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Far-Infrared Spectra of Iron-Doped MgO†

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The far-infrared absorption spectra of two iron-doped MgO samples were measured at 4.2, 20.3, and 77.4°K, using a large grating spectrometer. A line at 105.0 cm^{-1} was observed with a peak absorption coefficient of 1.5 cm^{-1} and a width of $\simeq$9.0 cm^{-1} at 20.3°K. This line is attributed, with the aid of oxidation and reduction data, to $MgO:Fe^{2+}$ at cubic sites. The transition $\Gamma_{5g}\rightarrow\Gamma_{3g}$, Γ_{4g} of $MgO:Fe^{2+}$ would be expected from crystal-field theory to be at around 200 cm^{-1}. However, Ham has postulated that vibronic effects could displace these levels to a position near 100 cm^{-1}. The location of the levels Γ_{3g}, Γ_{4g} at $\simeq$100 cm^{-1} would account for both anomalous quadrupole splitting in the Mössbauer spectrum of $MgO:Fe^{2+}$ at $T<14$°K and the rates of spin-lattice relaxation in the ground state. This prediction is now confirmed. Other lines were also observed in one or both of the samples investigated, but they are not related to the 105-cm^{-1} line. The origin of these lines is also briefly discussed.

I. INTRODUCTION

THE free-ion electronic configuration of Fe^{2+} is $3d^6$. The low-lying energy levels of this ion at cubic site in MgO according to static crystal-field theory[1] are shown in Fig. 1. The lowest electronic term under the cubic crystalline field of the MgO lattice is $^5T_2$. First- and second-order spin-orbit interactions further split this degenerate electronic state into six levels, the lowest three of which are labeled in octahedral double-group notation by Γ_{5g} (threefold degenerate), Γ_{3g} (twofold), and Γ_{4g} (threefold), respectively. (The states Γ_{3g} and Γ_{4g} are split by second-order spin-orbit interaction.) The positions of the Γ_{3g} and Γ_{4g} states are given by crystal-field theory to lie at $\Delta\sim2|\lambda|$ above the Γ_{5g} level where λ is the spin-orbit parameter.[1] Using the free-ion value $|\lambda|=100$ cm^{-1}, we have $\Delta\sim200$ cm^{-1}. The separation of levels Γ_{3g} and Γ_{4g} has the value $6\lambda^2/\Delta$ as given by crystal-field theory.[1] Since $\lambda^2/\Delta\sim1$ cm^{-1} for Fe^{2+} in MgO,[2] the separation of Γ_{3g} and Γ_{4g} is therefore $\sim$6 cm^{-1}. The ground-state paramagnetic resonance absorption of Fe^{2+} in MgO has been observed,[3,4] and it was found that resonance absorption is detectable only at very low temperatures ($\sim$4.2°K and below). This experimental result is consistent with the presence of a low-lying electronic level (or levels) in this system, even though its exact position cannot be determined, because at relatively high temperatures the excited Zeeman levels of the ground state (Γ_{5g}) can relax very rapidly through a two-phonon or Orbach process[5] so that the resonance absorptions to these excited Zeeman levels become too broad to be detected.

Recently, Pipkorn and Leider[6] and also Frankel and Blum[7] reported the observation of an anomalous quadrupole splitting in the Mössbauer spectrum of $MgO:Fe^{2+}$ below 14°K. It was pointed out by Ham[8] that such a splitting at low temperatures is explicable simply on the basis of crystal-field theory, as the result of the electric-field gradient produced at the nucleus by the valence electrons of Fe^{2+}, combined with the effect of random strains in the MgO crystals and suitably long electronic relaxation times. Ham inferred a value for the relaxation time among the three components of the Γ_{5g} ground state from the disappearance of the quadrupole splitting above 14°K and suggested that this relaxation time might be accounted for on the basis of an Orbach process involving a level at $\sim$100 cm^{-1}. He therefore predicted that the position of the first excited state (or states) of Fe^{2+} at cubic sites in MgO should be $\sim$100 cm^{-1} from the ground state instead of $\sim$200 cm^{-1} as calculated from static crystal-field theory. Since there are no sharp lines in the optical spectrum of $MgO:Fe^{2+}$ (Ref. 2), the only way to determine the actual position of the first excited states (Γ_{3g}, Γ_{4g}, or both) is by observing the direct transition from the ground state to these excited states in the far-infrared region of the spectrum. This would also furnish a direct check on Ham's theory to explain the anomalous low-temperature Mössbauer spectrum of $MgO:Fe^{2+}$.

II. EXPERIMENTAL TECHNIQUE

The far-infrared measurements were made using a large grating spectrometer, covering the spectral region from 10 cm^{-1} to 220 cm^{-1}, which has been described previously.[9] Figure 2 shows the experimental arrangement used in the present experiment. The spectrometer output is monochromatic far-infrared radiation

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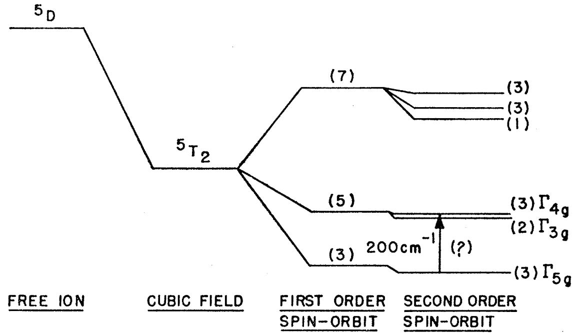

Fig. 1. Low-lying energy levels of MgO:Fe^{2+}.

(chopped at 10 cps), that is conveyed via a 1.1-cm. i.d. aluminum light pipe to the absorbing sample mounted at the bottom of a large metal Dewar. The sample-mounting technique will be described later. A crystalline quartz window separates the high-vacuum Dewar compartment from the relatively low-vacuum spectrometer tank[10] and allows grating to be changed while the Dewar remains at low temperatures. After passing through the sample, the radiation is conveyed by light pipe to the Texas Instruments germanium bolometer detector which operates at 4.2°K. The detector output (an electrical signal) is amplified approximately 1000-fold by the preamplifier and then fed into the signal channel of the Princeton lock-in amplifier. The lock-in amplifier reference channel receives a reference signal (chopped at 10 cps by the same chopper that chops the far-infrared signal) from the spectrometer so that the lock-in amplifier will amplify only those signals from the preamplifier that lie within a certain bandwidth (determined by a RC time constant) about the chopper frequency of 10 cps. The slowly varying dc output of the lock-in amplifier is recorded on chart paper.

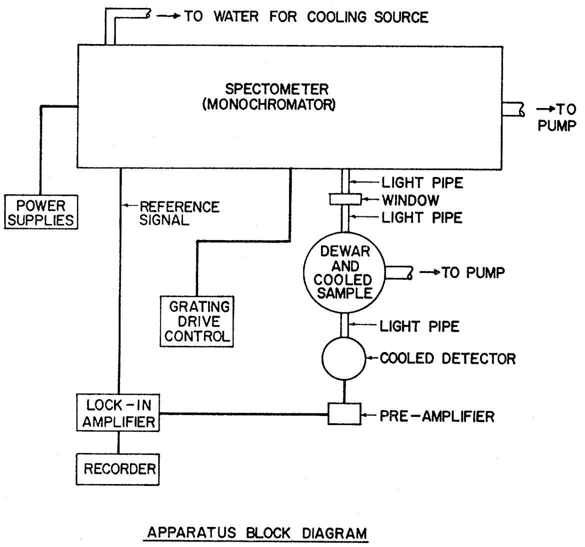

Fig. 2. Block diagram of the far-infrared spectrometer and auxiliary equipment.

The dimensions of the samples used in this experiment are typically 1 cm long and 1×1 cm in cross-sectional area. Because liquid hydrogen and liquid nitrogen absorb far-infrared radiation,[11] the samples cannot be cooled simply by immersion but have to be cooled by conduction. Special sample holders have been constructed for this purpose and are described in detail (together with sample-mounting techniques) elsewhere.[12] The temperature of the samples were monitored by means of a calibrated carbon resistor, and it was found that the sample temperatures were always within 0.5°K of the cryogenic liquid temperature. This difference is negligible for the purposes of this study.

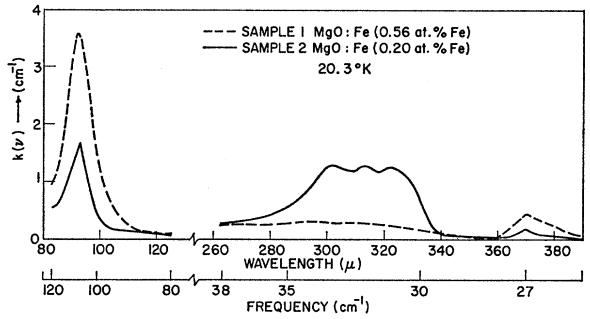

Fig. 3. Far-infrared absorption spectra of two iron-doped MgO samples at 20.3°K.

III. FAR-INFRARED SPECTRA

The far-infrared absorption spectra of two iron-doped MgO samples were taken following the experimental techniques described in Sec. II at liquid-hydrogen temperature. The far-infrared spectrum of a pure MgO sample was used as reference. The spectra obtained are shown in Fig. 3. The solid curve in this figure corresponds to the spectrum of a sample[13] containing approximately 0.20 at.% of Fe and the dashed curve corresponds to the spectrum of a more concentrated sample (~0.56 at.% of Fe).[14] Both samples showed a line at 105 cm^{-1}. The line in the less concentrated sample (hereafter known as sample No. 2) has a peak absorption at 20.3°K of ~1.5 cm^{-1} and a width of ~9

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[10] The entire spectrometer, including source and entrance optics, is housed in a large cylindrical aluminum tank. The latter can be evacuated to get rid of water vapor which absorbs far-infrared radiation.

[11] E. D. Nelson, J. Y. Wong, and A. L. Schawlow, Phys. Rev. **186**, 298 (1967).

[12] J. Y. Wong, Ph.D. dissertation, Stanford University, Stanford, Calif., 1967 (unpublished).

[13] This sample was obtained from Peter Llewellyn of Varian Associates, Palo Alto, Calif.

[14] This sample was obtained from D. N. Pipkorn and H. R. Leider of Lawrence Radiation Laboratory, Livermore, Calif.

cm^{-1}. The same line in the more concentrated sample (hereafter known as sample No. 1) has a peak absorption of 3.5 cm^{-1} at the same temperature, and its width is somewhat larger. This 105-cm^{-1} line is interpreted as the transition from Γ_{5g} to both Γ_{3g} and Γ_{4g}. The reason is as follows. We have looked at the far-infrared spectrum all the way to $\sim$220 cm^{-1} in frequency (the limit of our spectrometer) and no more lines were observed. As was pointed out in Sec. I, the separation of Γ_{3g} and Γ_{4g} is of the order of a few wave numbers. Since the resolution of our spectrometer in this particular frequency region is $\sim$2 cm^{-1}, we conclude that the separation of the Γ_{3g} and Γ_{4g} levels is actually less than $\sim$2 cm^{-1}. Since the separation of the Γ_{3g}, Γ_{4g}, and Γ_{5g} levels has been depressed by 100 cm^{-1} relative to Γ_{5g} from the static crystal-field value, it is conceivable, though rather surprising, that the separation between Γ_{3g} and Γ_{4g} levels is similarly depressed but to a slightly greater extent. We will postpone the discussion of this to a later section.

In addition to the 105-cm^{-1} line, a group of three lines was also observed in sample No. 2 at around 32 cm^{-1} (31.0, 32.0, and 32.9 cm^{-1}). Since this group of lines was not observed in sample No. 1, it cannot be due to iron impurities in MgO. Even though the temperature dependence of this triplet indicates that the splittings occur in the ground state and they are electronic lines, their origin is at present still unclear and will be discussed in a later section. There is yet another very weak line at 27 cm^{-1} which is present in the spectra of both samples. Since the strength of this line is roughly proportional to the square root of the amount of iron in these samples (even though the line is too weak for any quantitative correlation), it is likely that this line is due to pairs of iron impurities (Fe^{2+}, Fe^{3+} or Fe^{2+}—Fe^{3+}) in MgO. However, no further investigation of this line was carried out.

Because of the presence of the group of lines at around 32 cm^{-1} in sample No. 2, it is necessary for us to measure the far-infrared spectrum of this sample in greater detail to see if this group of lines and the 105-cm^{-1} line belong to the same or separate impurity systems. The spectra of this sample were taken at 4.2, 20.3, and 77.4°K and are shown in Fig. 4. No interconnecting lines at around 73 cm^{-1} were observed at 20.3 and 77.4°K. If the group of lines at around 32 cm^{-1} and the 105-cm^{-1} line belong to the same impurity system, one would expect to see interconnecting lines at $\sim$73 cm^{-1} at these temperatures. Hence, these two sets of lines belong to separate impurity systems in MgO and this finding is consistent with our assignment of the 105-cm^{-1} line.

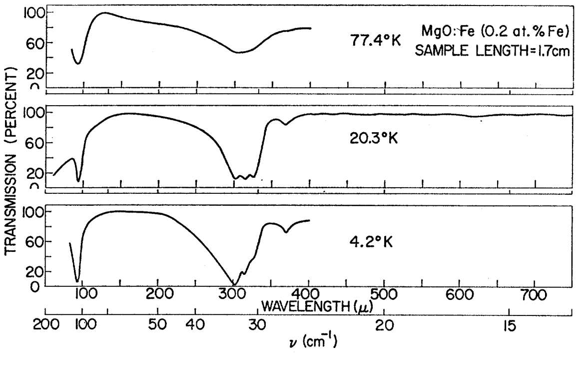

FIG. 4. Far-infrared absorption spectra of MgO:Fe (0.2 at. % Fe) at 4.2, 20.3, and 77.4°K.

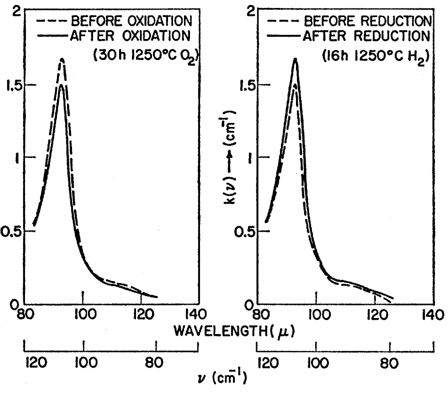

FIG. 5. Oxidation and reduction data on the 105-cm^{-1} line at 20.3°K.

IV. OXIDATION, REDUCTION, AND X-IRRADIATION DATA

In order to confirm our assignment of the 105-cm^{-1} line observed in both of the iron-doped MgO samples, a portion of sample No. 2 was oxidized at $\sim$1250°C by circulating molecular oxygen through the sample heated in a quartz tube inside an electric oven for approximately 30 h. The intensity of the 105-cm^{-1} line was monitored carefully before and after the oxidation and the result is shown in the left-hand portion of Fig. 5. The intensity of the line was seen to decrease upon oxidation as expected since some of the Fe^{2+} ions were converted into Fe^{3+} during the oxidation process. The same sample (namely, the portion after oxidation) was further reduced by circulating molecular hydrogen at $\sim$1250°C, and it was found that the intensity of the line increased as shown in the right-hand portion of Fig. 5. Again the result turned out to be what is expected since part of the Fe^{3+} ions (which are invariably present in a iron-doped MgO sample) were converted into Fe^{2+} ions during the reduction process. In short, the results of the oxidation and reduction experiments are consistent with the assignment of the 105-cm^{-1} line. The change in intensity of this line in these experiments appeared to be smaller than one would normally expect. This can be explained by the fact that the Fe^{2+} ions are very stable once they are formed in the MgO crystals because of the very high temperature (~3000°C) at which these crystals are grown. The temperatures used to oxidize or reduce the samples in our experiments (~1250°C) were relatively small compared with 3000°C and hence the conversion efficiency is probably rather poor.

We have also monitored the intensities of the group of lines at around 32 cm^{-1} before and after oxidation, and also before and after reduction, but in both instances we did not observe any detectable changes in the intensities of these lines.

We have also measured the far-infrared spectrum of sample No. 2 after it has been x-irradiated for ~8 h (50 kV and 5 mA) and compared it with the spectrum before irradiation. No significant changes in the irradiated spectrum were observed.

V. DISCUSSION

The observation of the 105-cm^{-1} line in two iron-doped MgO samples and the assignment of this line to the $\Gamma_{5g} \rightarrow \Gamma_{3g}$, Γ_{4g} transitions in $\mathrm{MgO{:}Fe^{2+}}$ support Ham's theory to account for the anomalous low-temperature Mössbauer spectrum of this system.[8] The position of the first excited state of $\mathrm{MgO{:}Fe^{2+}}$ as measured by far-infrared spectroscopy agrees very well with that predicted by Ham. The separations between the Γ_{3g}, Γ_{4g}, and Γ_{5g} levels and also that between Γ_{3g} and Γ_{4g} are partially quenched from the values predicted by static crystal-field theory. This is probably caused by the dynamic Jahn-Teller effect[15] operating in this system even though the ground-state g values agree with those calculated from static crystal-field theory. The fact that this is possible may appear to be somewhat surprising. However, a detailed dynamic Jahn-Teller calculation including both first- and second-order vibronic effects in d^1 impurity systems in $\mathrm{Al_2O_3}$ shows that this is indeed possible due to the complicated way the second-order terms come into calculation.[16] It would be interesting to carry out a detailed Jahn-Teller calculation on this system similar to that of $\mathrm{Al_2O_3{:}Ti^{3+}}$. However, the mathematics would be very much more involved.

The group of lines around 32 cm^{-1}, which appeared in only one of the samples, could be due to defects or other impurities in MgO. We have looked at two other MgO samples containing only vanadium and nickel as impurities respectively and no lines were observed in either of them. The origin of this group of lines is still unclear at the present time.

The assignment of the 105-cm^{-1} line is also consistent with the result of another independent experiment, namely, the measurements of the spin-lattice relaxation time for the ground state (Γ_{5g}) of $\mathrm{Fe^{2+}}$ at cubic sites in MgO as a function of temperature by Hartman *et al.*[17] They found that the low-temperature relaxation data can be described by a one-phonon direct process plus a two-phonon Orbach process. By fitting their data to these two processes they predicted the position of the first excited state of this system to be ~100 cm^{-1}. This also agrees with our direct measurement.

VI. CONCLUSION

The far-infrared spectra of two iron-doped MgO samples were measured at 20.3°K and a line at 105.0 cm^{-1} was observed in both of the samples. This line is interpreted as the $\Gamma_{5g} \rightarrow \Gamma_{3g}$ and Γ_{4g} transitions of $\mathrm{MgO{:}Fe^{2+}}$ at cubic sites. This is supported by oxidation and reduction data. The present assignment is also in good agreement with the position of the $\Gamma_{5g} \rightarrow \Gamma_{3g}$, Γ_{4g} transitions predicted by Ham to account for the quadrupole doublet in the Mössbauer spectrum of $\mathrm{MgO{:}Fe^{2+}}$ at $T < 14$°K and with the spin-lattice relaxation data on the ground state. A group of three lines at around 32 cm^{-1} was also observed in one of the samples and its origin is at present unknown and probably due to other impurities or defects in MgO. A very weak line at 27.0 cm^{-1} was also observed which could be due to pairs of iron impurities in magnesium oxide.

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