

Lattice Vibration Spectra. LIX. Single Crystal Infrared and Raman Studies of Spinel Type Oxides

H. D. LUTZ, B. MÜLLER, AND H. J. STEINER

Universität Siegen, Anorganische Chemie I, Postfach 101240 D-5900 Siegen, Federal Republic of Germany

Received April 9, 1990

The infrared reflection and Raman spectra of spinel type oxides $M\text{Cr}_2\text{O}_4$ ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$), $M\text{Fe}_2\text{O}_4$ ($M = \text{Ni}, \text{Cu}$), and Mn_3O_4 (single crystals, pressed pellets) including Kramers-Kronig analyses and oscillator-fit calculations are presented. The spectra are discussed with respect to the true space group and ionicities of these compounds as well as the vibrational modes, phonon energies, and resonance Raman effects compared with the respective spectra of spinel type halides, sulfides, and selenides. Because of the relatively high porosity of the pellets obtainable the true frequencies of the IR allowed phonons can only be determined from single crystal spectra. © 1991 Academic Press, Inc.

Introduction

Spinel type ternary oxides (space group $Fd\bar{3}m$) should exhibit four IR (species F_{1u}) and five Raman-allowed ($A_{1g} + E_g + 3F_{2g}$) lattice modes as predicted by group theory (1, 2). In the conventional IR absorption spectra of such oxides as, for example, $M^{\text{II}}\text{Cr}_2\text{O}_4$ and $M^{\text{II}}\text{Fe}_2\text{O}_4$, however, frequently more than four IR bands have been observed (3-5) and discussed in terms of structural features, especially with respect of the true space group of spinel type oxides, viz., $Fd\bar{3}m$ or $F4\bar{3}m$ (4, 5). Studies of the true transversal (TO) and longitudinal optical (LO) phonon frequencies as well as of the Raman spectra, especially those of single crystals, are scarce (6-9).

In order to prove whether the band splittings observed with the conventional IR experiment are actually owing to the distortion of the spinel structure we recorded the IR reflection spectra and the Raman spectra of both single crystals and polycrystalline

samples of various chromites and ferrites, and of tetragonally distorted hausmannite type Mn_3O_4 . From the reflection spectra the dispersion functions of the dielectric and optic constants were calculated by means of classical oscillator-fit methods and Kramers-Kronig analyses.

Experimental

The spinel type ternary oxides were prepared by (i) oxidation of sulfide spinels in a stream of oxygen at 800°C (10) (MnCr_2O_4 , CoCr_2O_4), (ii) melting a mixture of $M^{\text{II}}\text{Cl}_2$ with $\text{K}_2\text{Cr}_2\text{O}_7$ up to 1100°C (11) (CuCr_2O_4 , MgCr_2O_4 , NiCr_2O_4), (iii) fusing the binary oxides at 1300°C (12, 13) (ZnCr_2O_4 , CuFe_2O_4 , NiFe_2O_4), (iv) solid state reaction of stoichiometric amounts of Fe, Cr_2O_3 , and Fe_2O_3 in sealed quartz ampoules at 1200°C (14) (FeCr_2O_4), and (v) decomposition of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (15) (Mn_3O_4).

Single crystals of ZnCr_2O_4 , as large as 3 mm in diameter, and of CoCr_2O_4 , 2 mm,

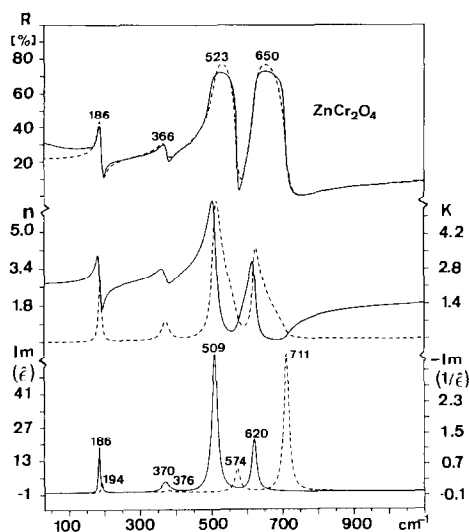


FIG. 1. Single crystal IR reflection spectrum of ZnCr_2O_4 : dashed line, oscillator-fit calculation; dispersion functions of the optic and dielectric constants n (—), k (---), $\text{Im}(\epsilon)$ (—), and $-\text{Im}(1/\epsilon)$ (---).

were grown by chemical vapor phase transport in quartz tubes from 1050 to 970 and 880°C, respectively, with chlorine as transporting agent (16).

For infrared measurements, disk like pellets were prepared by pressing the powdered samples at 1 GPa. The pellets (and single crystals) were embedded in a plastic material and polished with Al_2O_3 buffing powder as far as possible. The densities of the pellets only reached 55–60% of the values calculated from X-ray data. Sintering the pellets at temperatures up to 1500°C yields no improvement, at least in the case of the chromites.

The IR reflection spectra were recorded at near normal incidence using a Bruker IFS 114 Fourier transform interferometer (reference: Al mirror, resolution $< 4 \text{ cm}^{-1}$). Details of the experimental procedure and the conversion of the obtained spectra into the dielectric dispersion relations were given elsewhere (17, 18).

The Raman spectra were recorded on a

Dilor Omars 89 multichannel Raman spectrograph (spectral slit width $< 5 \text{ cm}^{-1}$). For excitation, the 514.5- and 647.1-nm lines of Ar^+ and Kr^+ ion lasers were employed. For details see (19). In the case of single crystals, the measuring geometries used were $a(zz)\bar{a}$ and $a(yy)\bar{a}$ (notation after Damen *et al.* (20)) (A_{1g} and E_g species), $a(z\bar{y})\bar{a}$ (F_{2g}), and $a(z'y')\bar{a}$ (E_g) with $y' = y + z$ ([011]) and $z' = -y + z$ ($[0\bar{1}1]$).

Results

The IR reflection spectra of ZnCr_2O_4 single crystals reveal four Reststrahlen bands (see Fig. 1) as predicted by group theory; the spectra of polycrystalline samples (pressed pellets) of ZnCr_2O_4 and of most other oxides show some more features (see Figs. 2 and

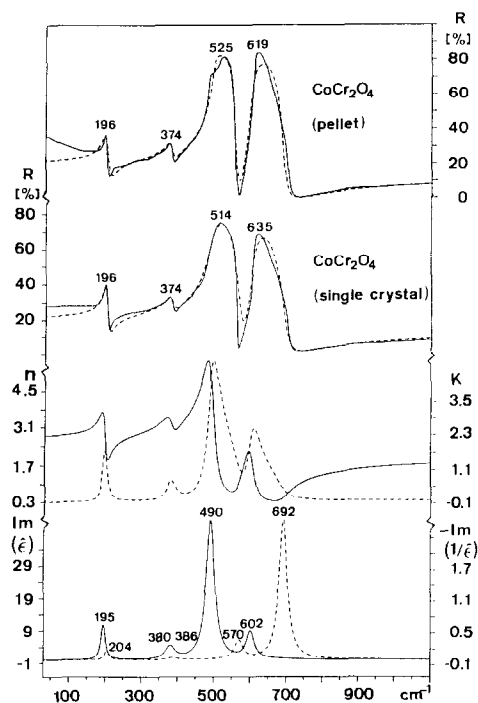


FIG. 2. IR reflection spectra of CoCr_2O_4 : single crystal and pressed pellet after density correction (see text) (for further explanations see Fig. 1).

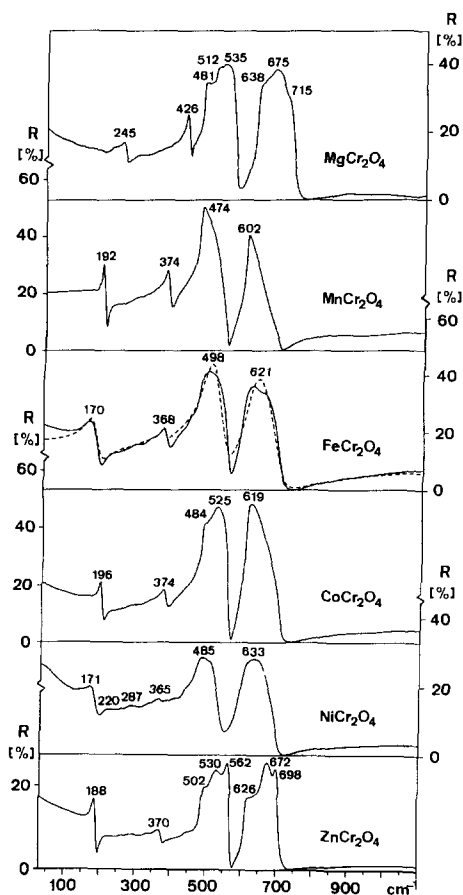


FIG. 3. IR reflection spectra of MCr_2O_4 ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$): pressed pellets (see Fig. 1).

3). The Reststrahlen bands of CuFe_2O_4 and NiFe_2O_4 with inverse spinel structure are relatively broad (see Fig. 4) owing to the breakdown of the translation symmetry because of the random distribution of the metal ions on the octahedral sites (see the discussion in (19)). The IR spectra of the tetragonally distorted (space group $I4_1/amd$) spinels CuCr_2O_4 and Mn_3O_4 (see Fig. 5) exhibit up to 12 Reststrahlen bands; allowed by group theory are 10 IR active modes (21).

The frequencies of the TO and LO zone center phonon modes were taken from the peak maxima of the $\text{Im}(\hat{\epsilon})$ and $-\text{Im}(1/\hat{\epsilon})$ dispersion relations, respectively (see Figs. 1

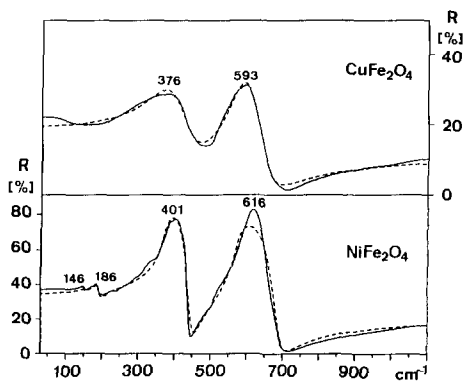


FIG. 4. IR reflection spectra of MFe_2O_4 ($M = \text{Ni}, \text{Cu}$) (see Fig. 1).

and 2). The data calculated by the oscillator-fit method and Kramers–Kronig analyses differ up to 10 cm^{-1} . As found for the corresponding sulfide and selenide spinels (18) the TO/LO splittings of the two low-energy modes are all small ($<10 \text{ cm}^{-1}$), those of the two high-energy bands are in the range of $50\text{--}100 \text{ cm}^{-1}$. These relatively large splittings, as compared to those of the corresponding sulfides ($<20 \text{ cm}^{-1}$), reflect the greater ionicity of oxides. Thus, the effective dynamic ionic charges (Szigeti charges) of the oxide ions calculated from the TO/LO splittings (procedure see Ref. (18)) are

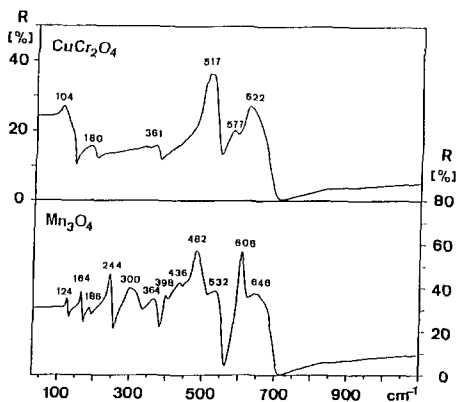


FIG. 5. IR reflection spectra of the tetragonally distorted spinels CuCr_2O_4 and Mn_3O_4 .

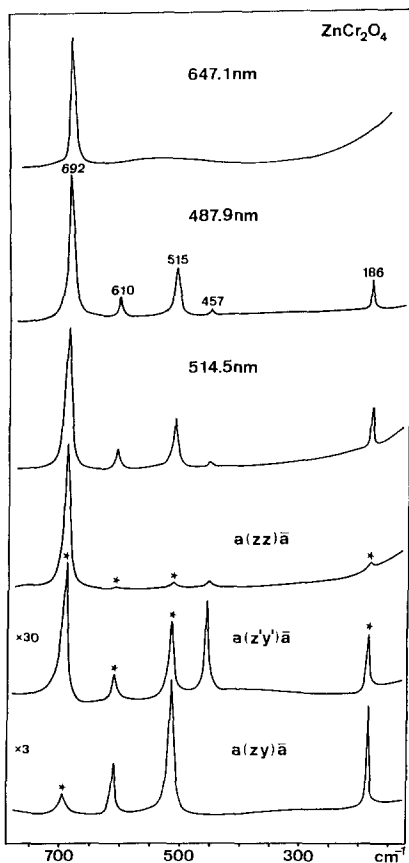


FIG. 6. Single crystal Raman spectra of ZnCr_2O_4 ((100) face) excited by radiation of different wavelengths with and without the use of polarization analyzers, respectively. Measuring geometries given by the notation of Damen *et al.* (20); y' : $[011]$; z' : $[0\bar{1}1]$; asterisks indicate incomplete extinctions.

-0.94 e (CoCr_2O_4) and -0.91 e (ZnCr_2O_4) compared to -0.4 – -0.5 e in the case of sulfide and selenide spinels (18).

The single crystal Raman spectra of ZnCr_2O_4 (see Fig. 6) reveal five bands, viz. at 692 cm^{-1} (A_{1g}), at 457 cm^{-1} (E_g), and at 610 , 515 , and 186 cm^{-1} (F_{2g}) as predicted by group theory for space group $Fd\bar{3}m$ (In the case of CoCr_2O_4 only three bands were observed, viz. 687 (A_{1g}), 516 , and 196 cm^{-1} (both F_{2g})). The relatively large amount of incomplete extinction is probably caused by

the microporosity of the crystal faces. The intensities of the Raman lines depend on the frequency of the laser light used (resonance Raman effect, which has also been observed in the case of sulfide spinels (19)). However, compared to the Raman spectra of sulfide spinels (19), the low intensity of the E_g mode is remarkable. The Raman spectrum obtained for NiFe_2O_4 confirms that reported by Graves *et al.* (8) during our experiments. From the 10 Raman bands allowed for the tetragonal Mn_3O_4 (21) only five were recorded (see Fig. 7).

Discussion

Assignments of the four IR-allowed phonon modes with respect to vibrations of the tetrahedral MO_4 and the octahedral MO_6 units of the spinel structure as established in the older literature (3, 4, 23) (as well as further interpretations of the spectra obtained) are not possible without lattice dynamical calculations. The IR-allowed modes are typical lattice vibrations with contributions of all atoms and forces of the spinel structure (see the discussion given in (22)). Nevertheless, some bands, e.g., the two reflection maxima at intermediated energies, are more affected by the nature of the octahedrally coordinated metals, the lowest-energy mode by the metals on the tetrahedral sites (22). The influence of the masses of the atoms involved on the band energies independently of the forces has been studied by isotopic substitution experiments (3).

Similar approaches hold for the Raman-

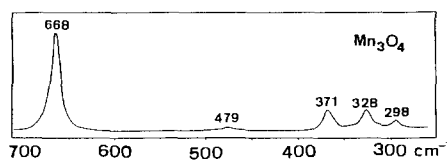


FIG. 7. Raman spectrum of Mn_3O_4 (pellet).

TABLE I

OSCILLATOR PARAMETERS, TO AND LO PHONON FREQUENCIES (cm^{-1}) OF SPINEL TYPE CHROMITES AND FERRITES (DATA TAKEN FROM PEAK MAXIMA OF THE DISPERSION RELATIONS OF THE IMAGINARY PART OF THE DIELECTRIC CONSTANT $\text{Im}(\hat{\epsilon})$ AND THE DIELECTRIC LOSS FUNCTION $-\text{Im}(1/\hat{\epsilon})$) OBTAINED BY OSCILLATOR-FIT CALCULATIONS (OF) AND KRAMERS-KRONIG ANALYSES (KKA), FOR MnFe_2O_4 AND ZnFe_2O_4 ; SEE (6)

| <i>j</i> | ρ_j | ω_j | γ_j | ω_{TO} | | ω_{LO} | |
|--|----------|------------|------------|----------------------|-----|----------------------|-----|
| | | | | OF | KKA | OF | KKA |
| ZnCr₂O₄, single crystal | | | | | | | |
| 1 | 0.052 | 186 | 0.045 | 186 | 186 | 194 | 194 |
| 2 | 0.024 | 370 | 0.064 | 370 | 372 | 376 | 377 |
| 3 | 0.165 | 509 | 0.038 | 509 | 506 | 575 | 574 |
| 4 | 0.043 | 621 | 0.026 | 621 | 624 | 711 | 711 |
| $\epsilon_x = 4.05$ | | | | | | | |
| ZnCr₂O₄, pellet | | | | | | | |
| 1 | | | | | 188 | | 194 |
| 2 | | | | | 374 | | 378 |
| 3 | | | | | 527 | | 570 |
| 4 | | | | | 633 | | 706 |
| CoCr₂O₄, single crystal | | | | | | | |
| 1 | 0.063 | 195 | 0.072 | 195 | 196 | 204 | 204 |
| 2 | 0.025 | 380 | 0.072 | 380 | 378 | 386 | 384 |
| 3 | 0.193 | 491 | 0.056 | 490 | 493 | 570 | 561 |
| 4 | 0.030 | 602 | 0.044 | 602 | 608 | 692 | 699 |
| $\epsilon_x = 3.81$ | | | | | | | |
| CoCr₂O₄, pellet | | | | | | | |
| 1 | | | | | 197 | | 202 |
| 2 | | | | | 379 | | 382 |
| 3 | | | | | 509 | | 557 |
| 4 | | | | | 613 | | 699 |
| CoCr₂O₄, pressed pellet after density correction of the reflection spectrum | | | | | | | |
| 1 | 0.070 | 196 | 0.090 | 196 | 196 | 207 | 203 |
| 2 | 0.021 | 378 | 0.052 | 378 | 378 | 383 | 382 |
| 3 | 0.176 | 493 | 0.029 | 493 | 491 | 560 | 558 |
| 4 | 0.030 | 598 | 0.028 | 598 | 609 | 689 | 701 |
| MgCr₂O₄, pellet | | | | | | | |
| 1 | | | | | 249 | | 253 |
| 2 | | | | | 428 | | 432 |
| 3 | | | | | 466 | | 503 |
| 4 | | | | | 498 | | 566 |
| 5 | | | | | 633 | | 725 |
| MnCr₂O₄, pellet | | | | | | | |
| 1 | | | | | 193 | | 198 |
| 2 | | | | | 376 | | 383 |
| 3 | | | | | 473 | | 540 |
| 4 | | | | | 602 | | 683 |
| FeCr₂O₄, pellet | | | | | | | |
| 1 | 0.068 | 171 | 0.190 | 170 | 170 | 184 | 183 |
| 2 | 0.004 | 373 | 0.032 | 374 | 375 | 376 | 379 |
| 3 | 0.083 | 495 | 0.081 | 495 | 495 | 540 | 550 |
| 4 | 0.045 | 615 | 0.084 | 614 | 608 | 691 | 693 |
| NiCr₂O₄, pellet | | | | | | | |
| 1 | | | | | 178 | | 187 |
| 2 | | | | | 222 | | 223 |
| 3 | | | | | 299 | | 301 |
| 4 | | | | | 370 | | 373 |
| 5 | | | | | 484 | | 537 |
| 6 | | | | | 610 | | 692 |
| NiFe₂O₄, pellet | | | | | | | |
| 1 | 0.010 | 151 | 0.100 | 151 | 151 | 152 | 153 |
| 2 | 0.036 | 189 | 0.066 | 189 | 188 | 192 | 191 |
| 3 | 0.396 | 376 | 0.060 | 376 | 380 | 444 | 440 |
| 4 | 0.175 | 572 | 0.056 | 562 | 580 | 686 | 686 |
| $\epsilon_x = 7.19$ | | | | | | | |
| CuFe₂O₄, pellet | | | | | | | |
| 1 | 0.146 | 387 | 0.275 | 384 | 392 | 438 | 444 |
| 2 | 0.067 | 577 | 0.127 | 576 | 576 | 652 | 656 |

allowed lattice modes. In the vibrational modes of species A_{1g} and E_g , only motions of the oxygen atoms are involved and, hence, some more conclusions can be drawn from the band frequencies observed. Thus, the breathing mode of the tetrahedral MO_4 units (A_{1g} species) is mainly influenced by bonding and repulsion effects of this unit, e.g., the covalency of the $M-O$ bond, as shown from Raman spectroscopic studies of spinel type sulfides (19) and chlorides (24). Lattice dynamical calculations of $ZnCr_2O_4$ (25), however, revealed that the octahedral $Cr-O$ valence and the tetrahedral $O-O$ repulsion force constants are even more relevant to the A_{1g} mode than the tetrahedral $Zn-O$ valence force constant. The energies of the A_{1g} modes increase on going from spinel type chromium selenides ($236-241\text{ cm}^{-1}$) (26, 27) and sulfides ($248-254\text{ cm}^{-1}$) (19) to the oxides ($685-699\text{ cm}^{-1}$) (7, 9, and this work). This increase is much larger than can be caused by the decreasing masses of anions involved. These findings therefore reflect the stronger forces, especially the repulsive ones, of the ternary oxides compared to those of sulfides, etc.

In the case of the ferrites MFe_2O_4 , which possess an inverse or partially inverse spinel structure, the number of the Raman bands observed (8) exceeds that predicted by group theory. These findings are obviously due to the lack of full translation symmetry in the case of inverse spinels (19) (see also the discussion given in (8)).

In the case of the chromites MCr_2O_4 , we suppose that the true space group is $F43m$ instead of $Fd\bar{3}m$ despite only scarce spectroscopic indications (powder spectra). This means that the site symmetry of the octahedrally coordinated metals, i.e., the chromium ions, is C_{3v} compared to D_{3d} for space group $Fd\bar{3}m$. This reduction of symmetry, however, has been confirmed by X-ray structure determination in the case of $MgCr_2O_4$ (28).

Because the true number of oscillators (Reststrahlen bands) present, i.e., four

(space group $Fd\bar{3}m$) or seven ($F43m$), and the frequencies belonging to them are not exactly known conversion of the reflection spectra into the dielectric dispersion relations by means of the oscillator-fit method is problematic. This fact may be the reason for the different phonon frequencies obtained by oscillator-fit and Kramers-Kronig analysis, respectively. The number of oscillators used for calculation is included in Figs. 1-3 and Table I.

The relatively low densities of the obtained pellets became apparent also with the reflection spectra, which strongly differ from those of single crystals (see Figs. 1-3). The same applies to the oscillator parameters and phonon frequencies derived (see Table I). This means that, in the case of spinel type oxides, the true phonon frequencies cannot be calculated from IR reflection spectra of polycrystalline samples, i.e., pressed pellets, opposite to the corresponding sulfides and selenides (18). Attempts to prepare more dense pellets by sintering techniques at elevated temperatures were not successful apart from Mn_3O_4 and $NiFe_2O_4$. However, some improvement can be obtained if the reflectivities recorded are corrected by density relations, i.e., ρ_{cal}/ρ_{exp} (see Table I).

Furthermore, in the case of the spectra of the pellets obtained, there are some band splittings and other spectral features that are not observed for the single crystal spectra (see Figs. 1-3). Therefore, caution must be used when the IR spectra of polycrystalline samples are interpreted.

Acknowledgments

The authors thank Prof. Dr. W. Laqua, Universität Giessen, for some experiments with the high-temperature furnace and the Fonds der Chemischen Industrie for financial support.

References

1. W. B. WHITE AND B. A. DE ANGELIS, *Spectrochim. Acta*, **23A**, 985 (1967).
2. H. D. LUTZ, *Z. Naturforsch.* **A24**, 1417 (1969).

3. J. PREUDHOMME AND P. TARTE, *Spectrochim. Acta* **27A**, 1817 (1971).
4. N. W. GRIMES AND A. J. COLLET, *Phys. Status Solidi B* **43**, 591 (1971).
5. E. Z. KATSNELSON, A. G. KAROZA, L. A. MEL-ESHCHENKO, V. V. PANKOV, AND B. G. KHAVKIN, *Phys. Status Solidi B* **141**, 599 (1987).
6. E. Z. KATSNELSON, A. G. KAROZA, L. A. MEL-ESHCHENKO, AND L. A. BASHKIROV, *Phys. Status Solidi B* **152**, 657 (1989).
7. J. M. MALEZIEUX, J. BARBILLAT, B. CERVELLE, J. P. COUTURES, M. COUZI, AND B. PIRIOU, *TMPM Tschermaks Mineral. Petrogr. Mitt.* **32**, 171 (1983).
8. P. R. GRAVES, C. JOHNSTON, AND J. J. CAMPANIELLO, *Mater. Res. Bull.* **23**, 1651 (1988).
9. K. F. MCCARTY AND D. R. BOEHME, *J. Solid State Chem.* **79**, 19 (1989).
10. H. D. LUTZ AND M. FEHER, *Spectrochim. Acta* **27A**, 357 (1971).
11. M. R. UDUPA, *Thermochim. Acta* **59**, 379 (1982).
12. F. MÜLLER AND O. J. KLEPPA, *J. Inorg. Nucl. Chem.* **35**, 2673 (1968).
13. A. NAVROTSKY AND O. J. KLEPPA, *J. Inorg. Nucl. Chem.* **30**, 479 (1973).
14. K. SIRATORI, *J. Phys. Soc. Japan* **23**, 948 (1967).
15. T. E. MOORE, M. ELLIS, AND P. W. SELWOOD, *J. Amer. Chem. Soc.* **72**, 856 (1950).
16. F. EMMENEGGER, *J. Crystal Growth* **3**, 4, 135 (1968).
17. D. M. ROESSLER, *Brit. J. Appl. Phys.* **17**, 1313 (1966).
18. H. D. LUTZ, G. WÄSCHENBACH, G. KLICHE, AND H. HAEUSELER, *J. Solid State Chem.* **48**, 196 (1983).
19. H. D. LUTZ, W. BECKER, B. MÜLLER, AND M. JUNG, *J. Raman Spectrosc.* **20**, 99 (1989).
20. T. C. DAMEN, S. P. S. PORTO, AND B. TELL, *Phys. Rev.* **142**, 570 (1966).
21. J. ARSENE, A. ERB, AND M. LENGLET, *Ann. Chim. Fr.* **6**, 399 (1981).
22. H. D. LUTZ AND H. HAEUSELER, *Ber. Bunsenges. Phys. Chem.* **79**, 604 (1975).
23. R. D. WALDRON, *Phys. Rev.* **99**, 1727 (1955).
24. K. WUSSOW, H. HAEUSELER, P. KUSKE, W. SCHMIDT, AND H. D. LUTZ, *J. Solid State Chem.* **78**, 117 (1989).
25. H. D. LUTZ AND J. HIMMRICH, unpublished results.
26. E. F. STEIGMEIER AND G. HARBECKE, *Phys. Kondens. Mater.* **12**, 1 (1970).
27. M. N. ILIEV, E. ANASTASSAKIS, AND T. ARAI, *Phys. Stat. Sol. (b)* **86**, 717 (1978).
28. R. J. HILLEARD, *J. Phys. C: Solid State Phys.* **8**, L193 (1975).