

Substitutional H^- -ion vibrations in the alkaline-earth oxides reduced at high temperatures

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The infrared absorption spectra of MgO, CaO, and SrO, crystals containing high concentrations of hydrogen are studied. Samples reduced at high temperatures and high pressures of the alkaline-earth vapor exhibit sharp absorption lines that can be attributed to the fundamental vibrations of substitutional H^- ions. In $MgO:H^-$ a first-harmonic line is also observed. A comparison is made with results for H^- ions in the alkali halides.

I. INTRODUCTION

Hydrogen appears in the alkaline-earth oxides in five basic forms or configurations: H_2 , OH^- , H, hydrides, and H^- . High-pressure hydrogen gas (H_2) has been found to be present in cavities in MgO, resulting in opacity of the crystal.¹ The source of the hydrogen is moisture sorbed in MgO powder prior to crystal growth. Hydroxyl ions (OH^-) are normally present as $-(OH)_2^{2-}$ precipitates, or as OH^- ions with the proton substituting for Mg^{2+} , Ca^{2+} , or Sr^{2+} .² These ions are normally monitored by infrared-absorption measurements. Atomic hydrogen (H) has been found in CaO following irradiation at 77 K by electron paramagnetic resonance.³ Hydrides, such as LiH, have also been observed in CaO.³ Lastly, H^- substituting for O^{2-} ions in the crystals can be expected in special situations.

A substantial body of literature exists concerning the vibrational properties of substitutional H^- and D^- impurities, also referred to as U centers, in the alkali halides.⁴⁻¹² These systems are perhaps the best understood examples of localized modes in ionic crystals. Some studies have also been performed on H^- and D^- ion vibrations in the alkaline-earth fluorides¹³ and in rare-earth trifluorides.¹⁴ Relatively little has been done on the high-temperature oxides, presumably because substitutional H^- ions can be produced only under severe temperature and pressure conditions. An exception is the work on CaO by Gourley and Vance¹⁵ and Vance and Mallard,¹⁶ who found that the luminescent regions of arc-melted CaO crystals exhibited sharp infrared-absorption lines near 900 cm^{-1} ; they tentatively attributed these lines, which

were intensity-correlated in different samples, to H^- vibrations.

The motivation of the present investigation is that the conditions that prevail in the operation of some energy-efficient devices, such as the Stirling engine, are the same as those which produce H^- ions, namely high temperatures and high pressures of a reducing gas. In the present work we investigate the infrared spectra of MgO, CaO, and SrO, and provide evidence that certain structure appearing in the low-frequency region arises from H^- ion vibrations.

II. EXPERIMENTAL PROCEDURES

The MgO, CaO, and SrO crystals used in the present study were grown by the arc-fusion method at the Oak Ridge National Laboratory.¹⁷ The respective starting materials were high-purity grade MgO powder from Kanto Chemical Company, Tokyo, Japan, and reagent grade $CaCO_3$ and $SrCO_3$ powder from Mallinckrodt Chemical Company. The typical chemical analyses of the MgO and CaO crystals, along with their starting materials, have been reported previously.^{17,18} The analysis of the $SrCO_3$ powder and the resulting SrO crystals is given in Table I. In general, all MgO, CaO, and SrO crystals are expected to contain hydrogen. For the latter two crystals, the concentrations are inherently high. In the case of MgO, large variations of hydrogen content can be obtained. MgO powder presoaked with water produced crystals that are very cloudy, due to the presence of cavities containing high-pressure H_2 gas.¹ On the other extreme, MgO crystals with un-

TABLE I. Chemical analyses of Mallinckrodt SrCO₃ powder and the resulting SrO crystals. Methods of characterization include wet chemistry, neutron activation analyses, flame photometry, atomic absorption spectroscopy, and arc-emission spectrochemical techniques. The analyses are semiquantitative, to be interpreted as approximations only (< means below the limit of detection).

Element	SrCO ₃ powder	SrO crystal	Element	SrCO ₃ powder	SrO crystal
Ag	< 1	< 1	Mo	< 1	< 1
Al	3	< 3	Nb	< 5	< 5
B	1	1	Nd	70	≤ 1
Ba	10	3	Ni	< 3	< 3
Be	< 1	< 1	Pb	< 3	< 3
Bi	< 3	< 3	Pt	< 20	< 20
Ca	200	200	Rb	< 3	< 3
Cd	< 10	< 10	Sb	< 5	< 5
Co	< 5	< 5	Si	5	< 5
Cr	3	< 1	Sn	< 3	< 3
Cs	< 10	< 10	Ta	< 10	< 10
Cu	< 1	< 1	Ti	2	< 1
Fe	3	< 1	V	< 1	< 1
K	< 3	< 3	W	< 10	< 10
Li	< 1	< 1	Zn	< 50	< 50
Mg	5	3	Zr	< 5	< 5
Mn	70	10			

detectable or barely detectable OH⁻ concentrations can be produced when grown in a special way.¹⁷

Infrared absorption measurements were made with a Perkin-Elmer Spectrophotometer Model 580. Low-temperature measurements were made with a custom-made cryostat fitted with KBr windows. Oxygen-vacancy concentrations were estimated from optical-absorption measurements performed with a Cary 17D spectrophotometer.

III. RESULTS

The method used to produce H⁻ ions in all three materials involves a process commonly referred to as "additive coloration." This process produces anion (oxygen) vacancies, viz., a stoichiometric excess of cations. If hydrogen impurities are present in the crystal, it is expected that they can be trapped at oxygen-vacancy sites and form H⁻ ions. In practice, crystals containing hydrogen are heated at high temperatures (2000–2400 K) and high pressures of magnesium or calcium vapor (4–7 atm) in a tantalum bomb, followed by rapid cooling. The process is more aptly called "subtractive coloration" since the experimental evidence indicates that the stoichiometric imbalance is due to removal of oxygen ions from the

crystal rather than absorption of cations from the vapor. A similar conclusion was drawn from studies in Al₂O₃.¹⁹

A. Magnesium oxide

The infrared spectrum of a very cloudy MgO crystal, containing the maximum hydrogen concentration available in this laboratory, is shown in Fig. 1. The crystal had been heated in air at 1450 K for 10 min and quenched in order to maximize the 3296-cm⁻¹ line at the expense of the 3700-cm⁻¹ band.²⁰ The former is due to the OH⁻ stretching vibration of the V_{OH⁻} center (configuration: OH⁻—[Mg vacancy]—O²⁻) and the latter corresponds to that for Mg(OH)₂ precipitates.² We also show the part of the spectrum around 1000 cm⁻¹; no sharp absorption lines appear in this region.

After reduction in the tantalum bomb at ~ K, a very cloudy crystal became less cloudy. At such elevated temperatures, the pressure of H₂ in the cavities is about 10³ atm (Ref. 1) and some hydrogen probably diffused out of the sample during the reduction. Soluble hydrogen remaining in the crystal changed its configurations, as shown in Fig. 2. The 3296- and 3700-cm⁻¹ absorption bands disappeared, and sharp lines at 1024, 1032, and

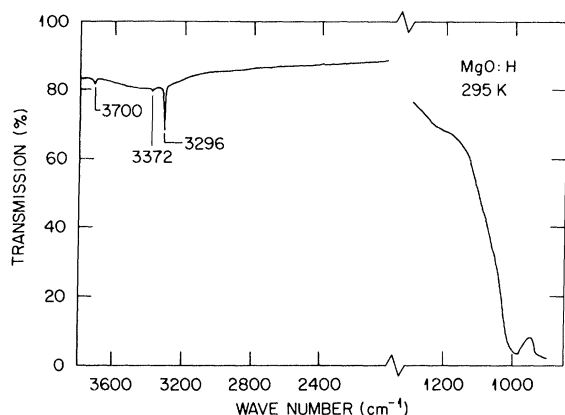


FIG. 1. Infrared spectrum of a cloudy MgO crystal with high hydrogen content, measured at 295 K. The sample thickness was 0.6 mm. The sample had been heated in air at 1450 K for 10 min prior to fast cooling in order to maximize the 3296 cm^{-1} band.

1053 cm^{-1} emerged. The intensity of these lines depends strongly on both the initial hydrogen content, as monitored by the cloudiness of the crystal and the OH^- bands, and the temperature for the reduction. The relative intensities of the lines, however, were roughly constant from sample to sample. Higher reduction temperature produces higher anion-vacancy concentration, as determined by the absorption coefficient of the 5.0 eV (250 nm) band. A very cloudy crystal reduced at the rela-

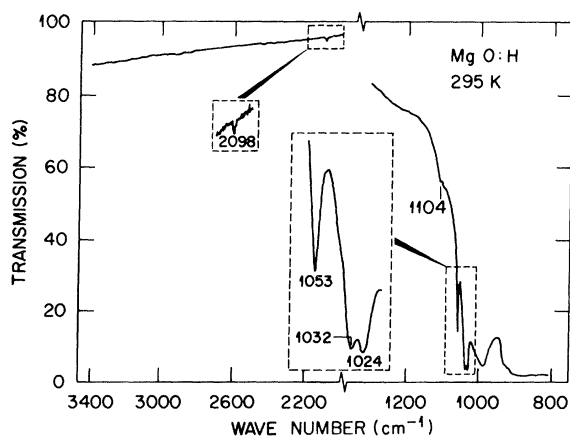


FIG. 2. Room-temperature spectrum of an MgO crystal with high hydrogen content after reduction at 2400 K in a tantalum bomb. The sample thickness was 0.6 mm. In the small inset, the band at 2098 cm^{-1} is magnified 5 \times in the vertical direction. The large inset is enlarged 2 \times and 5 \times in the horizontal and vertical directions, respectively.

tively lower temperature of ~ 2000 K exhibited lines of low intensity. The same was true for a crystal with low hydrogen content "bombed" at 2400 K. The unusually large intensity of the three lines shown in Fig. 2 was obtainable only for a very cloudy crystal reduced at 2400 K. The concentration of oxygen vacancies in this crystal was $\sim 2 \times 10^{18} \text{ cm}^{-3}$. Also, our results showed that for crystals with a given hydrogen content, the more intense the three-line series, the lower the intensity of the 3296 cm^{-1} band, and vice versa. We attribute these lines to the fundamental vibrations of substitutional H^- ions.

It is interesting to note that a low-intensity signal at 2098 cm^{-1} can be seen in Fig. 2. This line was detectable only for very cloudy crystals that were bombed at 2400 K. We attribute this line to the first-harmonic vibration for the 1053- cm^{-1} absorption. Since it is impossible to detect the fundamental D^- lines, because they would be submerged at 700–750 cm^{-1} under the very strong absorption in this region, we searched for the first-harmonic vibration for the D^- ions. While our deuterated crystals had a concentration ratio of OD^-/OH^- equal to 4, the deuterium (and hydrogen) content was low. In spite of the reduction of the deuterated samples at 2400 K, no structure could be seen near 1500 cm^{-1} , which is where the first-harmonic vibration for the D^- ions is expected to be, and no H^- harmonic signal was observed at 2098 cm^{-1} .

The spectrum of the same crystal measured at 80 K is shown in Fig. 3. The three lines attributed to the H^- ions narrowed and the peaks shifted approximately 3 cm^{-1} to 1027, 1034, and 1056 cm^{-1} . The low-intensity line at 2098 cm^{-1} at room temperature also narrowed and shifted 8 cm^{-1} to 2106 cm^{-1} . Hence, the evidence for this signal being the first harmonic for the H^- ions is (a) intensity correlation with the 1056- cm^{-1} line, (b) doubling of the frequency, and (c) the larger 8 cm^{-1} shift relative to that of the fundamental H^- vibration.

Some very weak structure observed at about 1104 cm^{-1} at 295 K (see Fig. 2) became more pronounced at 80 K and can be clearly resolved at 1092, 1100, and 1107 cm^{-1} . These lines were observable only in the very cloudy crystals which were reduced at 2400 K. Therefore, it appears that some correlation exists between the H^- impurities and these lines. In analogy with the situation in KCl ,¹² it may be possible that $\text{H}^- \text{H}^-$ pairs on adjacent $\langle 110 \rangle$ anion sites are the cause of these

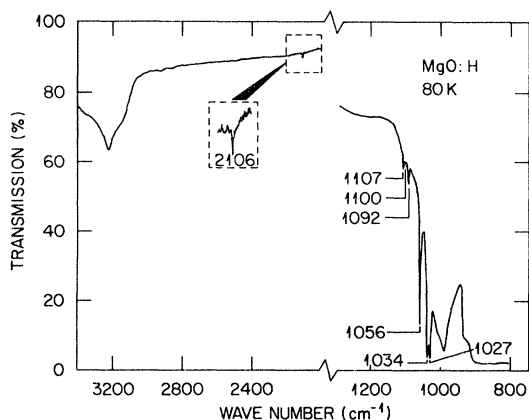


FIG. 3. Spectrum of the same sample as that shown in Fig. 2, measured at 80 K. In the inset, the band at 2106 cm^{-1} is magnified $5\times$ in the vertical direction.

transitions. Also, it is noted that these lines experienced a significant increase in intensity after the samples had been annealed in a graphite crucible at 1475 K for 10 min and subsequently slow cooled. Rapid cooling had the opposite effect.

B. Calcium oxide

CaO crystals are normally cloudy and the opacity is more pronounced than in MgO. The cloudiness arises from reactions involving hydroxyl ions from $\text{Ca}(\text{OH})_2$ in the powder and CO_2 evolved from the CaCO_3 powder.¹⁷ Therefore, CaO crystals usually contain an abundance of hydrogen impurities.

The room-temperature spectrum of an as-grown CaO sample, approximately 0.6 mm thick, is shown in Fig. 4. The broad band centered at 3640 cm^{-1} is associated with $\text{Ca}(\text{OH})_2$ formed mainly

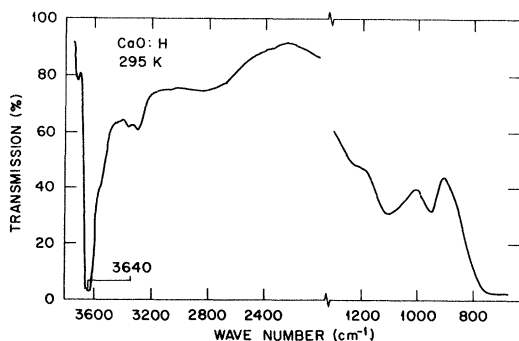


FIG. 4. Room-temperature spectrum of an as-grown CaO:H crystal. The sample thickness was 0.6 mm.

on the sample surface.¹ By removing the surface region via abrasion on a SiC paper, this absorption band can be drastically reduced and a narrower band centered at 3645 cm^{-1} due to $\text{Ca}(\text{OH})_2$ precipitates¹ in the bulk is observed. At 80 K (cf. Fig. 5), this broad $\text{Ca}(\text{OH})_2$ band shifts toward higher frequency and can be resolved into at least two bands, observable at 3650 and 3690 cm^{-1} . No absorption lines were observed in the region near 900 cm^{-1} .

After reduction at $\sim 2100\text{ K}$ in $\sim 5\text{ atm}$ of Ca vapor, similar CaO crystals became clearer and exhibited an orange color when exposed to room light. Placed in the dark, they emit a persistent orange luminescence corresponding to the $^3P \rightarrow ^1S$ transition of the two-electron anion vacancy.²¹ The spectra of a typical crystal, measured at 80 and 295 K, are shown in Fig. 5. At room temperature, two lines not seen in the spectrum of the as-grown crystal are observed at 880 and 911 cm^{-1} . At 80 K these peaks shift upward 5 cm^{-1} to 885 and 916 cm^{-1} , respectively. These values agree extremely well with those reported by Gourley and Vance¹⁵ for crystals "accidentally colored" during crystal growth. We support their conclusion that these lines are due to the vibrations of substitutional H⁻ ions. A search was carried out for a signal around 1800 cm^{-1} , corresponding to the first harmonic for H⁻ ions. Several crystals were examined, including some heated at 2300 K . None showed any evidence of the first-harmonic vibration.

C. Strontium oxide

Like CaO, as-grown single crystals of SrO inherently contain an abundance of hydrogen. The

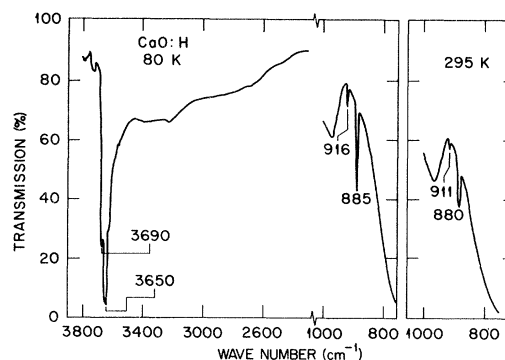


FIG. 5. Spectrum of a CaO:H crystal after reduction in a tantalum bomb at 2100 K , measured at 80 and 295 K. The sample thickness was 0.6 mm.

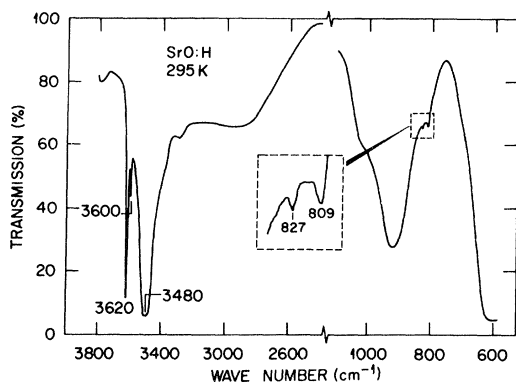


FIG. 6. Room-temperature spectrum of a SrO:H crystal after reduction in a tantalum bomb at 2100 K. The sample thickness was 0.6 mm. The inset is magnified $5\times$ in both the horizontal and vertical directions.

infrared spectrum displays strong absorption in the OH^- region. (A spectrum is not shown, but is similar to that on the left in Fig. 6 for a reduced sample.) At 295 K two sharp lines at 3620 and 3600 cm^{-1} are adjacent to a broad band centered at about 3480 cm^{-1} . After abrading off the surface region, the intensity of the two lines decreased considerably and the 3480 cm^{-1} band sharpened and shifted toward 3500 cm^{-1} . These values agree with those reported by Briggs (3612, 3590, and 3490 cm^{-1}) after his samples were annealed in hydrogen at 1500 K for 12 h.¹

After reduction at 2100 K in a tantalum bomb, SrO crystals exhibited a room-temperature spectrum shown in Fig. 6. The OH^- portion of the spectrum did not change appreciably. However, two sharp lines appeared at 809 and 827 cm^{-1}

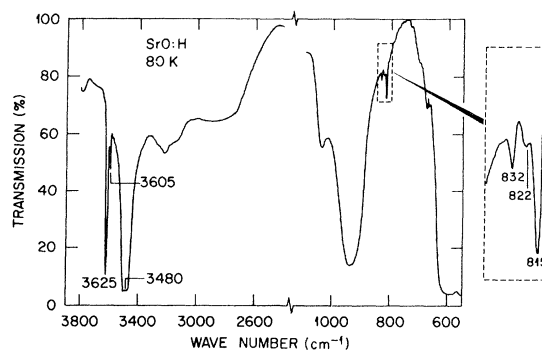


FIG. 7. Spectrum measured at 80 K for the same crystal whose spectrum is shown in Fig. 6. The inset is magnified $5\times$ in both directions.

which were not present prior to the reduction. At 80 K these two lines became more pronounced and shifted about 5 cm^{-1} to 815 and 832 cm^{-1} , respectively, as shown in Fig. 7. Also, a weaker signal at 822 cm^{-1} became evident. These lines are attributed to H^- ions in SrO. Attempts were made to find the first harmonic for the H^- ions in the neighborhood of 1650 cm^{-1} , but no line was observed.

IV. DISCUSSION AND CONCLUSIONS

Table II summarizes our data on absorption lines attributed to substitutional H^- -ion vibrations in MgO, CaO, and SrO. In each of the three oxides the fundamental H^- -ion vibrations produce two or more sharp, closely spaced lines, whose intensities in a given crystal are comparable, but not necessarily equal or rationally related. This may indicate a lowering of the point-group symmetry

TABLE II. Substitutional H^- -ion vibrational frequencies in MgO, CaO, and SrO. Units are cm^{-1} . The numbers in parentheses are estimated relative intensities within each series of lines.

	H^- lines		Other lines	
	80 K	295 K	80 K	295 K
MgO	1056 (0.9) 1034 (1.0) 1027 (0.9) 2106 (<0.1)	1053 (0.9) 1032 (1.0) 1024 (0.9) 2098 (<0.1)	1092 (1.0) 1100 (0.3) 1107 (0.8)	1104
CaO	885 (1.0) 916 (0.3)	880 (1.0) 911 (0.3)		
SrO	815 (1.0) 822 (0.3) 832 (0.3)	809 (1.0) 827 (0.3)		

TABLE III. H⁻ local-mode frequencies in the alkaline-earth oxides and the alkali halides, in units of cm⁻¹. The first column, ω , gives the experimental values; for MgO, CaO, and SrO, these are arithmetic averages of the 80-K data in Table II, and for the alkali halides, they are averages of the values compiled in Table 7-1 of Ref. 8. The second column, labeled ω_{md} , lists frequencies calculated by treating the substitutional H⁻ ion as a mass defect, that is, as an impurity having a different mass, but the same charge and the same interactions with its neighbors, as the ion it replaces. The shell models used for the mass-defect calculations are those in Refs. a–i. The last column lists the ratios of the observed H⁻ ion frequencies to the maximum phonon frequencies ω_{max} in the pure-host crystal.

	ω	ω_{md}	$\omega/\omega_{\text{md}}$	$\omega/\omega_{\text{max}}$
MgO ^a	1039	1745	0.595	1.44
CaO ^b	901	1465	0.615	1.61
SrO ^c	823	1268	0.649	1.71
NaCl ^d	563	808	0.697	2.17
KCl ^d	501	735	0.682	2.37
RbCl ^d	475	738	0.644	2.75
NaBr ^e	497	766	0.649	2.47
KBr ^f	447	712	0.628	2.71
RbBr ^g	424	685	0.619	3.29
NaI ^e	427	696	0.614	2.50
KI ^h	380	678	0.560	2.70
RbI ⁱ	360	688	0.523	3.36

^aM. J. L. Sangster, G. Peckham, and D. H. Saunderson, *J. Phys. C* **3**, 1026 (1970); model B in Table 3.

^bD. H. Saunderson and G. E. Peckham, *J. Phys. C* **4**, 2009 (1971); model II in Table 3.

^cK. H. Reider, R. Migoni, and B. Renker, *Phys. Rev. B* **12**, 3374 (1975); model I in Table III.

^dG. Raunio and S. Rolandson, *Phys. Rev. B* **2**, 2098 (1970); model II in Tables I and II.

^eJ. S. Reid, T. Smith, and W. J. L. Buyers, *Phys. Rev. B* **1**, 1833 (1970); model II in Table II.

^fR. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, *Phys. Rev.* **131**, 1030 (1963); model VI in Tables II and III.

^gS. Rolandson and G. Raunio, *J. Phys. C* **4**, 958 (1971); model IV in Table 3.

^hG. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, *Phys. Rev.* **147**, 577 (1966); model III in Table II.

ⁱG. Raunio and S. Rolandson, *Phys. Status Solidi* **40**, 749 (1970); model 2 in Table 3.

around the H⁻ ion from O_h to a less symmetric configuration, which in turn may be due to local charge compensation as discussed by Gourley and Vance.¹⁵ The observation of the first harmonic in

MgO is further evidence of reduced symmetry around the H⁻ ion in that crystal, since as pointed out in Ref. 15, the first harmonic is not an optically allowed transition in O_h symmetry. It is also possible, particularly in MgO where two sets of three lines are observed at 80 K (cf. Fig. 3), that H⁻ ions are present in local environments of slightly different symmetries. Satellite lines arising from this effect have been observed in the alkali halides⁷ and the alkaline-earth fluorides.¹³

In the alkali halides,^{4–11} the alkaline-earth fluorides,¹³ and rare-earth trifluorides,¹⁴ one-phonon sidebands of the fundamental H⁻-ion vibrational lines are seen. These arise from the anharmonic coupling between the H⁻ local mode and the perturbed lattice modes of its neighbors. Because of this coupling, the absorbed light can create a local-mode phonon and also create (higher-frequency sideband) or destroy (lower-frequency sideband) a lattice phonon. In a given crystal, the sideband structure is the same for D⁻ as for H⁻, although the fundamental peak is shifted down by a factor of very close to $1/\sqrt{2}$. We have not observed one-phonon sidebands of the H⁻ lines in MgO, CaO, or SrO, but our experiments were not sufficiently definitive to absolutely rule them out.

Table III compares our results for H⁻ ion vibrations in the alkaline-earth oxides with results in the alkali halides. The tabulation includes (average) observed values ω for the local-mode frequency and values ω_{md} calculated by treating the H⁻ ion as an isotopic mass impurity, having the same charge and interactions with other ions in the crystal as the ion it replaces (O^{2-} , Cl^- , Br^- , I^-). While this is not a very good approximation, as the table demonstrates, the ratio $\omega/\omega_{\text{md}}$ provides a rough measure of how the forces between the H⁻ ion and its neighbors differ from those between an O^{2-} ion and its neighbors in the host. The last column in the table shows how far above the maximum vibrational frequency in the perfect host crystal the H⁻ line lies. This is much lower in MgO, CaO, and SrO than in the alkali halides listed because of the smaller mass ratio $M(H):M(O)$.

In the alkali halides, the H⁻ ion has the same charge as the ion it replaces. Two major factors contribute to the reduction of the local-mode frequency from the value found by treating the H⁻ ion as a mass defect. The first is a large decrease in the short-range repulsive interaction of the defect with its nearest neighbors. When only this effect is included, as in Ref. 7 for KBr:H⁻ and

KI:H, a decrease of the order of 50% in the first-neighbor central-force constant is required to fit the experimental data. The second major factor is the different polarizability of the H^- ion, whose importance has been emphasized by Bilz *et al.*⁶

In the oxides, the H^- impurity not only has different interactions with its neighbors and a different polarizability from O^{2-} , it has a different charge. The details of the (unknown) charge compensation determine the very long-range nature of the electrostatic disturbance. In the alkali halides, the evidence^{7,11} is that the first neighbors of the H^- ion relax inward by a few percent because of the reduction in ionic size and in the short-range repulsive interactions. In the oxides, the first neighbors probably relax outward because of the reduced Coulomb attraction. We have performed model semi-classical, Mott-Littleton calculations^{22,23} for H^- in MgO that indicate that this occurs. Using first-nearest-neighbor host interaction parameters from Sangster,²⁴ and taking the pre-exponential Born-Mayer parameter B_{+-} for the H-Mg interaction to be half that for O-Mg, we find that the first-neighbor Mg^{2+} ions relax outward by 4.7% and the fourth-neighbor O^{2-} ions relax inward by 2.9%.

In view of the significant physical differences between substitutional H^- ions in the oxides and the alkali halides, it is somewhat surprising that the observed frequencies are so similar relative to the mass-defect values. The only noticeable difference in the results for ω/ω_{md} for the oxides and halides is that for the former, this ratio increases slightly with increasing cation mass, while for the latter, it decreases. Figure 8 is a log-log plot of local-mode

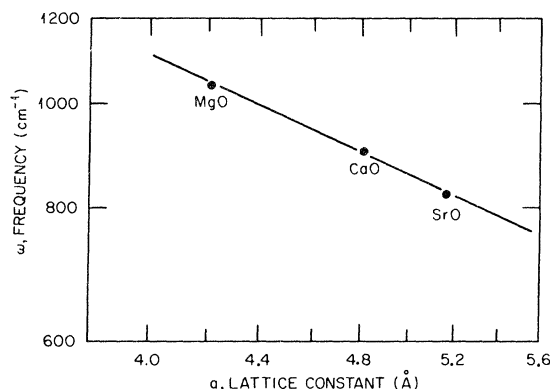


FIG. 8. Ivey plot of H^- -ion vibrational frequency versus lattice constant in the alkaline-earth oxides.

frequency versus lattice constant, which to a good approximation is a straight line as in the alkali halides,^{8,10} and has about the same slope as the corresponding plot⁸ for NaCl, KCl, and RbCl.

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¹A. Briggs, Ph.D. thesis, University of Bradford, 1970, unpublished; *J. Mater. Sci.* **10**, 729 (1975).

²See A. E. Hughes and B. Henderson, *Defects in Crystal-line Solids I*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972), and references therein.

³B. Henderson and H. T. Tohver, *Phys. Status Solidi* **51**, 761 (1972).

⁴B. Fritz, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon, London, 1965), p. 485; in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 480.

⁵R. Fieschi, G. F. Nardelli, and N. Terzi, *Phys. Rev.* **138**, A203 (1965).

⁶H. Bilz, D. Strauch, and B. Fritz, *J. Phys. Radium* **27**, Suppl. C2-3 (1966).

⁷T. Timusk and M. V. Klein, *Phys. Rev.* **141**, 664 (1966); T. Gethins, T. Timusk, and E. J. Woll, Jr., *Phys. Rev.* **157**, 744 (1967).

⁸M. V. Klein, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968), p. 429.

⁹D. Kühner and M. Wagner, *Z. Phys.* **207**, 111 (1967).

¹⁰H. Dötsch and S. S. Mitra, *Phys. Rev.* **178**, 1492 (1969).

¹¹R. F. Wood and B. N. Ganguly, *Phys. Rev. B* **7**, 1591 (1973).

- ¹²M. de Souza, A. Gongora, M. Aegerter, and F. Lüty, Phys. Rev. Lett. 25, 1426 (1970); M. de Souza and F. Lüty, Phys. Rev. B 8, 5866 (1973).
- ¹³R. J. Elliott, W. Hayes, G. D. Jones, H. F. MacDonald, and C. T. Sennett, Proc. R. Soc. (London) A289, 1 (1965).
- ¹⁴G. D. Jones and R. A. Satten, Phys. Rev. 147, 566 (1966).
- ¹⁵J. T. Gourley and E. R. Vance, Phys. Status Solidi B 77, K85 (1976).
- ¹⁶E. R. Vance and W. C. Mallard, Phys. Status Solidi B 91, K155 (1979).
- ¹⁷M. M. Abraham, C. T. Butler, and Y. Chen, J. Chem. Phys. 55, 3752 (1971).
- ¹⁸Y. Chen, D. L. Trueblood, O. E. Schow, and H. T. Tohver, J. Phys. C 3, 2501 (1970).
- ¹⁹K. H. Lee and J. H. Crawford, Jr., Appl. Phys. Lett. 33, 273 (1978); G. S. White, K. H. Lee, and J. H. Crawford, Jr., *ibid.* 35, 1 (1979).
- ²⁰W. A. Sibley, C. M. Nelson, and Y. Chen, J. Chem. Phys. 48, 4582 (1968).
- ²¹B. Henderson, S. E. Stokowski, and T. C. Ensign, Phys. Rev. 183, 826 (1969); B. Henderson, Y. Chen, and W. A. Sibley, Phys. Rev. B 6, 4060 (1972).
- ²²I. M. Boswarva and A. B. Lidiard, Philos. Mag. 16, 805 (1967); I. M. Boswarva, *ibid.* 16, 827 (1967).
- ²³M. Mostoller and R. F. Wood, Phys. Rev. B 7, 3953 (1973).
- ²⁴M. J. L. Sangster, J. Phys. Chem. Solids 34, 355 (1973).