

Evidence for an Isotopic Shift in the Electron-Spin-Resonance Absorption Spectrum of Fe^{3+} in Calcite*

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The hyperfine structure spectrum of trivalent iron located substitutionally for calcium in calcite has been studied at a wavelength of 3 cm. At 77°K, the hyperfine splitting tensor of Fe^{57} has been found to be isotropic with a value $A = (-11.23 \pm 0.04)$ Oe. This result was obtained from data taken on seven separate fine structure transitions, five at $\theta = 0$ and two at $\theta = \frac{1}{2}\pi$. An analysis of the hyperfine structure components taken at $\theta = 0$ has shown that aside from the fact that Fe^{57} has a nuclear spin of $\frac{1}{2}$, its fine structure spectrum is measurably different from that of Fe^{56} whose nucleus has zero spin. The difference in the two fine structure spectra can be explained by a shift in the crystal-field constants of Fe^{57} with respect to Fe^{56} with no measurable shift in the spectroscopic splitting factor. The shifts in B_2^0 and B_4^0 for Fe^{57} using the values for Fe^{56} as references are given by $\delta B_2^0 = (2.0 \pm 0.2) \times 10^{-2}$ Oe and $\delta B_4^0 = (-1.3 \pm 0.7) \times 10^{-4}$ Oe. Spectral shifts due to Fe^{54} relative to Fe^{56} have also been detected and found to be opposite in sign and approximately twice the magnitude of the shifts due to Fe^{57} . These measurements were repeated at 4.2, 50, and 112°K and to within experimental errors, the results exhibited no temperature dependence.

I. INTRODUCTION

IN many respects, calcite is a host highly suited for studying electron-spin-resonance absorption spectra of magnetic ions. Its symmetries, being noncubic, provide maximum degeneracy removal between Kramers doublets, and hence allow interesting information to be obtained from the spectra, while its high degree of crystalline perfection contributes to the occurrence of narrow resonance absorption lines. Another feature of the structure is its almost complete absence of nuclear magnetic moments. The total abundance of naturally occurring nuclei in calcite having nonzero magnetic moments is of the order of 2%. Finally, the structure is capable of supporting impurities whose ionic charge states differ from those of the host ions as evidenced by the observed spectra of trivalent iron and CO_2^- molecule ions.¹⁻³ The principal limitations of the structure are its instability at high temperatures, making ionic diffusion of impurities very difficult, and the fact that no synthetic single-crystal specimens have as yet been produced in sizes sufficiently large to be of interest to electron-spin-resonance absorption spectroscopy.

Some of the resonance absorption lines displayed by calcite are as narrow as 0.03 Oe between half-intensity points.^{2,3} This structure is useful for studying those subtleties in electron-spin-resonance absorption spectra that may otherwise be obscured in structures whose ultimate resonance absorption linewidths are limited by interactions with host ion nuclei having nonzero magnetic moments. In this report results are presented of an analysis and phenomenological interpretation of an anomalous hyperfine structure spectrum due to trivalent Fe^{57} in calcite. It is hoped that these results may

prove to be of some value in understanding specific interactions between a magnetic impurity ion and its host lattice.

II. EXPERIMENT

Single crystals of calcite used in this study were obtained through the courtesy of Dr. E. Olsen of the Chicago Natural History Museum. By a chemical analysis the concentrations of iron and manganese were shown to be five parts per million by weight. Specimens were cut from single crystal blocks into parallelepipeds having cross sections of 0.6×0.6 cm and lengths of 2.0 cm. Cuts were taken so as to leave the crystal $[111]$ direction perpendicular to the axis of the parallelepiped, while the basal plane of the parallelepiped was set at an azimuthal angle of $\phi = 0$, where ϕ is measured from the carbonate ion C-O bond direction. Specimens were mounted along the axis of a cylindrical cavity resonator operating in the TE_{011} mode whose loaded Q was of the order of 5000. The spectrometer was operated at 3-cm wavelength using a 30-Mc/sec superheterodyne detector and a signal oscillator locked to the resonance frequency of the specimen cavity resonator. Zeeman field strengths were determined from a nuclear-resonance absorption magnetometer using an electronic counter for readout.

III. RESULTS

The spin Hamiltonian used in analyzing the hyperfine structure spectrum of trivalent Fe^{57} located substitutionally for calcium in calcite is given by

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + (B_4^3 O_4^3)^* + \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \beta^n \mathbf{H} \cdot \mathbf{g}^n \cdot \mathbf{I}, \quad (1)$$

where the O_n^m are electron-spin operators of degree n having m -fold rotational symmetry and where the remaining symbols have their conventional spectroscopic meaning. When the Zeeman field vector is oriented

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² S. A. Marshall and A. R. Reinberg, *Phys. Rev.* **132**, 134 (1963).

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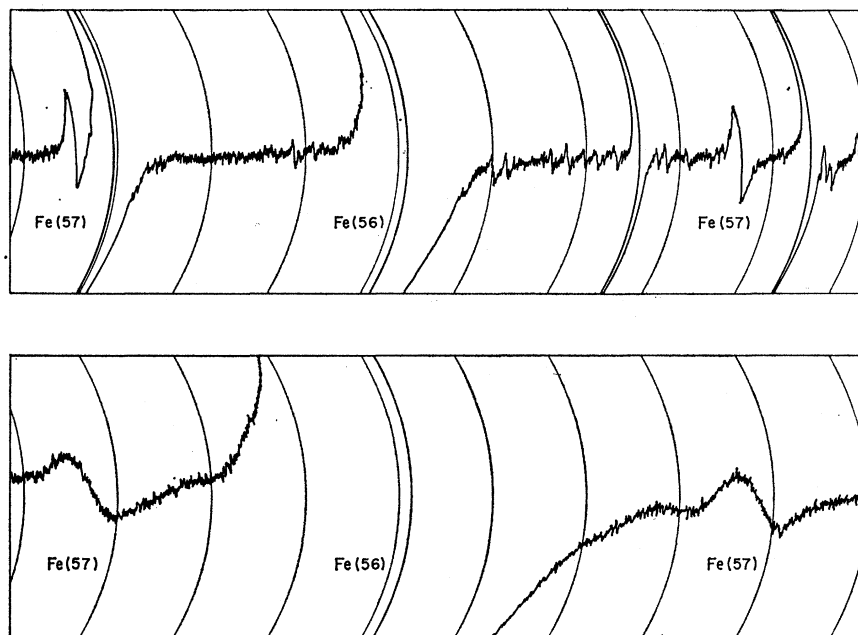


FIG. 1. First derivative chart recorder tracings of the (a) $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ and (b) $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ transitions of Fe^{3+} .

parallel to the crystal $[111]$ direction, the six eigenvalues of the above Hamiltonian with $I=0$ are given by

$$\begin{aligned}
 E(\pm\frac{5}{2}) &= \pm g_{11}\beta H + B_2^0 + 90B_4^0 \\
 &\quad + [(\pm\frac{3}{2}g\beta H + 9B_2^0 - 30B_4^0)^2 + 90|B_4^3|^2]^{1/2}, \\
 E(\pm\frac{3}{2}) &= \pm\frac{3}{2}g_{11}\beta H - 2B_2^0 - 180B_4^0, \\
 E(\pm\frac{1}{2}) &= \mp g_{11}\beta H + B_2^0 + 90B_4^0 \\
 &\quad - [(\mp\frac{3}{2}g_{11}\beta H + 9B_2^0 - 30B_4^0)^2 + 90|B_4^3|^2]^{1/2},
 \end{aligned} \quad (2)$$

where the spin states labeling of the eigenvalues refer to the high Zeeman field limit. At 77°K , the parameters of the fine structure spin Hamiltonian are given by $g_{11} = g_{\perp} = 2.0030$, $B_2^0 = 343.24$ Oe, $B_4^0 = -0.69102$ Oe, and $|B_4^3| = 15.6$ Oe.² The magnetic hyperfine interaction term for Fe^{57} in various host lattices is known to be the order of 10 Oe⁴⁻¹⁰ and thus small compared to the fine structure energy terms. The complete eigenvalue problem can consequently be solved using perturbation theory. With the Zeeman field oriented parallel to the crystal $[111]$ direction, $\theta=0$, the problem can, to some degree, be simplified since the nuclear Zeeman term does not contribute to energy level differences, and $A_{11}S_zI_z$ coming from $\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$ can be incorporated in the zeroth-

order spin Hamiltonian leaving only $\frac{1}{2}A_{\perp}(S_+I_- + S_-I_+)$ as the perturbation. Thus, all terms of the zeroth-order spin Hamiltonian, with the exception of $B_4^3O_4^3$ and its complex conjugate, yield diagonal matrix elements while the term $\frac{1}{2}A_{\perp}(S_+I_- + S_-I_+)$ yields only off-diagonal matrix elements which connect the states (M_s, M_I) to the states $(M_s \pm 1, M_I \mp 1)$. If B_4^3 and A_{\perp} were vanishingly small, the spin Hamiltonian at $\theta=0$ would be rigorously diagonal meaning that the eigenfunctions would be pure spin vectors and the eigenvalues would, in general, be linear functions of the Zeeman field strength.

In performing the work for this report, the resonance absorptions due to the isotope Fe^{57} , which has a natural abundance of 2.2%, were observed by using phase sensitive lock-in type detection. With the Zeeman field modulated at an amplitude of not more than one-quarter of a linewidth, first derivatives of the resonance absorption lines were displayed on a strip chart recorder, see Fig. 1. By repeated trials, it was found that the field position of the peak of a resonance absorption could be reproduced to within ± 0.02 Oe. For data taken at either $\theta=0$ or $\frac{1}{2}\pi$, a set of three measurements were made which constituted a run. These were the two Fe^{57} hyperfine structure resonance absorption field strength positions and the associated Fe^{56} fine structure field position. During a run, the frequency of the spectrometer signal oscillator was monitored and only those data were accepted when the frequency remained constant to within ± 10 kc/sec corresponding to a Zeeman field strength uncertainty of the order of 0.004 Oe. Associated with these three field positions are two field differences $\Delta H_+ = H_+ - H_0$ and $\Delta H_- = H_0 - H_-$, see Fig. 2. In zeroth order, $\Delta H_+ + \Delta H_-$ should yield the magnitude of the

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⁸ E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. **6**, 117 (1961).

⁹ W. M. Walsh and L. W. Rupp, Jr., Phys. Rev. **126**, 952 (1962).

¹⁰ A. Rauber and J. Schneider, Z. Naturforsch. **17a**, 266 (1962).

hyperfine structure parameter A while the hyperfine structure asymmetry defined as $\Delta H_+ - \Delta H_-$ should vanish, assuming the fine structure constants of the Fe⁵⁷ spin Hamiltonian to be identical with those of Fe⁵⁶.

At $\theta=0$ and with $T=77^\circ\text{K}$ the data showed that, except for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition, the hyperfine structure asymmetries were nonvanishing and that these asymmetries were unaccounted for by perturbation theory. After making corrections to the observed hyperfine structure splittings arising from the term $\frac{1}{2}A_1(S_+I_- + S_-I_+)$, such corrections being dominated by second-order terms and from a slight line shape asymmetry due to superposition of the Fe⁵⁶ and Fe⁵⁴ spectra, the resulting asymmetries showed a certain regularity. Table I lists these asymmetries and shows that while the asymmetry for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ fine structure transition vanishes, to within experimental limits, the asymmetries for the two transitions $M_s = -\frac{5}{2} \rightarrow -\frac{3}{2}$ and $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ are of equal magnitude and sign while the asymmetries for the two transitions $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ and $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$ are of equal magnitude but of opposite sign.

An examination of Table I and the fine structure eigenvalue expressions given by Eqs. (2) points to a rather convincing phenomenological interpretation of the observed Fe⁵⁷ hyperfine structure asymmetries. To develop this interpretation, it may be assumed that energy terms in the fine structure spin Hamiltonian proportional to B_4^3 are negligible compared to energy terms proportional to B_2^0 and B_4^0 . This is not too restrictive an assumption provided none of the transitions in question occur near the field strength at which the states $M_s = -\frac{5}{2}$ and $M_s = \frac{1}{2}$ begin to mix heavily; see Fig. 1(a) of Ref. 2. In this approximation, the eigenvalues given in Eqs. (2) for the states $M_s = \pm\frac{5}{2}$ and $\pm\frac{1}{2}$ reduce to $[\pm\frac{5}{2}g_1\beta H + 10B_2^0 + 60B_4^0]$ and $[\pm\frac{1}{2}g_1\beta H - 8B_2^0 + 120B_4^0]$, respectively, while the eigenvalues for the states $M_s = \pm\frac{3}{2}$ remain unchanged. Taking eigenvalue differences and dividing through by $g_1\beta$ to get the spin Hamiltonian parameters in field strength units, the approximate resonance absorption field strength expressions are given by,

$$\begin{aligned} H(-\frac{5}{2} \rightarrow -\frac{3}{2}) &= H_0 + 12B_2^0 + 240B_4^0, \\ H(-\frac{3}{2} \rightarrow -\frac{1}{2}) &= H_0 + 6B_2^0 - 300B_4^0, \\ H(-\frac{1}{2} \rightarrow \frac{1}{2}) &= H_0, \\ H(\frac{1}{2} \rightarrow \frac{3}{2}) &= H_0 - 6B_2^0 + 300B_4^0, \\ H(-\frac{3}{2} \rightarrow -\frac{5}{2}) &= H_0 + 12B_2^0 + 240B_4^0, \end{aligned} \quad (3)$$

where $H_0 = h\nu/g_1\beta$ and where the $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$ transition does not occur at a wavelength of 3 cm. If the parameters of the fine structure Hamiltonian of Fe⁵⁷ are different from those of Fe⁵⁶, the mean field position of an Fe⁵⁷ hyperfine doublet will be shifted from the associated Fe⁵⁶ fine structure field position in a predictable manner. To simplify the interpretation of the Fe⁵⁷ hyperfine structure asymmetries, it may be seen from Table I that since

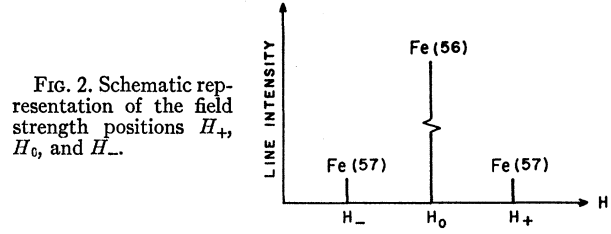


FIG. 2. Schematic representation of the field strength positions H_+ , H_0 , and H_- .

no asymmetry is observed for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition, the parameter g_{11} for Fe⁵⁷ must be, to within measurement error, equal to that for Fe⁵⁶. The asymmetries observed in the Fe⁵⁷ hyperfine structure spectrum can therefore be related to slight shifts in B_2^0 and B_4^0 . In this approximation, Eqs. (3) show that the field shifts of the centers of the Fe⁵⁷ doublets relative to the associated Fe⁵⁶ fine structure field position are predicted to be equal in magnitude and sign for the two transitions $M_s = -\frac{5}{2} \rightarrow -\frac{3}{2}$ and $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ while they are predicted to be of equal magnitude but of opposite sign for the two transitions $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ and $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$. The corrected Fe⁵⁷ hyperfine structure asymmetries, which are just twice these field shifts, are seen to be in agreement with the shifts predicted by variations in B_2^0 and B_4^0 . The best fit shifts in the Fe⁵⁷ fine structure parameters with reference to the Fe⁵⁶ parameters are given by $\delta g_{11} = 0$, $\delta B_2^0 = (2.0 \pm 0.2) \times 10^{-2}$ Oe, and $\delta B_4^0 = (-1.3 \pm 0.7) \times 10^{-4}$ Oe. The relative shifts, which are perhaps of more interest, are given by $\delta B_2^0/B_2^0 = 0.58 \times 10^{-4}$ and $\delta B_4^0/B_4^0 = 1.9 \times 10^{-4}$.

In the last column of Table I are listed the corrected values of $\Delta H_+ + \Delta H_-$ which correspond to the hyperfine splitting tensor component A . The five values of A_{11} , arrived at from the data and on the assumption that A is less than zero, are seen to be in agreement to within ± 0.04 Oe. When A is assumed to be greater than zero, the five values of A_{11} are found to exhibit a scatter of the order of ± 0.4 Oe. A_{11} and A_{\perp} for Fe⁵⁷ are concluded to be less than zero. The sign of the hyperfine interaction is seen to be the same as that of other ions of the first transition series. The observed hyperfine interaction corresponds to a field at the nucleus of 570K Oe which

TABLE I. Hyperfine structure splitting data given in oersteds for Fe⁵⁷ obtained at $\theta=0$ and $T=77^\circ\text{K}$ for each of the five fine structure transitions.

Transition	$(\Delta H_+ + \Delta H_-)^a$	$(\Delta H_+ - \Delta H_-)^a$	δ^b	$-A_{11}^b$
$-\frac{5}{2} \rightarrow -\frac{3}{2}$	11.29	0.41	0.43	11.24
$-\frac{3}{2} \rightarrow -\frac{1}{2}$	11.16	0.34	0.33	11.20
$-\frac{1}{2} \rightarrow \frac{1}{2}$	11.04	0.10	0.00	11.22
$\frac{1}{2} \rightarrow \frac{3}{2}$	11.05	-0.22	-0.32	11.25
$-\frac{3}{2} \rightarrow -\frac{5}{2}$	11.11	0.39	0.41	11.24

^a As experimentally observed.

^b δ and A_{11} are given by $(\Delta H_+ - \Delta H_-)$ and $(\Delta H_+ + \Delta H_-)$, respectively, to which are added perturbation and line shape asymmetry corrections.

TABLE II. Line shape asymmetries for the five Fe^{3+} fine structure transitions. The asymmetry is defined as the difference between the high-field and low-field extrema of the line shape first derivative.

Transition	Asymmetry (in parts/1000)
$-\frac{5}{2} \rightarrow -\frac{3}{2}$	30 ± 5
$-\frac{3}{2} \rightarrow -\frac{1}{2}$	25 ± 5
$-\frac{1}{2} \rightarrow \frac{1}{2}$	0 ± 5
$\frac{1}{2} \rightarrow \frac{3}{2}$	-25 ± 6
$\frac{3}{2} \rightarrow \frac{5}{2}$	30 ± 5

again is comparable per unpaired electron spin to that observed in other iron group ions.¹¹

In addition to data taken at 77°K, the measurements at $\theta=0$ were repeated on all five transitions at $T=50^\circ\text{K}$ and on the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$, $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$, and $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$ transitions at $T=4.2$ and 112°K . No measurable variations were observed in either the hyperfine structure splittings or spectral shifts over this temperature range.

In an attempt to establish whether the observed hyperfine structure asymmetries due to Fe^{57} are indeed an isotope effect and not the consequence of a nonvanishing nuclear spin, an investigation was made of the shapes of each of the five Fe^{3+} fine structure transitions at $\theta=0$. The object of this investigation was to see if the nonmagnetic nucleus Fe^{54} which is 5.9% naturally abundant exhibits an isotopic spectral shift and if such a shift can be correlated to the isotopic shift due to Fe^{57} . If the displacement of the Fe^{54} fine structure spectrum relative to Fe^{56} were of the same order of magnitude as the previously observed displacements between the Fe^{56} and Fe^{57} fine structure lines, then the displacement would be insufficient to resolve the Fe^{54} and Fe^{56} spectra but would produce a measurable line shape asymmetry in the composite resonance line. The results of the investigation are summarized in Table II which gives for each Fe^{3+} fine structure transition at $\theta=0$, the sign and magnitude of the asymmetry in the first derivative of the resonance absorption line shape. This asymmetry is defined as the difference between the high- and low-field extrema intensities of the line shape first derivative. Needless to say, there are numerous pitfalls to assigning relevance to slight asymmetries in line shapes and especially in the spectrum of Fe^{3+} in calcite. To begin with, each Fe^{3+} fine structure resonance absorption is split into a doublet pattern at polar angles other than $\theta=0$ and $\frac{1}{2}\pi$. Thus, by not being exactly at one of these orientations, asymmetry in the resonance absorption can result from a slight doublet splitting. Such an effect is however quite predictable as is the sign of the resulting asymmetry.^{2,12-14} Another source of spurious line shape

asymmetry is the occurrence of a faint but unrelated resonance absorption beneath the one of interest. Such a possibility can be investigated by preferentially shifting the field position of the Fe^{3+} resonance absorption through a slight change in the angle θ . Finally, it is possible that the spectrometer is adjusted so as to artificially produce an asymmetric line shape. This too can be checked by tracing through a resonance absorption which is known to be symmetric. The aforementioned possible sources of line shape asymmetry were shown to be negligible.

Once having adjusted the spectrometer to produce a first derivative recorder tracing symmetric to five parts in one thousand of one of the Mn^{2+} resonance absorptions which are known to be symmetric at $\theta=0$, each of the five Fe^{3+} fine structure transitions were carefully recorded under conditions of minimum saturation and modulation broadening. The results shown in Table II, indicate that the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition of Fe^{3+} exhibits no asymmetry in excess of five parts in one thousand while the two transitions $M_s = -\frac{5}{2} \rightarrow -\frac{3}{2}$ and $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ exhibit asymmetries of equal magnitude and sign, and the two transitions $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ and $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$ exhibit asymmetries which are of equal magnitude but of opposite sign. The asymmetries in the five Fe^{3+} fine structure resonance absorptions can qualitatively and to some extent quantitatively be interpreted on the basis of a slight displacement of the Fe^{54} spectrum with reference to that of Fe^{56} . The spectral shift of the Fe^{54} lines relative to the Fe^{56} lines which best fits all five asymmetries is one which is of opposite sign and between 1.5 and 2.5 times the magnitude of the shift of Fe^{57} .

The measured line shape asymmetry in a composite Fe^{54} and Fe^{56} fine structure line enables the field displacement between the two resonance peaks to be obtained. This displacement amounts to a few hundredths of an oersted and has been accounted for in the data given in Table I.

IV. CONCLUSION

The anomalous asymmetry of the hyperfine splitting of the Fe^{57} spectrum relative to the Fe^{56} spectrum, together with the observed displacement between the spectra of the zero-spin isotopes Fe^{56} and Fe^{54} , suggests that spectral shifts are not simply a consequence of a nonvanishing nuclear spin but more a consequence of the differing nuclear masses of the isotopes. The influence of nuclear mass is manifested by slight variations in the parameters of the spin Hamiltonian for the different isotopes.

Analysis of the observed isotope shift is hampered by the fact that there is at present no generally established theory for the interaction S -state ions with crystalline fields. One process which may be operative in causing an isotopic spectral shift is that, at a given temperature, the amplitude of oscillation of an ion in its host lattice

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¹⁴ L. M. Materese and C. Kikuchi, *J. Chem. Phys.* **23**, 601 (1960).

will depend upon ionic mass. Since ions of differing isotopic mass will have unequal amplitudes of oscillation, they will consequently sample the crystalline electric fields in different manners.¹⁵ Such oscillations would have to occur in nonsymmetric modes since small changes of oscillation amplitude in symmetric modes would cause no changes in the sampling of the electric field. A complete description of the dependence of the shift of the crystalline field parameters of the spin Hamiltonian on isotope mass differences would require

¹⁵ A. L. Schawlow, *J. Appl. Phys.* **33**, 395 (1962).

detailed information on the relevant vibrational energy levels. The lack of any temperature dependence of the observed shift over the range 4.2–112°K suggests, however, that only the zero-point vibrational states of the ground electronic level need be considered.

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Oxygen Vacancies and Electrical Conduction in Metal Oxides*

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Oxygen vacancies and their effects on electrical conduction in some metal oxides were considered through an exact solution of the equilibrium relations between oxygen partial pressure in the ambient gas and concentrations of oxygen vacancies and conduction electrons in the oxide. The mass-action law was assumed but no state of ionization of oxygen vacancies was neglected. Concentrations of electrons in conduction states and total oxygen vacancies were considered. The results, which possess considerable complexity not contained in the usual limiting-case solutions, were compared with pertinent experiments.

I. INTRODUCTION

ELECTRICAL conductivity σ and concentrations of oxygen vacancies, $[V_A]_{\text{tot}}$, in some solid metal oxides such as TiO₂, Nb₂O₅, and CeO₂ show a dependence on oxygen partial pressure P at constant temperature T according to the laws

$$\sigma = C_1(T)P^{-1/n}, \quad (1)$$

and

$$[V_A]_{\text{tot}} = C_2(T)P^{-1/m}, \quad (2)$$

where $C_1(T)$ and $C_2(T)$ are functions of temperature and n and m are constants. It has been reported that n has values $n=5$ for CeO₂,¹ $n=4$ for Nb₂O₅,² $n=5$ or $n=6$ for TiO₂,³ and that n can take on various nonintegral values.⁴ It has also been reported that m has values $m=6$ or $m=2$ for TiO₂,^{5,6} and $m=6$ for Nb₂O₅.⁷

It has generally been concluded that Eq. (1) with $n=5$ is not compatible with a defect model wherein oxygen vacancies are the sole source of conduction electrons. This conclusion has been reached on the basis that the oxygen-vacancy model leads to Eq. (1) with $n=4$ if all oxygen vacancies are singly ionized, and to Eq. (1) with $n=6$ if all oxygen vacancies are doubly ionized.^{2,3,5,7,8} Because of this, interstitial cations,^{1,3,8} or associated vacancies⁹ have been postulated as conduction electron sources in order to explain experimental results which appear to follow the law of Eq. (1) with $n=5$.

The purpose here is to treat the oxygen-vacancy model exactly, not making any assumption about the states of ionization of oxygen vacancies. Because both electrical-conductivity measurements and gravimetric determination of oxygen-vacancy concentration are used to determine the defect structure, concentrations of both conduction electrons and oxygen vacancies are considered. The case discussed is that of pure oxide with oxygen vacancies being the only source of conduction electrons. Thus, impurity atoms and all other sources of carriers including intrinsic formation of electron-hole pairs are not considered here. It is assumed that there is only one type of conduction state for the electrons and that electrons are the only carriers. After the characteristics of the oxygen-vacancy defect model

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