JOURNAL OF SOLID STATE CHEMISTRY **19**, 155–160 (1976)

A Systematic Study of Magnetic Order in Divalent Europium Perovskites

J. E. GREEDAN*, CHAI-LING CHIEN†, AND RICHARD G. JOHNSTON‡

**Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada*; †*Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218*; ‡*Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802*

Received April 5, 1976; in revised form May 27, 1976.

The magnetic properties of a series of cubic perovskite materials, $Eu(Al_{0.5}Ta_{0.5})O_3$, $Eu(Mg_{0.5}W_{0.5})O_3$, and $Eu(Lu_{0.5}Ta_{0.5})O_3$ have been investigated using bulk magnetic and Mössbauer techniques. $Eu(Al_{0.5}Ta_{0.5})O_3$ is a ferromagnet ($T_c \sim 5°K$, $\theta_c = +8°K$), $Eu(Lu_{0.5}Ta_{0.5})O_3$ is an antiferromagnet ($T_N = 4.0$, $\theta_c = -8°K$), while $Eu(Mg_{0.5}W_{0.5})O_3$ is probably antiferromagnetic ($T_N = 2.8°K$, $\theta_c = -1°K$). These data are compared with the known properties of $EuLiH_3$ and $EuTiO_3$ and a sharp drop in θ_c as a function of increasing lattice constant is noted. A molecular field theory analysis of the data yields two possible sets of *nn* (J_1) and *nnn* (J_2) exchange constants for each compound which are compared with existing theories.

Introduction

The magnetic properties of the cubic perovskite $EuTiO_3$, have been considered anomalous since the original investigation by McGuire *et al.* (*1*) disclosed that this material was an antiferromagnet with a type *G* magnetic structure, $T_N = 5.3°K$, $\theta_c = +3.8°K$. A molecular field theory analysis of the above data yielded surprising values for the exchange constants, J_1/k (nearest neighbors) = $-0.021°K$ and J_2/k (next nearest neighbors) = $+0.040°K$. The negative J_1 was unexpected in that the *nn* Eu^{2+} distance in $EuTiO_3$ (3.90 Å) lies between that for EuO (3.63 Å) and EuS (4.20 Å), both ferromagnets for which J_1 is relatively large and positive. As the next nearest neighbor interaction is of the 180° cation–anion–cation type the positive value of J_2 is not in accord with the usual superexchange theory. The properties of $EuTiO_3$ appear to be even more anomalous in comparison with $EuLiH_3$, also a cubic perovskite material, with an Eu^{2+} *nn* distance of 3.79 Å. This material is a ferromagnet with $T_c = 37.6°K$, $\theta_c = +40°K$, $J_1/k = +0.8 \pm 0.2°K$, and $J_2/k = \pm 0.05°K$ (*2*, *3*).

The different magnetic properties of $EuTiO_3$, EuO, and $EuLiH_3$ have been rationalized in part by Chien et al. (*4*). They assume that J_1 has the form suggested by Goodenough (*5*) and Kasuya (*6*), $J_1 \sim J_{intra}b^2/U^2$, where *b* is a transfer integral between *nn* cations dependent on overlap, *U* is the energy separation between 4*f* and 5*d* levels of appropriate symmetry, and J_{intra} is the intra-atomic Hund's rule coupling constant.

It is further assumed that *b* is roughly comparable for EuO, $EuLiH_3$, and $EuTiO_3$, which leads to the conclusion that wide differences in J_1 are due to wide differences in *U*. *U* in turn is determined by the magnitude of the crystal field splitting, Δ, of the 5*d* levels into e_g and t_{2g} sublevels, *U* varying inversely with Δ. The point charge model, despite its obvious limitations, has the virtue that quantitative calculations are straightforward and these in-

Printed in Great Britain

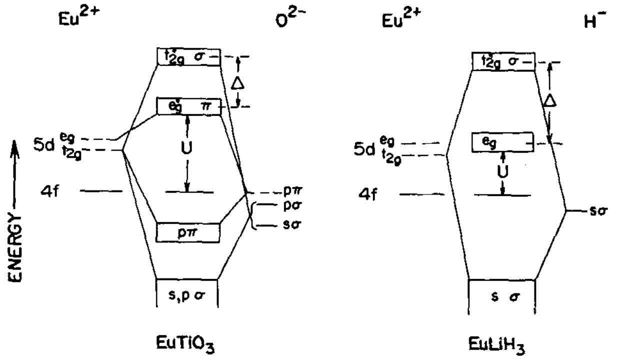

FIG. 1. Schematic relationships between Δ, the crystal field splitting of the 5*d* levels, and U, the promotional energy for the Goodenough–Kasuya (G–K) exchange interaction, for $EuTiO_3$ and $EuLiH_3$ assuming a tight-binding band model.

dicate that Δ for EuO and $EuLiH_3$ is about an order of magnitude greater than for $EuTiO_3$ (*4*).

The situation of $EuLiH_3$ vis à vis $EuTiO_3$ also can be understood qualitatively by means of a tight-binding band model, as illustrated in Fig. 1. Here Δ is the difference between $\sigma^*_{t_{2g}}$ and $\pi^*_{e_g}$ band centers. As H^- lacks *p*-orbitals, the e_g^* band for $EuLiH_3$ will be relatively low-lying, resulting in a larger Δ and a smaller U than for $EuTiO_3$. In either model the relationship between Δ and U is the same, but for the tight-binding approach the width of each 5*d* subband is proportional to the appropriate transfer integral, b_{e_g} or $b_{t_{2g}}$.

Different authors have emphasized the possible contribution of mechanisms other than the Kasuya–Goodenough mechanism to J_1. For example, *nn* Eu^{2+} ions also can be connected via a 90° cation–anion–cation (c–a–c) interaction in both the NaCl(EuO) and perovskite ($EuTiO_3$, $EuLiH_3$) structures (*1*). It has been pointed out that the number of 90° c–a–c linkages in $EuTiO_3$ is twice that for EuO. If the 90° interaction is negative this would contribute to a smaller J_1 in $EuTiO_3$ than in EuO. Indeed, if the *G–K* mechanism is diminished by crystal field effects, the negative interaction may be dominant. The 90° c–a–c interaction is expected to be absent in $EuLiH_3$ as the relevant anion H^- has no available *p*-orbitals.

In order to learn more about the puzzling magnetic behavior of divalent europium perovskites it would be advantageous to study systems in which more precise control over the exchange parameters b and U can be exercised. Such an opportunity is perhaps afforded by compounds of the type $Eu(M_{0.5}M'_{0.5})O_3$, cubic perovskite materials in which M and M' may exhibit various combinations of valence the average of which is 4+. By careful choice of M and M', the Eu^{2+} *nn* distance, and thus b, can be varied without affecting the gross crystal symmetry. Also, according to point charge arguments, Δ will decrease with increasing lattice constant and thus U will increase. From the tight-binding band viewpoint the main effect of an increasing lattice constant will be to decrease b_{e_g} and thus also the e_g bandwidth, which leads to an increasing U. Finally, it is desirable that the anion, in this case O^{2-}, be common throughout the series and that if possible the mean electronegativity of the M and M' cations be roughly constant and roughly equal to that of Ti in order to facilitate comparison with $EuTiO_3$.

The materials chosen for this study are $Eu(Al_{0.5}Ta_{0.5})O_3$, $Eu(Mg_{0.5}W_{0.5})O_3$, and $Eu(Lu_{0.5}Ta_{0.5})O_3$, all of which are cubic perovskite materials covering a range of lattice parameters which includes that of $EuTiO_3$.

Experimental

Preparation of materials. $Eu(Al_{0.5}Ta_{0.5})O_3$ and $Eu(Mg_{0.5}W_{0.5})O_3$ were prepared as described previously (7). $Eu(Lu_{0.5}Ta_{0.5})O_3$

was prepared by two different solid-state reactions:

$$EuO + \tfrac{1}{4}Lu_2O_3 + \tfrac{1}{4}Ta_2O_5 \rightarrow Eu(Lu_{0.5}Ta_{0.5})O_3,$$

$$\tfrac{1}{2}Eu_2O_3 + \tfrac{1}{4}Lu_2O_3 + \tfrac{3}{20}Ta_2O_5 + \tfrac{2}{10}Ta \rightarrow Eu(Lu_{0.5}Ta_{0.5})O_3.$$

The reactants were mixed, pelletized, sealed under argon into molybdenum crucibles, and fired at 1700°C for 12 hr. Single-phase materials were generally obtained without regrinding and only single-phase materials were used for X-ray and magnetic measurements.

X-ray characterization. Precision lattice parameters were determined as described previously (*7*).

Magnetic measurements. Magnetic data were obtained using a PAR vibrating sample magnetometer in the temperature range from 1.2 to 300°K and in applied fields from 100 Oe to 30 kOe. Calibration was carried out using $Hg[Co(SCN)_4]$ and a small sphere of high purity Ni. Samples consisted of sintered disks or spheres attached to the vibrating probe with low-temperature varnish.

Mössbauer measurements. Mössbauer spectra were determined as described previously (*3*).

Results and Discussion

As shown in Table I all of these materials except $Eu(Lu_{0.5}Ta_{0.5})O_3$ have the $(NH_4)_3FeF_6$ modification of the perovskite structure in which the *M* and *M′* ions are ordered on the sixfold site, leading to a doubling of the primitive cubic cell. Table I also includes values of Δ calculated on the point charge model using methods described previously (*4*). Note the nearly identical Eu^{2+} *nn* distance for $Eu(Al_{0.5}Ta_{0.5})O_3$ and $EuTiO_3$ and that the calculated Δ values behave in the expected manner.

The low-temperature magnetic properties of these phases are shown in Figs. 2, 3, and 4. From the low field magnetization–temperature curves, Fig. 2, $Eu(Al_{0.5}Ta_{0.5})O_3$ appears to be a ferromagnet with T_c somewhat above 4.2°K. T_c for $Eu(Al_{0.5}Ta_{0.5})O_3$ can be estimated as about 5°K by extrapolation of the Mössbauer hyperfine fields (proportional to zero-field magnetization), assuming a molecular field dependence, as shown in Fig. 4. $Eu(Lu_{0.5}Ta_{0.5})O_3$ appears to be an antiferromagnet with $T_N = 4.0$°K. $Eu(Mg_{0.5}W_{0.5})O_3$ apparently orders antiferromagnetically at 2.8°K. This ordering temperature is confirmed by Mössbauer effect measurements, Fig. 4. The magnetization curve for this material is characteristic of an antiferromagnet in a field which exceeds the spin-flop field. The field dependence of the magnetization at 1.2°K for each of the materials is shown in Fig. 3. The curve for $Eu(Al_{0.5}Ta_{0.5})O_3$ is typical for ferromagnets while the curve for $Eu(Lu_{0.5}Ta_{0.5})O_3$ is typical for antiferromagnets with small exchange fields showing effects which may

TABLE I

STRUCTURAL DATA AND CALCULATED Δ VALUES FOR DIVALENT EUROPIUM PEROVSKITES

Compound	Space group	a_0 (Å)	Eu^{2+}-Eu^{2+} *nn* distance (Å)	Δ (eV)
$EuLiH_3$	*Pm3m*	3.797	3.797	1.00
$Eu(Al_{0.5}Ta_{0.5})O_3$	*Fm3m*	7.794	3.897	0.22
$EuTiO_3$	*Pm3m*	3.904	3.904	0.21
$Eu(Mg_{0.5}W_{0.5})O_3$	*Fm3m*	7.901	3.951	0.20
$Eu(Lu_{0.5}Ta_{0.5})O_3$[a]	*Pm3m*[a]	4.100	4.100	0.17

[a] This material is also probably ordered, but the very small difference in atomic number between Lu and Ta ($\Delta Z = 2$) renders it unlikely that superlattice lines can be observed by X rays.

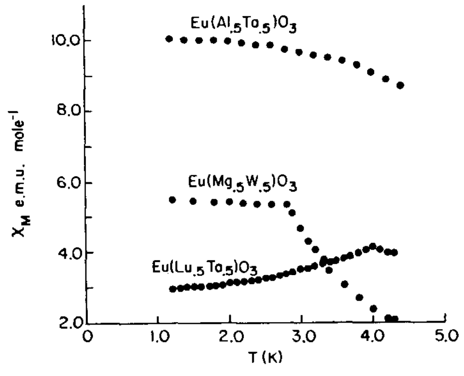

FIG. 2. Low-temperature susceptibility data for the perovskites Eu($M_{0.5}M'_{0.5}$)O_3 at an applied field of 410 Oe.

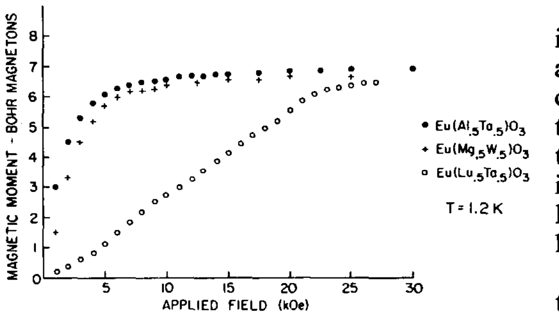

FIG. 3. Field dependence of the magnetization for the perovskites Eu($M_{0.5}M'_{0.5}$)O_3 at a temperature of 1.2°K.

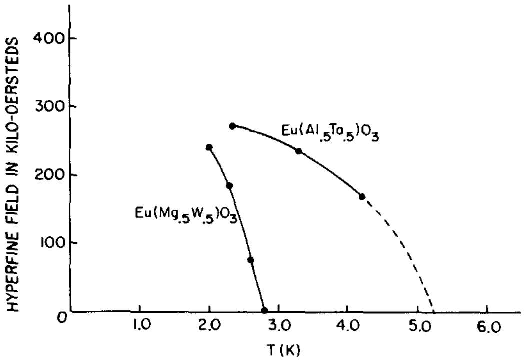

FIG. 4. ^{151}Eu hyperfine fields from the Mössbauer effect as a function of temperature.

be due to spin-flopping in the region up to 7 kOe. Eu($Mg_{0.5}W_{0.5}$)O_3 has an unusual but not impossible field dependence for an antiferromagnet with low spin-flop and exchange fields.

Susceptibility data, collected in the region from 4.2 to 300°K, were analyzed using the Curie–Weiss Law and these results together with those from Figs. 2 and 3 are summarized in Table II. Note that the values of C_M, the molar Curie constant, are very near the theoretical value of 7.87 and that saturation moments are very close to 7 μ_B suggesting very little contamination by Eu^{3+}. The signs of θ_c for Eu($Al_{0.5}Ta_{0.5}$)O_3 and Eu($Lu_{0.5}Ta_{0.5}$)O_3 are consistent with ferromagnetism in the former and antiferromagnetism in the latter while the small negative value for Eu($Mg_{0.5}W_{0.5}$)O_3 is further evidence for antiferromagnetism in this material.

To begin an interpretation of these data it is of interest to consider the variation of the algebraic sum of J_1 and J_2, i.e., the Weiss constant, $\theta_c = (2S(S+1)/(3k))(6J_1 + 12J_2)$, throughout the series. In Fig. 5 we plot θ_c vs the primitive cubic lattice parameter, a_0 (this is also the *nn* Eu^{2+}–Eu^{2+} distance) for all known divalent europium perovskites which have been well characterized.

The sharp drop in θ_c in going from $EuLiH_3$ to Eu($Al_{0.5}Ta_{0.5}$)O_3 may be attributed to a sharp decline in J_1. It is misleading to attribute this entirely to a decrease in b, the transfer integral, because of the aforementioned change in Δ, and thus U, in going from $EuLiH_3$ to Eu($Al_{0.5}Ta_{0.5}$)O_3 and the different properties of the H^- and O^{2-} anions. It we focus attention on the oxides, a less dramatic but nonetheless marked decline in θ_c is observed from a positive value in Eu($Al_{0.5}Ta_{0.5}$)O_3 which passes through zero near Eu($Mg_{0.5}W_{0.5}$)O_3 and attains a definitely negative value for Eu($Lu_{0.5}Ta_{0.5}$)O_3. This trend is not subject to a unique interpretation at present because of a lack of information on J_1 and J_2 separately. The set of $\{J_1, J_2\}$ consistent with these data is not, however, infinite. Information on the ordering temperatures together with the molecular field theory can be used to drastically reduce the number of possibilities.

For the simple cubic magnetic lattice appropriate to the perovskite structure Cofta (*8*), Adamowicz (*9*), ter Haar and Lines (*10*) have derived the following relationships,

TABLE II

Summary of Magnetic Data for Divalent Europium Perovskites $Eu(M_{0.5}M'_{0.5})O_3$

Compound	C_M	θ_c (°K)	T_N or T_c (°K)	Saturation moment at 1.2°K in Bohr magnetons
$Eu(Al_{0.5}Ta_{0.5})O_3$	7.95	+8 ± 1	~5, T_c	6.85
$Eu(Mg_{0.5}W_{0.5})O_3$	7.90	−1 ± 1	2.8 } T_N	6.70
$Eu(Lu_{0.5}Ta_{0.5})O_3$	7.73	−8 ± 1	4.0	—

assuming only near neighbor, J_1, and next near neighbor, J_2, interactions:

$$T_c = \theta_c = \frac{2}{3}\frac{S(S+1)}{k}(6J_1 + 12J_2) \tag{1}$$

$$T_{N1} = \frac{2}{3}\frac{S(S+1)}{k}(-6J_1 + 12J_2) \tag{2}$$

$$T_{N2} = \frac{2}{3}\frac{S(S+1)}{k}(2J_1 - 4J_2) \tag{3}$$

$$T_{N3} = -\frac{2}{3}\frac{S(S+1)}{k}(2J_1 + 4J_2). \tag{4}$$

Relationship (1) is exact for θ_c and also holds approximately for the ferromagnetic ordering temperature, T_c. In addition, three types of antiferromagnetic order are predicted, type G (T_{N1}), type A (T_{N2}), and type C (T_{N3}). The nomenclature adopted here is that of (*5*). In Fig. 5 we plot a phase diagram relating values of θ_c/T_N to the J_2/J_1 ratios permitted for each type of ordering. Comparing our experimental values for θ_c/T_N (Table III) with Fig. 6, we see that type C ordering is unlikely and can be eliminated from consideration. Indeed to our knowledge, type C ordering has never been observed for any real material. Both type G and type A ordering are possibilities for $Eu(Mg_{0.5}W_{0.5})O_3$ and $Eu(Lu_{0.5}Ta_{0.5})O_3$. Simultaneous solution of Eqs. (1) and (2) and (1) and (3) give two distinct sets of exchange parameters for both compounds, as shown in Table III.

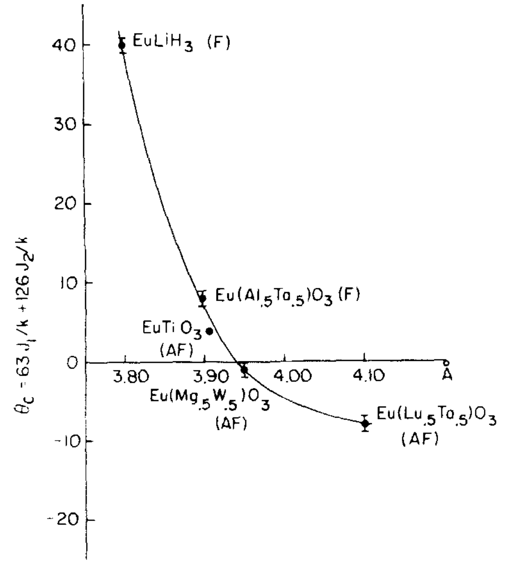

FIG. 5. The variation of θ_c as a function of the primitive cubic cell parameter a_0 for the series of well-characterized Eu^{2+} perovskites.

Lacking neutron diffraction data on the type of *AF* ordering for these compounds it is impossible to choose between the quite different sets of parameters. It is still of interest to examine the dependence of J_1 and J_2 on distance and Δ for each set and compare these to existing theories.

For type G order J_1 is always negative and becomes more so with an increase in lattice constant. This is qualitatively consistent with a model in which J_1 is determined by competing positive and negative exchange mechanisms with the negative interaction dominant. Let us assume that the negative interaction is relatively insensitive to lattice constant at least within this narrow range. If the positive contribution is the G–K interaction it will decrease with increasing lattice constant due to a decrease in b (decrease in overlap) and an increase in U (decrease in Δ). Thus, the net J_1 will become more negative with increasing distance. The situation with J_2 is more puzzling as this parameter changes sign

TABLE III

EXCHANGE PARAMETERS FOR DIVALENT EUROPIUM PEROVSKITES OBTAINED FROM THE MOLECULAR FIELD THEORY ASSUMING TYPE G OR TYPE A ORDER

Compound	Type G J_1/k (°K)	Type G J_2/k (°K)	Type A J_1/k (°K)	Type A J_2/k (°K)	θ_c/T_N
$Eu(Al_{0.5}Ta_{0.5})O_3$	—	—	—	—	
$EuTiO_3$	−0.021	+0.040	—	—	+0.717
$Eu(Mg_{0.5}W_{0.5})O_3$	−0.030 ± 0.008	+0.007 ± 0.009	+0.059 ± 0.008	−0.037 ± 0.003	−0.35 ± 0.3
$Eu(Lu_{0.5}Ta_{0.5})O_3$	−0.095 ± 0.016	−0.016 ± 0.004	+0.032 ± 0.008	−0.079 ± 0.003	−2.0 ± 0.3

from positive to negative with increasing distance. Such behavior for J_2, 180° c–a–c, is anticipated by Kasuya (*6*), who predicts that J_2 may also result from competition between a positive interaction dominant at short Eu–O distances and a negative interaction dominant at longer Eu–O distances. For type *A* order, J_1 remains positive but decreases with increasing a_0 which is consistent with a dominant *G–K* mechanism. J_2 becomes more negative with increasing distance, which is the same dependence as for the type *G* alternative.

It is clear that the set of parameters for type *G* order is more consistent with the known properties of $EuTiO_3$. Given the remarkably similar distance for $EuTiO_3$ and $Eu(Al_{0.5}Ta_{0.5})O_3$ it may, however, be difficult to reconcile the ferromagnetic order found in the latter within a single theory for all of these materials. In order that $Eu(Al_{0.5}Ta_{0.5})O_3$ be ferromagnetic, J_1 must be positive. By reasonable extrapolation one predicts from the type *G* parameter set that J_1/J_2 is positive and $J_1/J_2 < 1$, while from the type *A* set J_1/J_2 is probably negative and $(J_1/J_2) > 1$. Thus, data on J_1/J_2 for $Eu(Al_{0.5}Ta_{0.5})O_3$ would provide very useful information and together with the magnetic structures of $Eu(Mg_{0.5}W_{0.5})O_3$ and $Eu(Lu_{0.5}Ta_{0.5})O_3$ should permit this problem to be resolved.

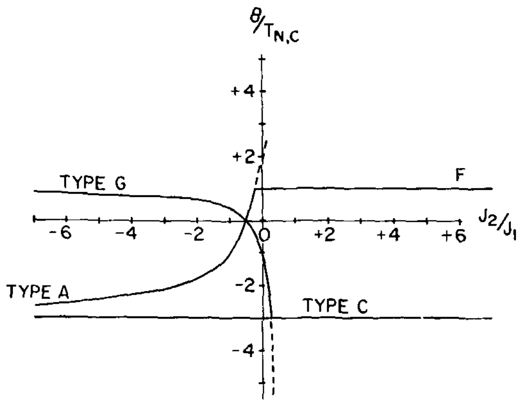

FIG. 6. A molecular field theory phase diagram relating $\theta/T_{N,c}$ and J_2/J_1 for the simple cubic magnetic lattice. Adapted from (*9*).

Acknowledgments

We wish to thank the NRC of Canada for partial support of this work, Mr. J. Niemanis for the magnetic measurements and Professors C. V. Stager and M. F. Collins for useful discussions.

References

1. T. R. McGUIRE, M. W. SHAFER, R. J. JOENK, H. A. ALPERIN, AND S. J. PICKART, *J. Appl. Phys.* **37**, 981 (1966).
2. J. E. GREEDAN, *J. Phys. Chem. Solids* **32**, 819 (1971).
3. C. L. CHIEN AND J. E. GREEDAN, *Phys. Lett.* **36A**, 197 (1971).
4. C. L. CHIEN, S. DE BENEDETTI, AND F. DE S. BARROS, *Int. J. Mag.* **5**, 361 (1974).
5. J. D. GOODENOUGH, "Magnetism and the Chemical Bond," pp. 146–167, Interscience, New York (1963).
6. T. KASUYA, *IBM J. Res. Dev.* **14**, 214 (1970).
7. J. E. GREEDAN, G. J. McCARTHY, AND CAROL SIPE, *Inorg. Chem.* **14**, 775 (1975).
8. H. COFTA, *Acta Phys. Polon.* **19**, 759 (1960).
9. L. ADAMOWICZ, *Acta. Phys. Polon.* **22**, 195 (1962).
10. D. TER HAAR AND M. E. LINES, *Philos. Trans. Roy. Soc. London, Ser. A* **254**, 540 (1962).