01 Jan 1974

I.R. Lattice-Vibration Spectra of MnF2

James Roger Weaver
Missouri University of Science and Technology, weaverjr@mst.edu

C. A. Ward

G. S. Kovener

Ralph William Alexander
Missouri University of Science and Technology, ralexand@mst.edu

Recommended Citation

I.R. LATTICE–VIBRATION SPECTRA
OF MnF$_2^*$

J. H. WEAVER, C. A. WARD, G. S. KOVENER
and R. W. ALEXANDER

Department of Physics and Graduate Center for Materials Research, University of Missouri, Rolla
Rolla, Mo. 65401, U.S.A.

Abstract—The room temperature reflectivity of MnF$_2$ has been measured in the far i.r. between 50 and 800 cm^{-1}. The reflectivity spectra show four i.r.-active modes which can be identified as E_u and A_{2u} modes. The spectra also show structure which might be related to multiphonon effects. The dielectric functions were determined by fitting the reflectivity data with classical oscillator parameters.

Recent studies of the i.r.-active[1] and Raman-active[2] phonon modes of MnF$_2$ have provided a good qualitative understanding of the lattice dynamics of uniaxial MnF$_2$. Far i.r. and Raman experiments have revealed magnon and multimagnon modes of antiferromagnetically ordered MnF$_2$. Detailed information concerning the magnitudes of the dielectric response functions at room temperature, however, is lacking. Such information is crucial for a detailed study of surface electromagnetic wave propagation on anisotropic MnF$_2$[3]. The results discussed here provide reliable dielectric functions and reveal previously unreported structure in the reflectivity which may be related to multiphonon effects.

The divalent fluorides MnF$_2$, CoF$_2$, FeF$_2$, NiF$_2$, ZnF$_2$ and MgF$_2$ crystallize in a rutile structure, D_{4h}, with 6 atoms per unit cell and an irreducible representation of $A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$ [4, 5]. Of the 11 fundamental modes of vibration, 4 are Raman active[2] (A_{2g}, B_{1g}, B_{2g} and E_g) and 4 are i.r. active[1, 6–8]. Three of the optic modes have symmetry E_u and can be excited by radiation polarized with the electric field vector perpendicular to the $\hat{c}$-axis, $\mathbf{E} \perp \hat{c}$, while the fourth has symmetry A_{2u} and interacts with radiation polarized with $\mathbf{E} \| \hat{c}$.

Far i.r. reflectivity measurements were performed between 50 and 800 cm^{-1} using a Beckman (RIIC) FS-720 Fourier transform spectrometer operated in a symmetric mode. Two large, oriented, single crystals of MnF$_2$ with exposed basal plane and another plane containing the a- and c-axes (CA) planes were obtained from Optovac and were polished to quarter-wave (Na doublet) flatness. The measurements were performed at near-normal incidence at room temperature using a wire grid polarizer when studying the CA face. The basal plane reflectivity was also measured at 45° with s- and p-polarized radiation. The reflectivity of a polished Al sample of the same geometry mounted symmetrically on the sample holder was used as a standard. Suitable filtering extended the range of the interferometer beyond the cut-off of the conventional black Polyethylene lens. The apodized resolution was 4 cm^{-1}.

The reflectivity spectra of MnF$_2$ are shown in Figs. 1 and 2. Three strong features are apparent for $E \perp c$ and one for $E \| c$, in qualitative agreement with the results of Parisot[1]. Additional fine structure is observed which Parisot was not able to resolve, presumably because the reflectivity was small in that spectral region.

The weak features of Fig. 1 are difficult to explain but are believed to be genuine. The reflectivity, $R(\nu)$, has a dip at the reststrahl peak near 180 cm^{-1}, a plateau near 230 cm^{-1} and a distinct foot at about 280 cm^{-1}. These features were observed with both samples, and the reflectivity of the basal plane was indistinguishable from that of the CA plane measured at near-normal incidence with polarized light. The polarized 45° data revealed the same features and satisfied the requirement that R_s^2 (45°) = R_p(45°). Finally, the dielectric function was
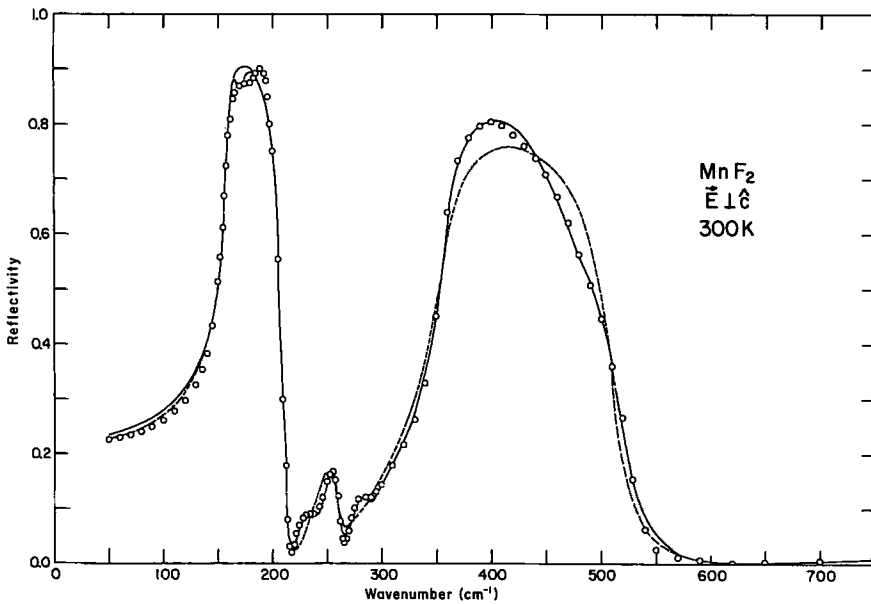
Fig. 1. Near-normal incidence reflectivity of MnF_2 with $\vec{E}\perp\hat{c}$. The data are represented by circles, a three-phonon fit by the dashed line, and a best, seven-phonon fit by a solid line.
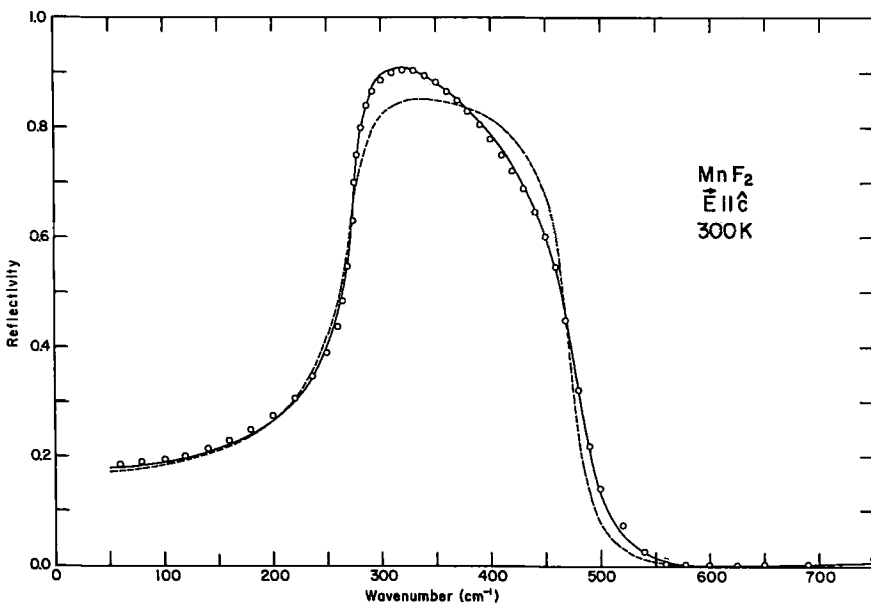

Fig. 2. Near-normal incidence reflectivity of MnF_2 with $\vec{E}\parallel\hat{c}$. The data are represented by circles, a single-phonon fit by the dashed line, and a best, three-phonon fit by a solid line.

calculated, as will be discussed shortly, and the 45° s- and p-polarized reflectivities were calculated. Comparison with the measured spectra was excellent. Other studies of the divalent fluorides[6–8] have revealed features which, while less clearly defined, are similar to those shown in Fig. 1.

The $R(\nu)$ spectra were Kramers–Kronig analyzed to determine the dielectric functions. The magnitudes of the calculated quantities were, however, strongly dependent on the high and low frequency extrapolations and were used only to obtain first approximations to the oscillator

parameters. The dielectric functions were assumed to be adequately described by classical, noninteracting harmonic oscillators so that

$$\bar{\epsilon}(\nu) = \epsilon_\infty + \sum_j \frac{s_j \nu_j^2}{\nu_j^2 - \nu^2 - i\gamma_j \nu_j \nu}, \qquad (1)$$

where ν_j is the frequency of the jth oscillator and s_j and γ_j are the strength and damping parameters, respectively. An iterative computer program was used to vary the phonon parameters to determine best fits to the experimental spectra. The results are shown in Figs. 1 and 2. For $E \perp \hat{c}$, a set of three oscillators was chosen to correspond to the E_u modes, and a single oscillator corresponding to A_{2u} was used for $E \parallel \hat{c}$. The fits shown are only partially satisfactory.

To improve the three-phonon fit of Fig. 1, a coupling parameter was introduced as discussed by Barker and Hopfield[9]. Two modes were assumed to have a coupled damping parameter, while the third was allowed to respond independently. The calculated spectra did not appreciably improve the fit shown in the figure. It is not known if a completely coupled, three-phonon system or frequency-dependent damping would give a better fit. In light of the new structure observed near 230 and 280 cm⁻¹, it appears that multiphonon or forbidden mode effects should be considered before coupling or frequency-dependent damping is pursued further.

The dip at the reststrahl peak near 180 cm⁻¹ is similar to what has been reported for numerous other I.R. active materials. Berreman[10] has attributed such reststrahl structure to domes or pits on the surface. Our crystals were flat to ~ 0·1 μm, but a measure of the presence or concentration of domes or inclusions is not available.

The reflectivity spectrum shown in Fig. 2 and that reported by Parisot[1] for $E \parallel \hat{c}$ show a distorted shoulder on the high frequency side of the reststrahl maximum. Similar shoulders have been observed for CoF₂[6], NiF₂[6], ZnF₂[8] and MgF₂[8]. For MgF₂, the shoulder was sufficiently pronounced that Barker[8] introduced a weak, forbidden mode to improve the oscillator fit. A two-phonon fit for MnF₂ did not give satisfactory agreement with experiment. (Distortion of the $R(\nu)$ spectrum arising from non-normal incidence or

Table 1. The oscillator parameters used to obtain reflectivity fits shown in Figs. 1 and 2

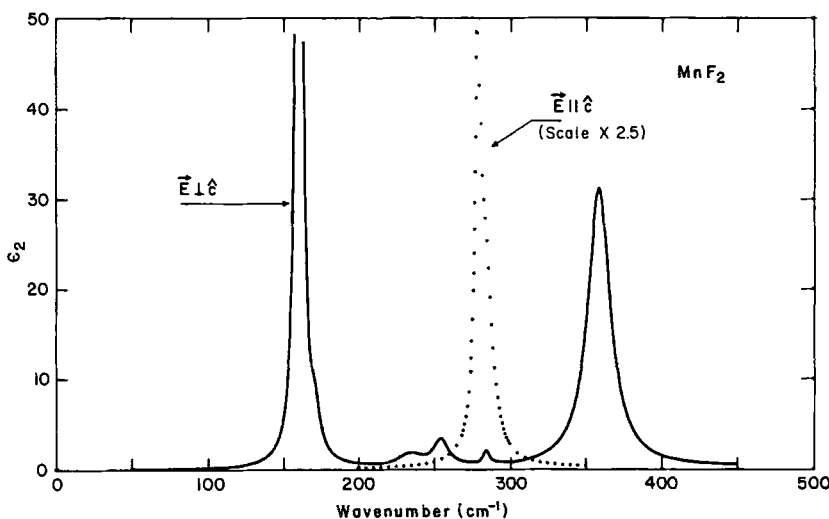| ν_j(cm⁻¹)	s_j	γ_j	$\bar{\nu}_j$(cm⁻¹)	s_j	γ_j
		$E \perp \hat{c}$			
(Three-phonon fit)			(Seven-phonon fit)		
160·0	3·774	0·0283	160·2	3·803	0·0254
			170·9	0·168	0·0425
			233·7	0·113	0·0837
251·4	0·224	0·0780	254·1	0·131	0·0459
			284·1	0·0256	0·0174
354·4	1·534	0·0725	358·9	1·539	0·0494
			470·7	0·041	0·2273
	$\epsilon_\infty = 1·92$			$\epsilon_\infty = 2·04$	
		$E \parallel \hat{c}$			
(Single-phonon fit)			(Three-phonon fit)		
277·2	3·735	0·0676	279·0	1·460	0·0129
			283·8	2·202	0·0389
			369·6	0·224	0·7333
	$\epsilon_\infty = 1·97$			$\epsilon_\infty = 2·01$	

Fig. 3. The imaginary parts of the dielectric functions of MnF₂: solid line for $E \perp \hat{c}$, dotted line for $E \parallel \hat{c}$.

incomplete polarization is believed to be small, particularly since no structure was observed for $E\|\hat{c}$ near 180 cm^{-1}.)

To obtain reliable dielectric functions from the reflectivity spectra of Figs. 1 and 2, additional oscillators were introduced, and the computer was allowed to search for a best fit. Seven oscillators produced the fit shown in Fig. 1 for $E\perp\hat{c}$ and three gave the excellent fit shown in Fig. 2 for $E\|\hat{c}$. The oscillator parameters used for the fits are given in Table 1. The non-normal incidence reflectivity was calculated with the $E\perp\hat{c}$ dielectric functions, and the agreement with experiment at 45° for s- and p-polarized radiation was excellent.

The imaginary parts of the dielectric functions for $E\perp\hat{c}$ and $E\|\hat{c}$ are shown in Fig. 3. For $E\perp\hat{c}$, two strong modes are clearly visible, as is the weak mode at 254·1 cm^{-1}; these can be attributed to the E_u modes. The identification of the additional features at 233 and 284 cm^{-1}; would be largely speculative in the absence of detailed phonon dispersion curves and temperature dependent studies of MnF$_2$ and must be postponed until such information is available. It is clear, however, that the spectra of MnF$_2$ are more complicated than previously reported.

REFERENCES

1. Parisot G., *C. R. Acad. Sci.* **B265**, 1192 (1967)
2. Porto S. P. S., Fleury P. A. and Damen T. C., *Phys. Rev.* **154**, 522 (1967).
3. Kovener G. S., Alexander R. W., Tyler I. L. and Bell R. J., to be published.
4. Narayanan P. S., *Proc. Ind. Acad. Sci.* **32A**, 279 (1950).
5. Moller K. D. and Rothschild M. G., *Far Infrared Spectroscopy*. Wiley-Interscience, New York, 1971.
6. Balkanski M., Moch P. and Parisot G., *J. Chem. Phys.* **44**, 940 (1966).
7. Hunt G. R., Perry C. H. and Ferguson J., *Phys. Rev.* **134**, A688 (1964).
8. Barker A. S., Jr., *Phys. Rev.* **136**, A1290 (1964).
9. Barker A. S., Jr. and Hopfield J. J., *Phys. Rev.* **135**, A1732 (1964).
10. Berreman D. W., *Phys. Rev.* **163**, 855 (1967).