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Infrared spectrum of FeF$_2$

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Résumé. — Les spectres de réflexion infrarouge à température ambiante sont présentés pour le composé FeF$_2$
de structure rutile. Ils sont analysés par deux méthodes : une méthode classique de réponse en terme d’oscillateurs,
et une analyse de Kramers-Kronig. Une faible bande supplémentaire apparaît dans le spectre correspondant à une
polarisation parallèle à l’axe. Une interprétation par un processus à deux phonons est proposée. Par contre, la
bande supplémentaire mise en évidence par l’analyse de Kramers-Kronig pour la polarisation perpendiculaire à
l’axe n’est pas expliquée.

Abstract. — Infrared reflectivity spectra at room temperature are presented for the rutile structure compound
FeF$_2$ and analysed by two methods : a classical oscillator response and a Kramers-Kronig analysis. A weak sup-
plementary sideband appears in the spectrum for polarization parallel to the axis. An interpretation by a two-
phonon process is proposed. The supplementary band revealed by the Kramers-Kronig analysis for polarization
perpendicular to the axis is however not explained.

Among the four fluoride compounds MgF$_2$, MnF$_2$, ZnF$_2$ and FeF$_2$, which crystallize with the rutile struc-
ture (P 42/mnm) ; iron fluoride is of particular inte-
rest : in addition to the direct magnon-phonon coupl-
ing observed by neutron scattering techniques [1]
a magnetostriiction induced coupling is observed
between the para-antiferromagnetic ordering and the
first order Raman spectrum of phonons [2]. Contrary
to the three other compounds the only infrared optical
measurements performed until now on this crystal
are a rather incomplete transmission spectrum [3].
A group character analysis shows that this material
should present three doubly degenerate infrared active
modes (3 $E_J$) with polarization perpendicular to the
four fold c axis and one non degenerate mode parallel
to the c axis (A$_{2u}$).

We report here our measurements on this material
at room temperature. A more complete analysis includ-
ing a model interpretation and temperature effects
will be given elsewhere.

1. Experimental. — The single crystal sample of
FeF$_2$ provided by Cristal Tec (Leti-Grenoble) was
oriented by X-rays then cut and polished by the usual
techniques. Our sample is optically clear and light
yellow in colour. A rectangular sample 15 by 10 by
4 mm was cut with c axis parallel to largest edge.

Room temperature reflection spectra were taken in
the range 350-5 000 cm$^{-1}$ with an infrared spec-
trometer built in our laboratory. The angle of incidence
was less than $6^\circ$. In the 40-400 cm$^{-1}$ frequency range
we used a Fourier transform spectrometer. The
measured reflectivities are shown in figures 1, 2.

2. Discussion. — Two methods have been used for
the analysis of the reflectivity spectra : one method

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Fig. 1. — Room temperature reflection spectra of FeF$_2$ for a
polarization parallel to the axis. The full line is the measured reflect-
itivity whereas the dashed line represents reflectivity calculated by
an oscillator model.
using classical oscillator dispersion theory and the other using a Kramers-Kronig analysis.

The first method consists in introducing 3 oscillators for the polarization perpendicular to the c axis (E_u modes) and one oscillator for the polarization parallel to the axis (A_2u mode) (plus one weak mode—see later). From this model it is possible to calculate the dielectric constant tensor $\varepsilon(\omega)$ and then the reflectivity spectrum for each of the two polarizations. By a fitting procedure, values for the strengths, frequencies and line widths of each oscillator are obtained so that the measured infrared reflectivity is correctly reproduced. The infinite dielectric constant was obtained by extrapolating measurements of the reflection index in the visible region using the Abbe refractometer. The results are shown in figures 1 and 2. The mode parameters are given in table I. We present, too, the longitudinal mode frequencies obtained with the values of dampings in response function equal to zero (Barker [5]).

The reflectivity is well described for the A_2u mode but is poorly described in the 200-300 cm\(^{-1}\) region for the polarization perpendicular to the c axis.

It is evident that the response function of this crystal cannot be simply described by a classical oscillator dispersion model.

To obtain the response function

$$\varepsilon(\omega) = \varepsilon_\infty + \sum \frac{\omega^2}{\omega^2 - \omega^2 - i \Gamma}$$

we apply a Kramers-Kronig analysis.

The phase shift of the electromagnetic field after reflection is given by [11]

$$\theta(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\ln R(\omega') - \ln R(\omega)}{\omega^2 - \omega'^2} d\omega'$$

We report the value obtained by K.K. analysis for $\varepsilon(\omega)$ in figures 3, 4 for the both polarizations.

We also report the value of $\varepsilon(\omega)$ obtained from the classical oscillators analysis.

For the polarization parallel to the c axis both analyses give nearly identical results, in particular we find the weak side band in the 430 cm\(^{-1}\) region (note that a weak supplementary oscillator has been introduced in the oscillator dispersion analysis).

However for the polarization perpendicular to the c axis the two analyses give very different results:

- in the 200-270 cm\(^{-1}\) region we obtain two peaks at 250 and 310 cm\(^{-1}\);
- the band at 420 cm\(^{-1}\) looks quite different.

We report in table I the values of the transverse
mode frequencies (taken at the peaks of $\tilde{E}(\omega)$) and of the longitudinal mode frequencies (taken at some of the zeros of the $\tilde{E}(\omega)$ function).

If we take into account the anharmonicity of the crystal the response to an electromagnetic field can be written as [6]

$$\tilde{e}(\omega) = \tilde{e}(\infty) + 4 \pi \chi_2(\omega)$$

with

$$\chi_2(\omega) = \sum_j \tilde{M}_j \tilde{M}_j G_j(\omega)$$

$\tilde{M}_j$ is the renormalized linear dipole moment and

$$G_j(\omega) = \frac{2 \omega_j}{\omega_j^2 - \omega^2 - 2 \omega \left[ \Pi_j(\omega) - \Pi_{jj} G_j(\omega) \right]}$$

where

$$\Pi_j(\omega) = \Delta_j(\omega) - i \Gamma_j(\omega)$$

is the self energy of the phonon $j$ and

$$\Pi_{jj}^2(\omega) = \Delta_j^2(\omega) - i \Gamma_j^2(\omega)$$

is a term which defines the coupling between the modes $j$ and $j'$. If the coupling between oscillators is not too strong we can neglect the $\Pi_{jj}^2$ terms.

In very anharmonic crystals or in a crystal with a density of modes having a very high value in some region the imaginary part of the self energy function may present strong maxima and the function $\tilde{E}(\omega)$ can present supplementary peaks. For instance, the band at 430 cm$^{-1}$ in the spectrum for polarization parallel to the $c$ axis is certainly due to a maximum in the $\Gamma_j(\omega)$ imaginary part of the self energy of the $A_{2u}$ phonon.

Such a side band appears in the infrared spectrum of MgF$_2$ at 556 cm$^{-1}$ [5], [8]. In this last case using the calculated phonon dispersion curves [9] together with the appropriate selection rules for two-phonon processes at the $\Gamma$ ($q = 000$), $X$ ($q = \frac{1}{2}00$), $M$ ($q = \frac{1}{4}10$) and $Z$ ($q = 00\frac{1}{2}$) points, one finds only two allowed combinations for the interpretation of the side band frequency and for a polarization parallel to the axis. These are two $X_1 \otimes X_2$ combinations:

- $X_1$ at 137 cm$^{-1}$ combined with $X_2$ at 413 cm$^{-1}$ and
- $X_1$ at 267 cm$^{-1}$ combined with $X_2$ at 296 cm$^{-1}$.

The sum of frequencies are 550 cm$^{-1}$ and 563 cm$^{-1}$, respectively. As the two modes implicated in the first process correspond precisely to very strong peaks in the one phonon density of states we believe that this combination is responsible alone for the observed side band intensity.

Applying the same arguments in the case of FeF$_2$ the corresponding combined modes are [10] :

- $X_1$ at 110 cm$^{-1}$ combined with $X_2$ at 319 cm$^{-1}$ and
- $X_1$ at 222 cm$^{-1}$ combined with $X_2$ at 255 cm$^{-1}$.

which give for the frequency sum 429 cm$^{-1}$ and 477 cm$^{-1}$, respectively. As the side band frequency
is 437 cm\(^{-1}\) in this case one obtains here a confirmation of the previous interpretation.

The spectrum for polarization perpendicular to the c axis may be explained in the same way by the self energy of Eu\(_{2}\) mode. We think that the Eu\(_{2}\) mode frequency is close to 310 cm\(^{-1}\). The complex line width, \(\Gamma_{\text{Eu}_2}(\omega)\), of this mode changes the shape of the Eu\(_3\) mode spectrum and produces a side band at 250 cm\(^{-1}\).

The interpretation of this side band is not clear at present and a systematic study of the temperature effects on the infrared spectrum seems to be desirable in order to clarify the origin of the side band. This study is presently being carried out.

References

[10] To be published.