YRuO_6 and the Electronic Properties of the Series $M_2^{2+}X^{3+}Ru^{5+}O_6$ (M = Ca, Sr, Ba; X = La, Y)

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Profile analysis of constant-wavelength powder neutron diffraction data has been used to refine the crystal structure of the ordered perovskite Ca_2YRuO_6. The material is monoclinic (space group $P2_1/n$) with a disordered arrangement of calcium and yttrium on the A site and one of the B sites, such that the formula is best written as $Ca_{1.43}Y_{0.57}[(Ca_{0.57}Y_{0.43})Ru]O_6$. Low-temperature neutron diffraction experiments showed that the material is a Type I antiferromagnet at 2.5 K with an ordered magnetic moment of $1.2(1)\mu_B$ per Ru^{5+}. It is suggested that the dominant factor in determining the electronic properties of the series $M_2^{2+}X^{3+}Ru^{5+}O_6$ (M = Ca, Sr, Ba; X = La, Y) is the Ru–Ru separation distance.

Introduction

There are many well-known transition metal oxides, for example, MnO, in which the outer, unpaired d-electrons are effectively localized at a cation site. These materials are expected to be electronic insulators and to undergo a transition to a magnetically ordered state at low temperatures. At higher temperatures, their magnetic susceptibilities will follow the Curie–Weiss Law, with the effective magnetic moment being given by the spin-only formula, $\mu_{eff} = \sqrt{4S(S+1)}$, possibly modified for some orbital contribution. In the case of the octahedrally coordinated Ru^{5+} : $4d^3$ ions discussed in this paper, we would expect any orbital contribution to reduce the effective magnetic moment from the spin-only value of $3.87\mu_B$. There is another group of transition metal oxides, for example TiO, in which the outer d-electrons are itinerant. Consequently, these compounds are metallic conductors which exhibit temperature-independent Pauli paramagnetism. Clearly, any attempt to analyze the magnetic susceptibility of such a material in terms of Curie–Weiss behavior will lead to an excessively large (i.e., infinite) value for both the effective magnetic moment and the Weiss constant, θ. Whether the electrons in a particular material are localized or itinerant depends upon the relative strengths of the intraatomic electron correlations and the interatomic electron interactions. If the former are much greater than the latter we expect localized electron behavior; if the interatomic interactions are the stronger, then the system will be metallic (*1*). This paper concludes a series describing the

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family of ordered perovskites $M_2^{2+}X^{3+}Ru^{5+}O_6$ (M = Ca, Sr, Ba; X = La, Y) in which the two competing interactions are of approximately equal strengths. This was first shown to be the case in Ba_2LaRuO_6 and Ca_2LaRuO_6 (*2*) with the experimental evidence coming from two sources; magnetic susceptibility measurements and low-temperature neutron diffraction studies. The former revealed unusually high values for both the effective magnetic moment in the paramagnetic phase ($>4\mu_B$), and the ratio of the Weiss temperature to the Néel temperature ($\theta/T_N > 10$). Both of these observations are characteristic of a material which is intermediate between a localized-electron Curie–Weiss system and an itinerant-electron Pauli system. The neutron studies demonstrated that the dominant superexchange interaction was that between nearest-neighbor cations, consistent with the presence of half-filled t_{2g} orbitals and empty e_g orbitals on the Ru^{5+}: $4d^3$ ions in a pseudoface-centered cubic array. The feature of the neutron results which pointed to a very strong interatomic interaction, yet with the retention of an intraatomic interaction sufficiently strong to maintain antiferromagnetic ordering, was the much reduced value ($\sim 1.9\mu_B$) of the ordered magnetic moment on each Ru^{5+} ion. A reduction from the free ion value of the magnetic moment ($3\mu_B$) due to the covalent transfer of spin from the metal to the oxide ions along the superexchange pathway occurs in all antiferromagnets, but not to the extent found in Ba_2LaRuO_6 and Ca_2LaRuO_6. The ordered cation magnetic moment for Cr^{3+}: $3d^3$ in $LaCrO_3$, for example, is $2.8\mu_B$ (*3*). Thus, although these materials have nonmetallic electrical conductivities (*4*), there is some evidence to suggest that the interatomic interactions are sufficiently strong to render the localized-electron model inappropriate. However, although the ordered magnetic moment is likewise reduced in Sr_2YRuO_6 (*5*) the susceptibility data are consistent with a localized $4d^3$ electron configuration at the Ru^{5+} ions. It is thus apparent that the system M_2XRuO_6 lies close to the borderline between localized and itinerant electron behavior. Our aim is to determine the relative importance of the various factors which influence the strengths of the electronic interactions and to this end we have determined the crystal and magnetic structure of Ca_2YRuO_6, thus increasing the data available for the discussion of the effects of unit-cell volume, the acidity of M^{2+} and crystallographic distortions which can be found in this paper.

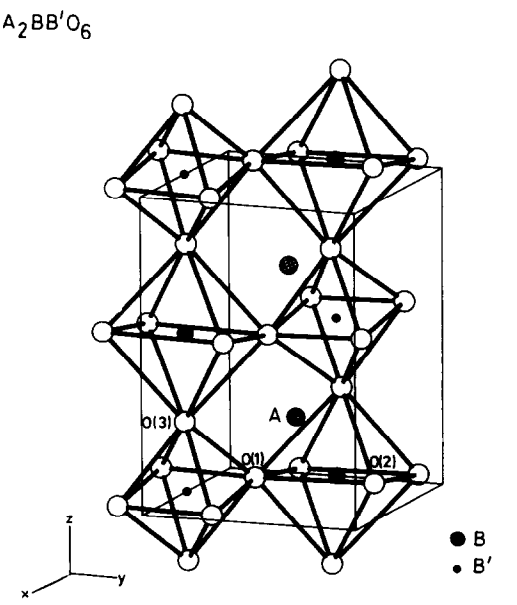

FIG. 1. The unit cell for the ordered, distorted perovskite $A_2BB'O_6$ showing the crystallographically distinct atoms.

Ca_2YRuO_6 was first prepared by Greatrex *et al.* (*4*). Their powder X-ray diffraction data indicated orthorhombic symmetry with an ordered, alternating arrangement of ruthenium and yttrium on the B sites of the perovskite-related unit cell drawn in Fig. 1. Mössbauer and magnetic susceptibility measurements indicated that the material orders antiferromagnetically with T_N = 16 K and θ = −176 K, giving a value of θ/T_N too large to be explained by a localized electron model, as is the value of $4.02\mu_B$

found for the effective magnetic moment at high temperature. There is therefore good reason to believe that Ca_2YRuO_6 must be treated as a strongly correlated, itinerant-lectron system similar to Ca_2LaRuO_6 and Ba_2LaRuO_6.

Experimental

A polycrystalline sample of Ca_2YRuO_6 was prepared by firing a pelleted stoichiometric mixture of calcium carbonate, yttrium sesquioxide, and ruthenium dioxide in air at 820°C for 6 hr and then for 5 days at 1100°C with regular grinding and repelleting. The reaction was carried out in a platinum crucible. The powder X-ray diffraction pattern of the product could be indexed using unit-cell parameters close to those reported previously (*4*). Analytical electron microscopy showed that the sample contained traces of a second phase, but it was present in too small a quantity to be identified in the X-ray pattern. Constant-wavelength powder neutron diffraction data were collected at room temperature and 2.5 K by operating the diffractometer Dla at ILL Grenoble at a wavelength of 1.909 Å with a monitor count of 3.94×10^4 (2.5 K) or 2.45×10^4 (room temperature) neutrons per 0.05° 2θ-step.

Results

The neutron diffraction patterns were analyzed by the profile analysis technique (*6*). The low-angle asymmetric peaks were excluded from the calculations which consequently analyzed 252 reflections in the angular range $30° < 2\theta < 140°$ using the scattering lengths: $b_{Ca} = 0.47$, $b_Y = 0.79$, $b_{Ru} = 0.73$ and $b_O = 0.58 \times 10^{-14}$ m. The background level was interpolated between regions where no Bragg peaks were observed.

The room-temperature data were used to refine the crystal structure of Ca_2YRuO_6 in the monoclinic space group $P2_1/n$. Rietveld analysis refined the unit-cell parameters to the values: $a = 5.5239(1)$, $b = 5.7770(1)$, $c = 7.9637(2)$ Å, $\beta = 90.23(1)°$. Here and throughout this paper the number in brackets is the estimated standard deviation in the last figure. Satisfactory agreement between the observed and calculated diffraction patterns was only obtained when the calcium and yttrium were allowed to disorder over the A site and one of the B sites in the ordered perovskite structure. The final occupation numbers and atomic parameters after refinement of 17 atomic parameters and 9 profile parameters are presented in Tables I and II. All the A-site cations were constrained to have the same isotropic temperature factor, as were the calcium and yttrium on the B site and the three oxygen atoms. The final observed, calculated, and difference profiles, corresponding to a weighted profile R-factor of 8.9%, are shown in Fig. 2. The most interesting bond lengths and bond angles are given in Table III.

TABLE I

ATOMIC POSITIONS AND ISOTROPIC TEMPERATURE FACTORS FOR Ca_2YRuO_6 AT ROOM TEMPERATURE

Atom	x	y	z	B (Å^2)
A site	0.5150(4)	0.5584(3)	0.2534(4)	1.25(6)
B site (Ca/Y)	0	½	0	0.10(9)
Ru	½	0	0	0.65(5)
O(1)	0.2129(4)	0.1797(4)	−0.0536(3)	0.81(2)
O(2)	0.3260(4)	0.7176(4)	−0.0661(3)	0.81(2)
O(3)	0.3860(3)	−0.0490(3)	0.2314(3)	0.81(2)

TABLE II

OCCUPATION NUMBERS FOR THE A-SITE AND DIAMAGNETIC B SITE IN Ca_2YRuO_6

Site	% Ca	% Y
A site	71.8(1.5)	28.2(3.5)
B (Ca/Y)	56.5(3.5)	43.5(4.6)

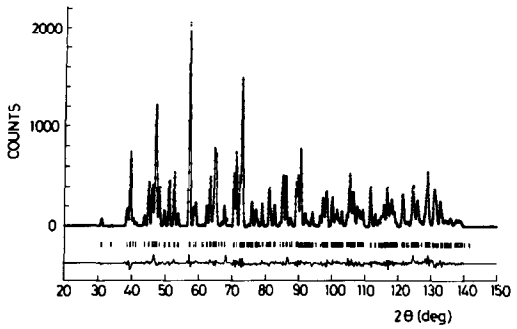

FIG. 2. The observed, calculated, and difference profiles for Ca_2YRuO_6 at room temperature. Reflection positions are marked.

The data collected at 2.5 K indicated that the sample was antiferromagnetically ordered at this temperature, but profile analysis showed that the room-temperature crystal structure was preserved in the magnetic phase. The strongest magnetic reflection occurred at $2\theta \sim 14°$ and was therefore too asymmetric to be used in profile analysis. The remaining magnetic peaks were very weak and we therefore chose to estimate the ordered magnetic moment by considering only the intensity of the low-angle peak. This method also removes the problem of fitting a form factor for the Ru^{5+} ion because at $2\theta \sim 14°$ it is a good approximation to assume a value of unity. The magnetic moment was calculated by comparing the intensity of the magnetic peak to those of the nuclear peaks, having first indexed the magnetic reflection and determined the type of antiferromagnetic ordering involved. The low-angle peak indexed as the {100} reflection in the pseudoface-centered cubic $\sqrt{2}a \times \sqrt{2}b \times c$ unit cell drawn in Fig. 3. This is consistent with the occurrence of Type I antiferromagnetism (*7*), as was found in Sr_2YRuO_6 and Ca_2LaRuO_6. In this type of magnetic structure, ferromagnetic (100) sheets are coupled antiferromagnetically along [100] with the spins lying in the (100) planes. The ordered magnetic moment was then calculated to be $1.2(1)\mu_B$ per Ru^{5+} ion. It should be noted that we have assumed that Ca_2YRuO_6 has a collinear magnetic structure. There may be noncollinear structures that would give the same powder diffraction pattern in the low-angle region.

Discussion

The most interesting feature of the crystal structure of Ca_2YRuO_6 is the disordered arrangement of the calcium and yttrium atoms, which can best be represented by writing the formula as $Ca_{1.43}Y_{0.57}[(Ca_{0.57}Y_{0.43})Ru]O_6$. Our previous studies (*2*, *5*) on Ca_2LaRuO_6, itself better written as CaLa$[CaRu]O_6$, and Sr_2YRuO_6 have found values of ~2.27 and 2.20 Å, respectively, for the metal–oxygen bond lengths at the diamagnetic B site. The values found in the present study lie between these two ex-

TABLE III

BOND LENGTHS (IN Å) AND BOND ANGLES (IN DEG.) IN Ca_2YRuO_6 AT ROOM TEMPERATURE

Ru–O(1) 1.941(4)	$B_{Ca/Y}$–O(1) 2.235(4)
Ru–O(2) 1.964(4)	$B_{Ca/Y}$–O(2) 2.260(4)
Ru–O(3) 1.970(3)	$B_{Ca/Y}$–O(3) 2.245(3)
O(1)–Ru–O(2) 90.8	O(1)–$B_{Ca/Y}$–O(2) 90.3
O(2)–Ru–O(3) 91.5	O(2)–$B_{Ca/Y}$–O(3) 94.1
O(1)–Ru–O(3) 91.1	O(1)–$B_{Ca/Y}$–O(3) 93.9

Note. Estimated standard deviation in bond angles is 1°.

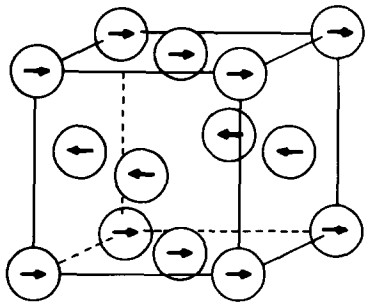

FIG. 3. The Type I magnetic unit cell of Ca_2YRuO_6. Only ruthenium ions are shown.

tremes and are thus consistent with the disordered cation arrangement. The observed arrangement presumably represents a compromise between two competing effects; first, the tendency for the more highly charged Y^{3+} ions to occupy the A site with its higher coordination number, and second, the tendency for the smaller ions, again Y^{3+}, to occupy the smaller, six-coordinate B site. The octahedron around the diamagnetic B site is significantly distorted with oxygen–oxygen distances ranging from 3.058 to 3.274 Å, whereas that around the Ru^{5+} is more regular (2.740 to 2.819 Å), as was found to be the case in the M_2XRuO_6 compounds studied previously (*2, 5*). The distortions reduce the coordination number of the A site from twelve to eight. The high-temperature factor of this site may be due to the disordered cation arrangement found there.

The Type I antiferromagnetism found in Ca_2YRuO_6 is consistent with a strong nearest-neighbor Ru–O–O–Ru superexchange interaction along the face-diagonal of the pseudocubic unit cell and a negligible next-nearest-neighbor interaction along the cell edge. Only in Ba_2LaRuO_6 (*2*) has this latter interaction been shown to be significant, presumably because, of all the diamagnetic B-site cations studied, only La^{3+} has energetically accessible orbitals which can take part in a superexchange interaction. The ordered magnetic moment ($1.2\mu_B$) found in Ca_2YRuO_6 is considerably lower than that found in Ba_2LaRuO_6, Ca_2LaRuO_6, or Sr_2YRuO_6 ($\sim 1.9\mu_B$), thus implying, in conjunction with the susceptibility data, that the electrons in this material are only very weakly correlated. We will now consider the various factors which may determine the extent of electron delocalization in these compounds in order to ascertain their relative importance. Ba_2LaRuO_6 will be omitted from this discussion in order that we may consider the three materials CaLa[CaRu]O_6, Sr_2[YRu]O_6, and $Ca_{1.43}Y_{0.57}$[$(Ca_{0.57}Y_{0.43})$Ru]O_6 which all have only one significant cation–cation interaction, that between nearest-neighbors. It is apparent from the magnetic susceptibility data (*4, 5*) that the $4d^3$:Ru^{5+} ions experience stronger intraatomic electron correlations in Sr_2YRuO_6 than in either of the other two materials, and this observation allows us to eliminate two possible factors. It has been suggested (*8*) that the greater the acidity of the A-site cation the more strongly that cation competes for the electron density on the oxide ions, and hence the less charge density is available to promote interactions between the magnetic B-site cations. Strontium is less acidic than any of calcium, yttrium, or lanthanum but the intercation interactions appear to be weaker in Sr_2YRuO_6 than in any of the other materials. The A-site acidity is therefore not the dominant factor which determines the electronic properties of these perovskites. Furthermore, the BO_6 octahedra in Sr_2YRuO_6 undergo smaller rotations from their ideal cubic orientations than do those in Ca_2YRuO_6 or Ca_2LaRuO_6. These rotations decrease the overlap of the oribtals along the superexchange pathway and should therefore lead to stronger interatomic interactions in Sr_2YRuO_6 than in either of the other materials. Thus, the degree of structural distortion does not appear to be the dominant factor. One parameter which does vary in a manner consistent with the electronic properties is the unit-cell volume, which takes the values of 272, 264, and 254 $Å^3$ in Sr_2YRuO_6, Ca_2LaRuO_6, and Ca_2YRuO_6, respectively. We therefore suggest that the most important factor in determining the behavior of these materials is the Ru–Ru distance, and that the magnetic superexchange, although actually mediated by the $p\pi$ orbitals on the intervening oxide ions, can be regarded as a direct exchange interaction which is very sensitive to the cation separation. The susceptibility and neutron data on Ca_2YRuO_6 both indicate the interatomic interactions in this material are very nearly strong enough to overcome

the intraatomic correlations and thus render the material metallic. The unit-cell volume is largely determined by the size of the A-site cation and we might expect a Ru(V) double-perovskite with only a slightly smaller A-site cation to show metallic behavior.

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