

LIGHT SCATTERING OF TRANSITION METAL IONS

II: Correlation of Electronic Raman Transitions and Magnetic Susceptibilities*

D. H. BOAL, J. T. HOFF, P. GRUNBERG,
J. PREUDHOMME, and J. A. KONINGSTEIN
Chemistry Dept., Carleton University, Ottawa, Canada

(Received 30 April; in revised form 14 August, 1973)

Abstract. Electronic Raman transitions to levels of divalent cobalt and iron ions of the compounds CoF_2 , Co_2GeO_4 and FeF_2 , Fe_2GeO_4 are discussed. From the position and wave functions of the low lying electronic levels it is possible to calculate the magnetic susceptibility of these compounds. Our calculations suggest that a reasonable agreement exists between the calculated value from the Raman spectra and the measured values of χ_m as function of the temperature of the samples.

1. Introduction

The observation of Raman transitions to energy levels of transition metal ions of solids, at temperatures above the Neel point, is a relatively new area of electronic Raman spectroscopy. It appears now that the intensity of such transitions is sufficiently high to permit a study of the positions of energy levels of compounds which contain small amounts of the ions [1–5]. In the case [4] of black Co_2GeO_4 the observed electronic transitions of Co^{2+} were used (i) to establish an energy level diagram and (ii) to evaluate the spin-orbit coupling parameter and the trigonal distortion parameter of the crystal field. This type of computation yields, apart from the position of low lying electronic levels, also the wave functions of such states and employing the latter data, it is straightforward to obtain values of the magnetic susceptibility χ_m of the compound as a function of the temperature. It is, however, worthwhile to recall that there are limitations in using this method to obtain values of χ_m . Not all crystals containing transition metal ions are suitable candidates for an investigation of the position of their low lying electronic levels by means of electronic Raman spectroscopy. The ions [7] should have a degenerate ground state for a site symmetry in the crystal of either O_h or T_d .

For the purpose of electronic Raman spectroscopy the interest focusses on the splitting of a ground term as a result of consideration of spin-orbit coupling and/or the effect of a surrounding of lower symmetry than O_h or T_d . From these considerations, Raman transitions are expected to occur between 10 cm^{-1} and 2000 cm^{-1} . The limits of detection of electronic Raman transitions to these states is then set primarily by Rayleigh scattering because the electronic transitions are formally allowed.

For instance, Co^{2+} is a suitable candidate if it is imbedded in a crystal with a local

* Research supported by the National Research Council of Canada.

site symmetry of O_h but not so for T_d . The ground term in the latter case is a ${}^4A_{2g}$ orbitally non-degenerate state which is not split to first order by either spin-orbit coupling or environments of lower symmetry. This state is, however, split by an external magnetic field. By and large many other transition metal ions satisfy the conditions mentioned above which permit the application of the method of electronic Raman spectroscopy as a tool to establish the positions of low lying electronic states which can be used to calculate the magnetic susceptibility. We report here the results of such a study for the compounds Fe_2GeO_4 , $CoGeO_4$, CoF_2 and FeF_2 .

2. The Raman Spectra of CoF_2 , FeF_2 , Co_2GeO_4 and Fe_2GeO_4

The Raman spectra of single crystals CoF_2 , FeF_2 , $CoGeO_4$ and Fe_2GeO_4 with shifts $< 2500\text{ cm}^{-1}$ contain two different types of transitions; the phonons and electronic effects. The germanates are normal spinels and belong to the space group O_h^7 and the cobalt and iron ions occupy sites of D_{3d} symmetry. The Raman active phonons of the normal spinels are of symmetry A_{1g} , E_g and T_{2g} ($3 \times$). In an earlier publication [4] of this laboratory the Raman spectra of a series of normal spinels were discussed which included Co_2GeO_4 . The spectrum of this cubic compound was studied employing a reflection technique and this method was also chosen to record and assign [8] the spectrum of Fe_2GeO_4 . The results are shown in Table I. Phonons

TABLE I
Phonons and electronic Raman transitions (cm^{-1}) of some compounds containing Co^{2+} and Fe^{2+}

Symmetry:	Phonons				Electronic transitions		
	T_{2g}	E_g	T_{2g}	A_{1g}	(O_h)		
CoO_4	—	302	643	757	229	900	961 ^a
Fe_2GeO_4	196	302	651	753	468(vw)	935(vw broad) ^b	

^a All transitions contain the species E_g .

^b Tensors not available.

Symmetry:	Phonons				Electronic transitions			
	B_{1g}	E_g	A_{1g}	B_{2g}	(D_{4h})			
CoF_2		256	370		787	1077	1252	1368 ^a
FeF_2	73	257	340	496	990	1116	1352(broad) ^b	

^a All transitions contain the species A_{1g} .

^b The tensors are a mixture of $A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g$.

The following are the temperatures for which the data were obtained:

CoF_2 , FeF_2 ; 80 K Co_2GeO_4 , Fe_2GeO_4 ; ~ 200 K.

For the phonons of the germanates see Reference 4.

For the phonons of the fluorides see Reference 7.

and electronic effects are distinguished from a consideration of (i) the position of corresponding phonons, (ii) their symmetry and (iii) the temperature dependent width at half height of the electronic Raman bands. From Table I it is seen that the frequency of phonons in both spinels is approximately equal and other Raman data for spinels suggest that the missing phonon of T_{2g} symmetry of Fe_2GeO_4 is situated $< 200 \text{ cm}^{-1}$. The energy level scheme for Fe^{2+} and Co^{2+} in the spinels is different from that for these ions in rutile fluorides, and this is reflected in the electronic Raman spectra of these compounds. Electronic transitions in Co_2GeO_4 have been reported [4] and

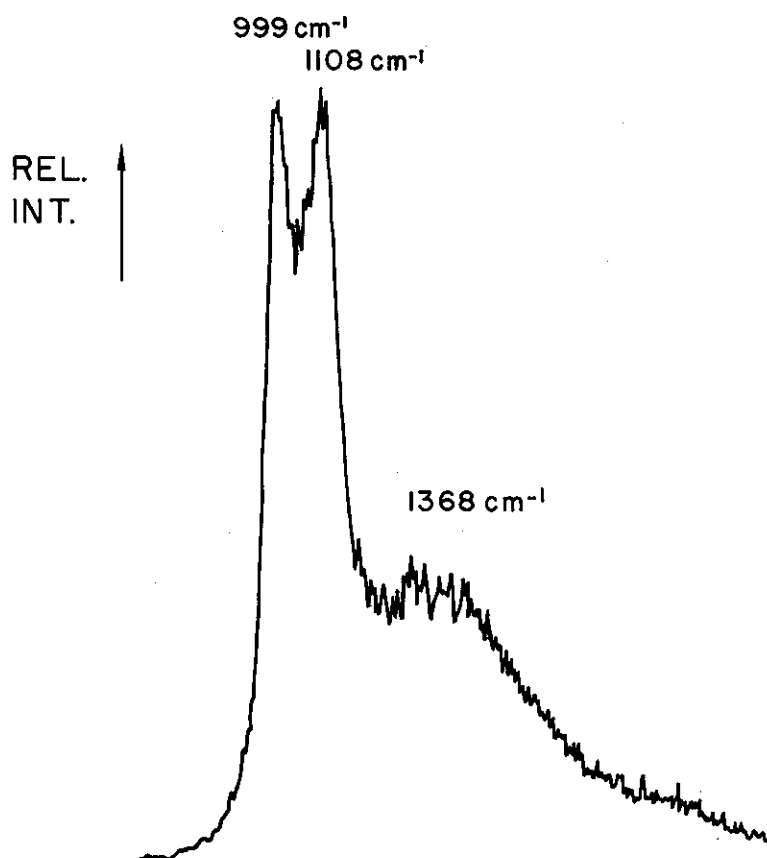
$$X' Y'$$


Fig. 1. Part of the 80K Raman spectrum of FeF_2 . X' and Y' refer to the local axes of the Fe^{3+} ion. The local axes can be brought parallel to the crystallographic a and b axes by a rotation of 45° around the local z axis (which is also the c -axis). For the complete Raman spectrum of FeF_2 see Figures 1 and 2 of Reference 19. The symmetry of the Raman lines given in Table I is derived from the measurement of the individual components of the scattering tensor.

discussed earlier and the data of Fe_2GeO_4 are reported here for the first time. In the latter compound the intensity of electronic effects is weak and the polarization measurements are incomplete.

The compounds FeF_2 and CoF_2 have the rutile structure and the Raman active phonons⁹ at $K \approx 0$ are of the species $A_{1g} + B_{1g} + B_{2g} + E_g$ of the space group D_{4h}^{14} . The position of some of the phonons and assignment is well known and all data are given in Table I. The position of the electronic Raman transitions above the Neel temperature of CoF_2 were recently observed [5, 6] and we report here also the relevant data of Fe^{2+} in FeF_2 . An absorption band at 1115 cm^{-1} was recorded in the infrared spectrum of FeF_2 and this band was assigned [10] to an electronic transition. Thus there is good agreement between the infrared and Raman measurements reported here*. The electronic Raman effect is very strong as can be seen in Figure 1. The Raman spectrum of this crystal was studied in the normal way and presently it is felt that the differences of intensities of FeF_2 and Fe_2GeO_4 is mainly due to the fact that the latter compound had to be studied in reflection of the laser light from the crystal. The spectra of Fe_2GeO_4 were excited with $\lambda_0 = 4880 \text{ \AA}$. The position of electronic Raman transitions given in Table I are for temperatures of the samples which are above the Neel temperature. However, both CoF_2 and FeF_2 become anti-ferromagnets below 37K and 78K and consequently changes in the Raman spectra do occur below these temperatures [6]. Thus, we would like to emphasize here that we are discussing scattering to either phonons or electronic states of the $3d$ configuration of single transition metal ions (the para magnetic state).

3. Electronic Levels, Wavefunctions and Magnetic Susceptibility

Iron in the $2+$ valency state has the electronic configuration $[\text{Ar}]3d^6$ and that for Co^{2+} is $[\text{Ar}]3d^7$. Thus the compounds CoF_2 and Co_2GeO_4 are Kramers salts in contrast to FeF_2 and Fe_2GeO_4 of which the electronic states do not split if the crystals are exposed to an external magnetic field.

Since for transition metal ions in solids L is no longer a good quantum number, it is customary to characterize the basis functions of Co^{2+} and Fe^{2+} by $|L_z, S_z\rangle$. For the $^4T_{1g}$ manifold of Co^{2+} six basis functions were chosen and for $^5T_{2g}$ of Fe^{2+} all fifteen are required to explain the degeneracy lifting effect of spin-orbit interaction combined with the effect of a field of rhombic symmetry [11] as happens to be the case for FeF_2 .

The Hamiltonian for the divalent iron and cobalt ions at the D_{3d} site of the spinel unit cell assumes the form [12].

$$\mathcal{H} = A(L \cdot S) + \delta(L_z^2 - \frac{2}{3}). \quad (1)$$

Here $\nu = F\lambda$ where F is a factor which measures the effect of mixing of 4F and 4P states of Co^{2+} . In the free ion $F = -\frac{3}{2}$. For Fe^{2+} this type of mixing does not occur

* A very intense Raman line with $\lambda\nu = 1082 \text{ cm}^{-1}$ was also observed recently by S. R. Chinn and H. J. Zeiger. Proceedings of the Magnetism Conference, *A.I.P. Conference Proceedings* 5, 344 (1971).

and $F=1$. The value of the spinorbit coupling parameter λ for an ion in a crystal is in general not equal to that for the free ion and mostly is found that $|\lambda_{\text{free ion}}| > |\lambda_{\text{crystal}}|$. A plot of the positions of low lying energy levels of Fe^{2+} vs δ/λ in a surrounding of D_{3d} symmetry and based on the form of the Hamiltonian given by Equation (1), is shown in Reference 18. It is true that only two electronic Raman transitions to levels of Fe^{2+} in Fe_2GeO_4 are detected and it seems somewhat presumptuous to use these data to obtain a value of δ/λ . However, if the condition is imposed that the

TABLE II
Parameters of Co^{2+} and Fe^{2+} ions in certain compounds

	$\lambda(\text{cm}^{-1})$	$A(\text{cm}^{-1})$	$\delta(\text{cm}^{-1})$	
Co_2GeO_4	-180	220	-350	
Fe_2GeO_4	-100	-100	+600	
	$\lambda^*(\text{cm}^{-1})$	$A^*(\text{cm}^{-1})$	$A(\text{cm}^{-1})$	$\varepsilon(\text{cm}^{-1})$
CoF_2	-163	236	524	-355
FeF_2	-95	-95	-1153	-95

λ^* and A^* are average values ($A_x = 248 \text{ cm}^{-1}$, $A_y = 215 \text{ cm}^{-1}$ and $A_z = 244 \text{ cm}^{-1}$).

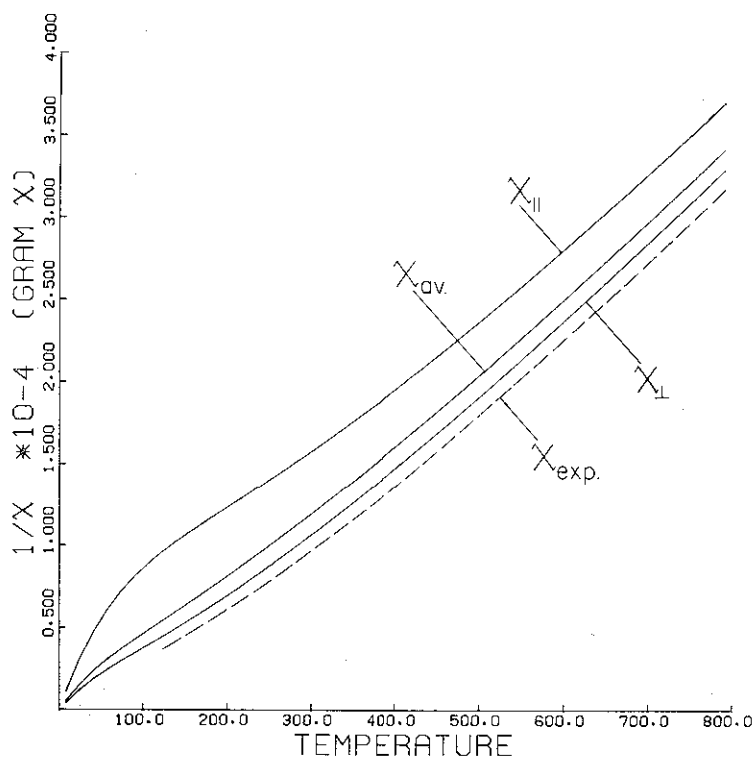


Fig. 2. Reciprocal magnetic susceptibility of Co_2GeO_4 vs T . The dotted line corresponds to the measured value by Blasse and Fast (Reference 15) of powdered Co_2GeO_4 .

value of the spin orbit coupling parameter for the crystal is less than or equal to that of the free Fe^{2+} ion, then it is found that the transition observed at 468 cm^{-1} terminates on the third excited state.

The transition at 935 cm^{-1} terminates then on the ninth excited state. The results of values of the trigonal distortion parameter δ , the spin orbit coupling parameter λ for the Fe^{2+} and Co^{2+} ions in the spinel crystals are given in Table II. The results of Co^{2+} have been taken from a recent paper of this laboratory. A value of δ for Fe_2GeO_4 has also been reported from a Mössbauer study of this compound [13]. The value $\delta=1150\text{ cm}^{-1}$ as found from these studies disagrees with $\delta=600\text{ cm}^{-1}$ obtained from the light scattering data. However, in arriving at such a large value of δ the effect of spin-orbit coupling was neglected and the energy level diagram of Fe^{2+} in Fe_2GeO_4 was thought to consist of a ground state ${}^5A_{1g}$ and one excited state 5E_g separated by δ .

From Table II is seen that $\delta\text{Fe}^{2+} > \delta\text{Co}^{2+}$ and this change is partly due to the fact of configuration interaction in the former and not in the latter. The Hamiltonian

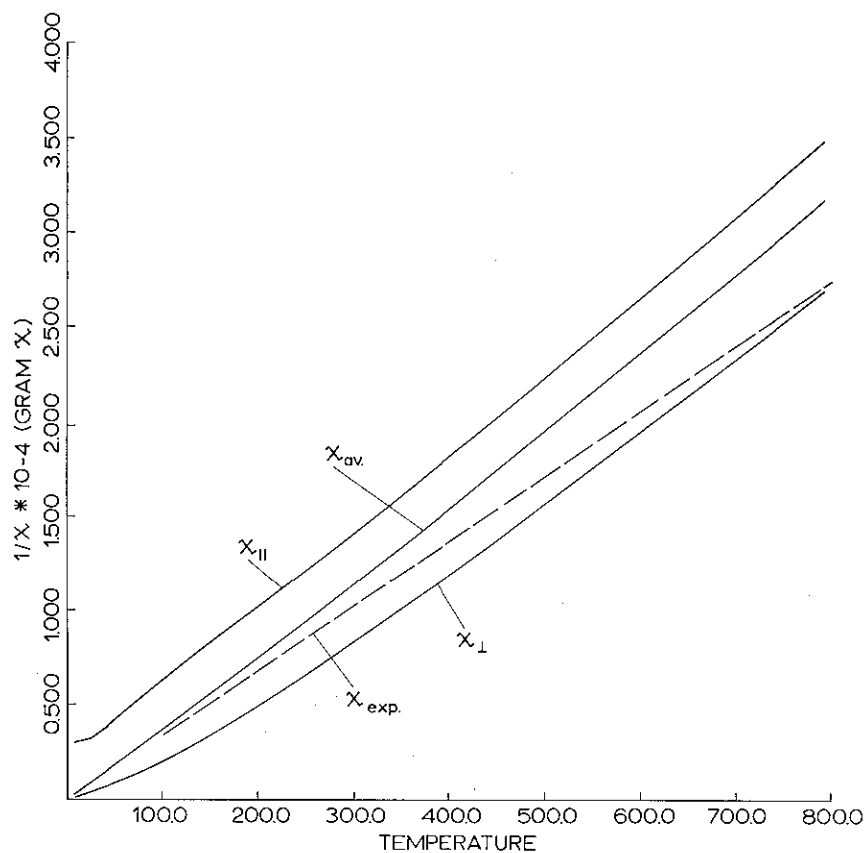


Fig. 3. Reciprocal magnetic susceptibility of Fe_2GeO_4 vs T . The dotted line represents the results of the measured value (Reference 15) of χ , the susceptibility of powdered Fe_2GeO_4 .

for the divalent cobalt and iron ions of CoF_2 and FeF_2 is more complicated in that the transition metal ions occupy sites of rhombic symmetry. This Hamiltonian assumes the form [11]

$$\mathcal{H} = A(L \cdot S) + \Delta(1 - L_z^2) + \varepsilon(L_x^2 - L_y^2), \tag{2}$$

where Δ is a tetragonal and ε a rhombic distortion parameter.

It has the usual meaning as in Equation (1). The appropriate secular determinants may again be diagonalized and similar to the case of the spinels, the computed eigenvalues may be compared with the observed energy of the eigenstates, which in turn permits the calculation of A , Δ and ε . In the case of CoF_2 additional experimental information is known; the g -factors of the groundstate have been measured for $\text{Co}^{2+} : \text{ZnF}_2$ [16]. By using a computer program based essentially on the Newton-Raphson method for iterative convergence the anisotropy of A could be established. For FeF_2 the g -factors were not used and a refinement of the calculations to yield A_x , A_y and A_z was not attempted. The results of the calculations are given in Table II.

The small anisotropy of A of CoF_2 permits one to arrive at an average value $A^* =$

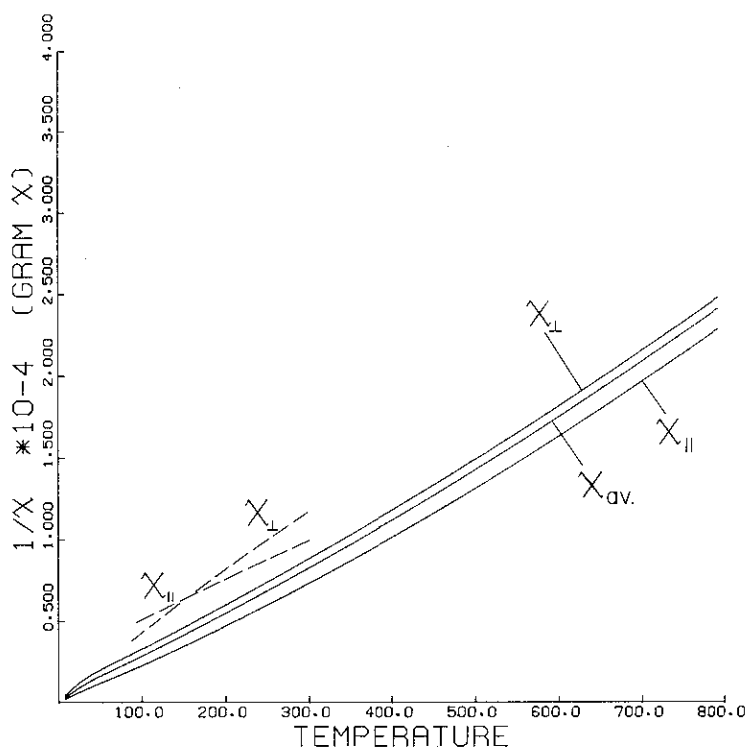


Fig. 4. The measured (Reference 16) and calculated value of the magnetic susceptibility of CoF_2 . χ_{\perp} and χ_{\parallel} refers to the situation that the external magnetic field is parallel or perpendicular to the four fold axes of the crystal. The calculated values of χ do not take into account magnetic ordering effects, and the solid curves can only be compared with the dotted curves for $T > 37\text{K}$.

$= 236 \text{ cm}^{-1}$ and in employing a value of $F = -1.45$ obtained from the optical spectrum [19] the value of $\lambda^* = -163 \text{ cm}^{-1}$; which compares to -178 cm^{-1} for the free ion 4F state and -152 for the 4P state. Similar to the case of the spinels it is seen that the distortion parameters for FeF_2 are smaller than those for CoF_2 . The reason that Δ and ϵ for CoF_2 and FeF_2 are not identical lies in the reduction of the matrices of crystal field potential inside the configurations appropriate for the two cases. If such a reduction is carried out then a correlation of the crystal field parameter is obtained [19].

Apart from the evaluation of the distortion parameters the eigenvectors of the electronic states follow from the diagonalization of the matrix. Such eigenvectors have already been published [4] for Co_2GeO_4 , they may be used to compute the magnetic susceptibility (χ_m) by using the expression of Van Vleck [14]. The results of such calculations are displayed in Figures 2, 3, 4, 5. It appears that the results obtained for Co_2GeO_4 and Fe_2GeO_4 are encouraging but discrepancies do exist for

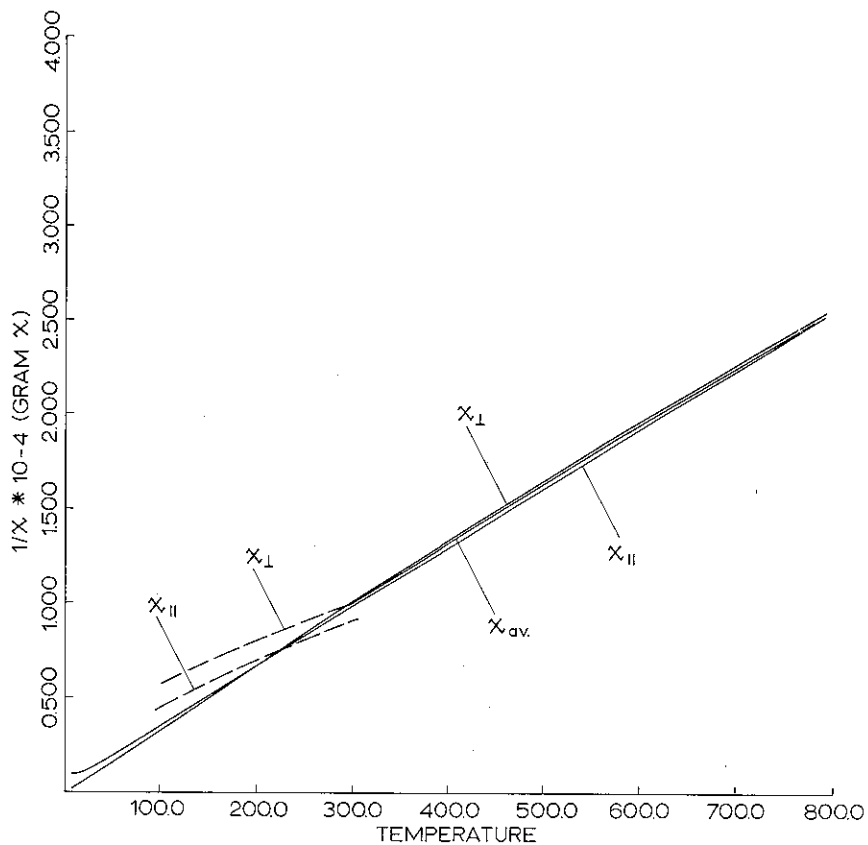


Fig. 5. Calculated (solid curve) and measured (Reference 17) (dotted curve) values of $1/\chi_{\text{Fe}_2}$ vs temperature. $\chi_{||}$ and χ_{\perp} refers to the situation that the external magnetic field is parallel or perpendicular to the four fold axis of the crystal. The solid curve is calculated for the case that magnetic ordering effects can be neglected which is only for $T > 78 \text{ K}$.

calculated and measured values of χ_m for CoF_2 and FeF_2 . Presently it is felt that the differences are related to the fact that magnetic ordering effects occur at higher temperatures for the fluorides than for the spinels. Such ordering effects are not taken into account in the calculations of the magnetic susceptibilities.

The differences are particularly evident for CoF_2 , because the crystal field parameters of this compound are known with greater precision than for the other crystals.

4. Concluding Remarks

An attempt has been made to use the technique of electronic Raman scattering to calculate magnetic susceptibilities of some transition metal ions in certain crystals. The data presented here seems to indicate that this technique cannot be ignored.

Compared to infra-red or fluorescence studies the electronic Raman spectra are *not* complicated by the occurrence of vibronic transitions and it appears also that the electronic transitions of FeF_2 are very intense, in fact, they are more intense than the intensity of the phonons and we note in passing that it is surprising to find that this part of the Raman spectrum was not mentioned in earlier publications on FeF_2 . At the same time we wish to state that, compared to the rare-Earth ions, our knowledge about the electronic effect of the transition metal ions is rather limited. The symmetry of the scattering tensor is presently under investigation, in particular, for the Fe^{2+} ion. Finally, in order to correlate E.P.R. and Raman spectroscopy, it is advantageous to go to situations where the dopance of transition metal ions is low. Here again, it seems that compounds doped with Fe^{2+} should be taken.

Acknowledgement

The authors wish to thank the National Research Council of Canada for financial support.

References

1. Azima, A., Grunberg, P., Hoff, J., Koningstein, J. A., and Preudhomme, J. M.: *Chem. Phys. Letters* **7**, 565 (1970).
2. Christie, J. H. and Lockwood, D. J.: *Chem. Phys. Letters* **8**, 120 (1971).
3. Christie, J. H. and Lockwood, D. J.: *Chem. Phys. Letters* **9**, 559 (1971).
4. Koningstein, J. A., Grunberg, P. A., Hoff, J. T., and Preudhomme, J. M.: *J. Chem. Phys.* **56**, 1 (1972).
5. Macfarlane, R. M. and Morawitz, H.: in *Light Scattering in Solids* (ed. by M. Balkansi), Flammarion Sciences, Paris (1971), p. 133; see also Moch, P., Gosso, J. P., and Daganthier, C.: p. 138.
6. Hoff, J. T., Grunberg, P. A., and Koningstein, J. A.: *Appl. Phys. Letters* **20**, 358 (1972).
7. Ballhausen, C. J.: *Introduction to Ligand Field Theory*, McGraw-Hill Book Company Inc. New York (1962).
8. Grunberg, P., Koningstein, J. A., and Van Uitert, L. G.: *J. Opt. Soc. Am.* **61**, 1613 (1971).
9. Porto, S. P. S., Fleury, P. A., and Damen, T. C.: *Phys. Rev.* **154**, 522 (1967).
10. Stout, J. W., Steinfeld, M. I., and Yuzuri, M.: *J. Appl. Phys.* **39**, 1141 (1968).
11. Gladney, H. M.: *Phys. Rev.* **146**, 253 (1966).
12. Lines, M. E.: *Phys. Rev.* **131**, 546 (1963).

13. Eibschütz, M., Ganiel, U., and Shtrikman, S.: *Phys. Rev.* **151**, 245 (1966).
14. Van Vleck, J. H.: *The Theory of Electronic and Magnetic Susceptibilities*, Oxford University Press, London (1932), p. 226.
15. Blasse, G. and Fast, J. F.: *Philips Res. Rept.* **18**, 393 (1963).
16. Lines, M. E.: *Phys. Rev.* **137**, 982 (1965).
17. Moriya, T., Motizuki, K., Kanamori, J., and Nagamiya, T.: *J. Phys. Soc. Japan* **11**, 211 (1956).
18. Griffith, J. S.: *The Theory of Transition Metal Ions*, Cambridge University Press (1961).
19. Hoff, J. T. and Koningstein, J. A.: *Chemical Phys.* **1**, 232 (1973).