The Canadian Mineralogist
Vol. 32, pp. 333-337 (1994)

ERNIENICKELITE, $NiMn_3O_7{\cdot}3H_2O$, A NEW MINERAL SPECIES FROM THE SIBERIA COMPLEX, WESTERN AUSTRALIA: COMMENTS ON THE CRYSTALLOGRAPHY OF THE CHALCOPHANITE GROUP

JOEL D. GRICE

Mineral Sciences Section, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

BLAIR GARTRELL

P.O. Box 116, Beverley, Western Australia 6304, Australia

ROBERT A. GAULT AND JERRY VAN VELTHUIZEN

Mineral Sciences Section, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

ABSTRACT

Ernienickelite is a new mineral species in the chalcophanite group from the SM7 pit, Siberia ultramafic complex, Western Australia, Australia. It occurs in a Ni–Co laterite as a rare constituent in cavities of quartz (chalcedony) associated with goethite, magnesite, a serpentine-group mineral, nimite and nontronite. It forms opaque, red-black plates to 0.5 mm in diameter and rosettes of plates up to 0.8 mm across. It is soft, $H \approx 2$, brittle with a splintery fracture, and characterized by a perfect {001} cleavage. $D_{calc.} = 3.83$ g/cm^3 and $D_{meas.} = 3.84$ g/cm^3. Uniaxial negative, $\omega > 2.00$, $\varepsilon = 1.97(2)$. It is trigonal, $R\bar{3}$ or $R3$, a 7.514(2), c 20.52(2) Å and $Z = 6$. The strongest X-ray-diffraction lines in the powder pattern [d in Å (I)(hkl)] are: 6.84(10)(003), 4.01(2)(104), 2.219(3)(214), 1.884(2)(217) and 1.575(2)(2,1,10). An analysis by electron microprobe gave: MnO_2 68.25, NiO 16.68, CoO 0.30, MgO 0.30, H_2O (according to stoichiometry of chalcophanite structure) 13.94, total 99.47 wt.%, which yields the empirical formula $(Ni_{0.87}Mg_{0.03}Mn_{0.04}Co_{0.02})_{\Sigma 0.96}Mn_3O_7{\cdot}3H_2O$, or simply, $NiMn^{4+}_3O_7{\cdot}3H_2O$. The crystal structures of ernienickelite and chalcophanite are compared to those of lithiophorite and cianciulliite. The X-ray powder-diffraction data for chalcophanite and aurorite are corrected, refined and indexed.

Keywords: ernienickelite, new mineral species, chalcophanite group, trigonal, laterite, Siberia ultramafic complex, Australia.

SOMMAIRE

La ernienickelite, découverte dans le puit SM7 du complexe ultramafique de Siberia, en Australie occidentale, est une nouvelle espèce minérale du groupe de la chalcophanite. On la trouve rarement sur les parois de cavités dans le quartz (calcédoine) des latérites à Ni–Co, en association avec goethite, magnésite, un minéral du groupe de la serpentine, nimite et nontronite. Elle se présente en rosettes de plaquettes jusqu'à 0.8 mm de diamètre. Il s'agit d'un minéral mou, d'une dureté de 2, cassant, ayant une fracture en éclats et un clivage {001} parfait. La densité calculée est 3.83, et la densité mesurée, 3.84. La ernienickelite est uniaxe négative, $\omega > 2.00$, $\varepsilon = 1.97(2)$. Elle est trigonale, $R\bar{3}$ ou $R3$, a 7.514(2), c 20.52(2) Å et $Z = 6$. Les cinq raies les plus intenses du cliché de diffraction X [méthode des poudres, d en Å (I)(hkl)] sont: 6.84(10)(003), 4.01(2)(104), 2.219(3)(214), 1.884(2)(217) and 1.575(2)(2,1,10). Une analyse à la microsonde électronique a donné: MnO_2 68.25, NiO 16.68, CoO 0.30, MgO 0.30, H_2O (selon la stoechiometrie des membres du groupe de la chalcophanite) 13.94, total 99.47% par poids, ce qui mène à la formule empirique $(Ni_{0.87}Mg_{0.03}Mn_{0.04}Co_{0.02})_{\Sigma 0.96}Mn_3O_7{\cdot}3H_2O$ ou, plus simplement, $NiMn^{4+}_3O_7{\cdot}3H_2O$. Nous comparons la structure cristalline de la ernienickelite et de la chalcophanite à celle de la lithiophorite et de la cianciulliite. Nous avons corrigé, affiné et indexé les données de diffraction X obtenues sur poudres de la chalcophanite et de l'aurorite.

(Traduit par la Rédaction)

Mots-clés: ernienickelite, nouvelle espèce minérale, groupe de la chalcophanite, trigonal, latérite, complex ultramafique de Siberia, Australie.

INTRODUCTION

Specimens of red, platy crystals in a chalcedony matrix were encountered during a field trip by one of the authors (B.G.) in the Kalgoorlie area of Western Australia. Upon further study, these have been determined to be a new mineral species, which is named ernienickelite in honor of Ernest (Ernie) H. Nickel for his outstanding contributions to research on the mineralogy and genesis of economic mineral deposits, particularly in Canada and Australia, and to his dedication to the formalization of mineral systematics in connection with his long-term appointment to the Commission of New Minerals and Mineral Names, International Mineralogical Association.

The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material, consisting of a few milligrams of crystals, has been deposited in the collection of the Canadian Museum of Nature under catalogue number CMN#81510.

OCCURRENCE

The lateritic Ni–Co deposits in the Kalgoorlie region of Western Australia are described in detail by Elias *et al.* (1981). The locality of the type material for ernienickelite is the SM7 open pit (named for the drillhole number that first intersected the nickel mineralization), approximately 4 km north of Siberia (former town) and 60 km north of Kalgoorlie (Lat. 30°20′S, Long. 121°0′E).

The Siberia complex, which hosts the SM7 pit, is a large ultramafic body comprising a part of the extensive Archean greenstone belt of the southeastern Yilgarn Block. The Archean succession is cut by a series of thin dolerite dykes of probable Proterozoic age. The area was severely lateritized to a depth of 60 m during Cretaceous to late Eocene time. Laterization of the dunite unit leached the Mg, leaving essentially pure quartz (chalcedony). Weathering of the dolerite dykes produced a clay assemblage that concentrated the Ni from percolating groundwater. The Ni was leached from the adjoining dunite. At the SM7 pit, both the Ni-rich clay and quartz laterite are mined and mixed to produce a flux used in the treatment of sulfide concentrates at the Kalgoorlie nickel smelter.

Ernienickelite is found as a rare constituent in cavities of quartz (chalcedony), associated with goethite, magnesite, a serpentine-group mineral, nimite and nontronite.

PHYSICAL AND OPTICAL PROPERTIES

Ernienickelite occurs as very thin, almost circular plates up to 0.5 × 0.5 × 0.02 mm (Fig. 1) and as rosettes composed of randomly oriented plates up to 0.8 × 0.5 × 0.5 mm. The mineral is almost black, but usually has a distinct red-brown cast. The streak is yellow-brown, and the luster, submetallic to vitreous. It does not fluoresce. Ernienickelite is opaque except in the thinnest of plates, where it is translucent. It is soft (Mohs hardness ≈ 2) and brittle, with a splintery fracture; it has a perfect {001} cleavage. The density, measured by suspension in Clerici solution, is 3.84(4) g/cm^3, which agrees well with the calculated density of 3.83 g/cm^3.

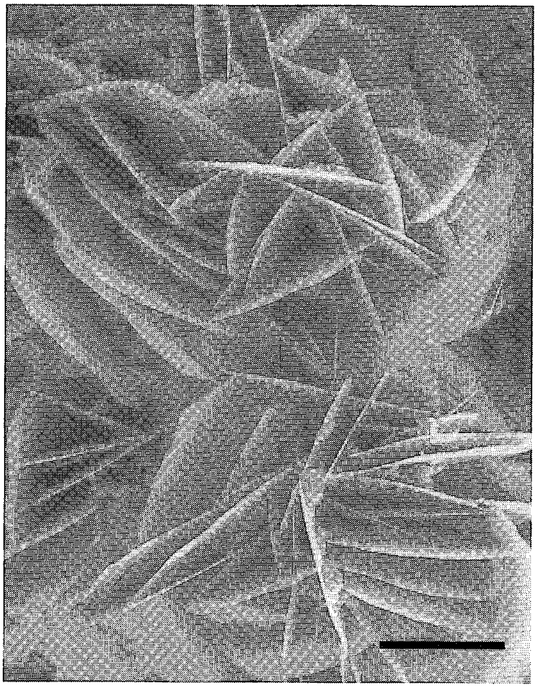

FIG. 1. Photomicrograph obtained by scanning electron microscopy showing a rosette of crystals of ernienickelite in quartz (chalcedony). Scale bar represents 100 μm.

Owing to the dense coloration of ernienickelite, optical measurements are difficult. It is uniaxial negative, with ω greater than 2.00, and ε equal to 1.97(2), measured with sodium light (gel-filtered, λ 590 nm). It seems to be nonpleochroic.

CHEMICAL COMPOSITION

Chemical analyses were performed on a JEOL 733 Superprobe using Tracor–Northern 5600 automation. The wavelength-dispersion mode was used. Data reduction was done with the Tracor–Northern Task series of programs using a conventional ZAF correction routine. The operating voltage was 15 kV, and the beam current was 0.020 μA. Owing to the extremely thin nature of the crystals (the plates are 20 μm thick), only very small areas received an adequate polish for analysis, allowing only a focused beam to be employed. A 100-s energy-dispersion scan indicated that no elements with Z greater than 8, other than those reported here, are present. The following elements were sought as well but not detected in the wavelength-dispersion mode: Na, Si, Ca, Fe, As, and Zn. Data for standards were collected for 50 s or 0.25% precision per element, whichever was attained first. Data for samples were collected for 25 s or 0.5% precision, whichever was attained first. Standards used were rhodochrosite (Mn$K\alpha$), synthetic nichromite (Ni$K\alpha$), synthetic cochromite (Co$K\alpha$) and diopside (Mg$K\alpha$). Two analyses on separate crystals gave average weight percentages of MnO_2 68.25 (68.42–68.08), NiO 16.68 (15.94–17.42), CoO 0.30 (0.48–0.22), MgO 0.30 (0.50–0.10), H_2O 13.94 (13.95–13.93), total 99.47. Because of insufficiency of material, the proportion of H_2O was calculated by stoichiometry based on the crystal structure of chalcophanite (Post & Appleman 1988). The empirical formula based on 10 atoms of oxygen is $(Ni_{0.87}Mg_{0.03}Mn_{0.04}Co_{0.02})_{\Sigma 0.96}O_7{\cdot}3H_2O$, and the ideal simplified formula is $NiMn_3O_7{\cdot}3H_2O$.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show ernienickelite to be trigonal, with possible space-groups $R\bar{3}$ or $R3$. Precession photographs of chalcophanite specimen NMNH C1814 from Sterling Hill, New Jersey were taken to compare with those of ernienickelite. This specimen of chalcophanite was used by Post & Appleman (1988) in their crystal-structure determination. Although the two sets of photographs are almost identical, twinning was observed on $(\bar{1}20)$ in ernienickelite.

The unit-cell parameters were refined from X-ray powder-diffraction data obtained with a 114.6-mm-diameter Debye–Scherrer camera with Cu$K\alpha$ (Ni-filtered) radiation (Table 1). The refined unit-cell parameters are a 7.514(2), c 20.52(2) Å, and the cell

TABLE 1. X-RAY POWDER DATA FOR ERNIENICKELITE, CHALCOPHANITE AND AURORITE

ERNIENICKELITE [1]				CHALCOPHANITE [2]				AURORITE [3]			
I obs	d,Å obs	d,Å calc	hkl	I obs	d,Å obs	d,Å calc	hkl	I obs	d,Å obs	d,Å calc	hkl
10	6.84	6.84	003	10	6.96	6.94	003	10	6.94	6.91	003
<1	6.22	6.20	101	1	6.23	6.25	101	2	6.20	6.20	101
<1	5.53	5.49	012								
2	4.01	4.03	104	5	4.08	4.08	104	5	4.06	4.05	104
1	3.44	3.47	015	6	3.50	3.51	015	7	3.45	3.45	006
<1	3.30	3.29	113	1	3.32	3.32	113	2	3.29	3.30	113
				<1	3.23	3.24	021	1	3.20	3.21	021
1	2.748	2.748	024	2	2.77	2.77	024	3	2.76	2.75	024
				<1	2.710	2.708	107	<1	2.70	2.695	107
1	2.533	2.529	116	4	2.570	2.575	205	5	2.540	2.543	116
1	2.442	2.442	211	2	2.460	2.461	211	4	2.450	2.442	211
1	2.394	2.392	122	2	2.410	2.411	122	4	2.400	2.393	122
3	2.219	2.218	214	5	2.240	2.237	214	5	2.230	2.222	214
<1	2.112	2.110	125	2	2.130	2.129	125	3	2.130	2.115	125
				<1	1.986	1.984	10•10	<1	1.980	1.975	10•10
2	1.884	1.884	217	3	1.900	1.904	217	4	1.899	1.892	217
<1	1.833	1.832	306	1	1.849	1.849	306	2	1.841	1.837	306
1	1.775	1.778	312,120	2	1.795	1.794	128,312	3	1.795	1.797	131
				<1	1.750	1.757	02•10	<1	1.748	1.748	02•10
<1	1.701	1.702	134	<1	1.715	1.717	134	1	1.712	1.704	134
<1	1.650	1.652	315	1	1.668	1.666	315	<1	1.668	1.654	315,226
2	1.575	1.575	21•10	4	1.597	1.594	21•10				
				<1	1.563	1.563	404	<1	1.563	1.569	11•12
								<1	1.560	1.552	404
<1	1.487	1.489	321	1	1.507	1.504	12•11	2	1.508	1.514	045
1	1.419	1.420	410	3	1.431	1.431	410	5	1.429	1.425	407
<1	1.391	1.390	413	<1	1.402	1.401	413	<1	1.398	1.404	235
<1	1.311	1.312	416	<1	1.324	1.323	416	1	1.321	1.313	416
				<1	1.308	1.309	051				
<1	1.258	1.259	12•14,10•16	1	1.279	1.271	054	1	1.277	1.279	40•10
								<1	1.234	1.232	333
<1	1.211	1.207	32•10								
								1	1.204	1.203	02•16
<1	1.180	1.178	425								
								1	1.144	1.144	31•14
<1	1.123	1.124	155					<1	1.119	1.113	22•15
<1	1.097	1.098	339								
								2	1.064	1.064	342
								1	1.036	1.035	345

1. 114.6 mm Debye-Scherrer camera, Cu$K\alpha$ radiation, visually estimated intensities, indexing based on a cell having $a = 7.514(3)$, $c = 20.517(4)$ Å. 2. Reindexed on the basis of d (Å) values reported in PDF 15-807 with the new cell $a = 7.570(3)$, $c = 20.816(4)$ Å. 3. Reindexed on the basis of d (Å) values reported in PDF 19-88 with the new cell $a = 7.514(4)$, $c = 20.734(5)$ Å.

volume *V*, 1003.4(7) Å^3; $Z = 6$. These cell parameters are slightly smaller than those calculated for the re-indexed pattern given by Berry & Thompson (1962) (PDF15–807) for chalcophanite; *a* 7.570(3), *c* 20.816(4) Å (Table 1). This decrease in cell parameters would be expected in the structure since Ni atoms are slightly smaller in size than Zn atoms.

DISCUSSION

At present, there are three confirmed species and one unnamed member (Potter & Rossman 1979b) in the chalcophanite group: chalcophanite, ideally $Mn_3^{4+}O_7\cdot3H_2O$, aurorite, $(Mn^{3+},Ag^+)Mn_3^{4+}O_7\cdot3H_2O$, a Mg-analogue of chalcophanite, $MgMn_3^{4+}O_7\cdot3H_2O$ (Potter & Rossman 1979b) and ernienickelite, $NiMn_3^{4+}O_7\cdot3H_2O$. Ostwald (1985) presented results of 30 electron-microprobe analyses of chalcophanite specimens. His data show a considerable variation in MnO_2, ZnO and NiO contents, and a more restricted variation in Fe_2O_3, MgO, CuO, CaO, BaO, Al_2O_3 and SiO_2. The aurorite species contains 7.50 wt.% Ag_2O and 1.30 wt.% PbO (Radtke *et al.* 1967). Thus the possibility of finding other species within the group seems likely.

Confusion as to the crystallography of the chalcophanite group arises from the crystal-structure determination of Wadsley (1955), who gave $P\bar{1}$ as the space group, with the cell parameters *a* 7.54, *b* 7.54, *c* 8.22 Å, α 90, β 117.2 and γ 120°. The atomic parameters of Wadsley (1955) were tested by MISSYM (LePage 1987, 1988), a computer program derived expressly to determine whether or not a crystal structure may in fact have higher crystallographic symmetry than considered. All atoms within his structure determination fall within 0.03 Å of having a 3-fold axis along [213], through ⅓,⅓,0 and a center of symmetry at ½,½,0. From this test, we can conclude that chalcophanite is trigonal. The proof is to be found in the structure refinement of Post & Appleman (1988) in space group $R\bar{3}$. Radtke *et al.* (1967) adopted the incorrect setting of Wadsley (1955) for aurorite; thus in Table 1 we include the cell-dimension refinement and X-ray powder-diffraction data of both chalcophanite and aurorite. The data reported in Table 1 show that all members of the chalcophanite group refine well with rhombohedral symmetry. The incorrect setting of Wadsley (1955) is easily understood upon studying the (*hk*0) precession photograph. Neither the *h*00 nor the *hh*0 reflections give a strong-intensity reciprocal row. In fact, the only set of intense reflections in this plane are 410 and its symmetry-related equivalents. This could mislead one to adopt another setting. On the X-ray powder-diffraction pattern (Table 1), 410 is the only *hk*0 type of reflection.

Ernienickelite formed in a mildly alkaline environment, (pH ≈ 9: Elias *et al.* 1981), and one that was highly oxidized by circulating groundwaters, as evidenced by the presence of Mn^{4+}. Potter & Rossman (1979a) tabulated most of the tetravalent manganese oxides. The two minerals that most closely resemble the chalcophanite group are todorokite, $MnMn_3O_7\cdot3H_2O$, and woodruffite, $ZnMn_3O_7\cdot3H_2O$. These minerals are likely isostructural, although only the todorokite structure has been solved (Post & Bish 1988) and shown to be a tunnel structure, quite different from that of chalcophanite. Interestingly, Elias *et al.* (1981) not only reported the Ni-analogue of chalcophanite, herein described as ernienickelite, but they also mention finding the "Ni and Co analogue of todorokite".

There are several manganese oxide minerals with a layered structure; these are reviewed in detail by Burns *et al.* (1983) and Giovanoli (1985). There are two structure types that resemble the chalcophanite – ernienickelite structure. Lithiophorite, $(Al,Li)Mn^{4+}O_2(OH)_2$, consists of fully occupied, brucite-like sheets of octahedra with alternating layers of $[MnO_6]$ and $[(Al,Li)(OH)_6]$ (Wadsley 1952). Cianciulliite, $Mn^{2+}(Mg,Mn)^{2+}Zn_2(OH)_{10}\cdot2\text{–}4H_2O$, has a layer of octahedra with one quarter of the octahedrally coordinated sites vacant. The structure consists of $[MnO_6]$ and $[(Mg,Mn)O_6]$ octahedra, a layer of $[ZnO_4]$ tetrahedra and a layer of H-bonded H_2O (Grice & Dunn 1991). The sequence of layers in the chalcophanite structure, Mn–O–Zn–H_2O–Zn–O–Mn, closely resembles that of cianciulliite, (Mn,Mg)–OH–Zn–(OH,H_2O)–Zn–OH–(Mn,Mg). Yet in chalcophanite the $[MnO_6]$ layer of octahedra can be regarded as intermediate between that of lithiophorite and cianciulliite, with one in seven of the octahedral sites vacant. The interesting crystal-chemical control here is the bond valence or Lewis strength. In both lithiophorite and chalcophanite, Mn^{4+} is a strong Lewis acid, but the layers of octahedra differ in response to site vacancies. In lithiophorite, the layer of $[Mn^{4+}O_6]$ octahedra is fully occupied, hence essentially neutral. The weak H-bonding afforded by the $[(Al,Li)(OH)_6]$ layer merely occurs in response to the Al:Li ratio, which creates a very weak Lewis acid. In contrast, the $[Mn^{4+}O_6]$ layer of octahedra in chalcophanite has vacancies, making it a stronger Lewis base overall. This stronger Lewis basicity is stabilized by direct bonding to the Zn (or Ni in the case of ernienickelite) layer of octahedra, which is a strong Lewis acid. In cianciulliite, the layer of octahedra has a much stronger Lewis basicity overall since the octahedra are occupied by the weak Lewis acids Mn^{2+} and Mg^{2+}, and there are even more cation vacancies in the layer than in chalcophanite. The net effect in cianciulliite is that Zn is only tetrahedrally coordinated, and each of the oxygen atoms has sufficient Lewis strength to attach a H atom. With this change in the structure, it is unlikely there will be a Ni-analogue of cianciulliite. Ni^{2+} has a higher crystal-field stabilization energy in octahedral coordination than in tetrahedral coordination. Therefore, it more readily adopts octahedral coordination. Zn^{2+} has no such site preference. In contrast, ernienickelite should form readily and may be relatively common in lateritic deposits of Ni.

ACKNOWLEDGEMENTS

The authors thank Mr. Mick Elias of the Western Mining Company for allowing B.J.G. to collect samples at the Siberia complex. Also, we are grateful to Dr. Pete Dunn, Smithsonian Institution, for providing the chalcophanite specimen for study. J.D.G. gratefully acknowledges funds from a Research Advisory Committee Grant, Canadian Museum of Nature. The authors appreciate improvements brought about by the comments of Jeffrey Post, Eugene Foord and R.F. Martin.

REFERENCES

BERRY, L.G. & THOMPSON, R.M. (1962): X-ray powder data for ore minerals. *Geol. Soc. Am., Mem.* **85**.

BURNS, R.G., BURNS, V.M. & STOCKMAN, H.W. (1983): A review of the todorokite – buserite problem: implications to the mineralogy of marine manganese modules. *Am. Mineral.* **68**, 972-980.

ELIAS, M., DONALDSON, M.J. & GIORGETTA, N. (1981): Geology, mineralogy, and chemistry of lateritic nickel–cobalt deposits near Kalgoorlie, Western Australia. *Econ. Geol.* **76**, 1775-1783.

GIOVANOLI, R. (1985): A review of the todorokite–buserite problem: implications to the mineralogy of marine manganese nodules: discussion. *Am. Mineral.* **70**, 202-204.

GRICE, J.D. & DUNN, P.J. (1991): The crystal structure of cianciulliite, $Mn(Mg,Mn)_2Zn_2(OH)_{10}{\cdot}2–4H_2O$. *Am. Mineral.* **76**, 1711-1714.

LEPAGE, Y. (1987): Computer derivation of the symmetry elements implied in a structure description. *J. Appl. Crystallogr.* **20**, 264-269.

________ (1988): MISSYM 1.1: a flexible new release. *J. Appl. Crystallogr.* **21**, 983-984.

OSTWALD, J. (1985): Some observations on the chemical composition of chalcophanite. *Mineral. Mag.* **49**, 752-755.

POST, J.E. & APPLEMAN, D.E. (1988): Chalcophanite, $ZnMn_3O_7{\cdot}3H_2O$: new crystal-structure determinations. *Am. Mineral.* **73**, 1401-1404.

________ & BISH, D.L. (1988): Rietveld refinement of the todorokite structure. *Am. Mineral.* **73**, 861-869.

POTTER, R.M. & ROSSMAN, G.R. (1979a): The tetravalent manganese oxides: identification, hydration, and structural relationships by infrared spectroscopy. *Am. Mineral.* **64**, 1199-1218.

________ & ________ (1979b): A magnesium analogue of chalcophanite in manganese-rich concretions from Baja California. *Am. Mineral.* **64**, 1227-1229.

RADTKE, A.S., TAYLOR, C.M. & HEWETT, D.F. (1967): Aurorite, argentian todorokite, and hydrous silver-bearing lead manganese oxide. *Econ. Geol.* **62**, 186-206.

WADSLEY, A.D. (1952): The structure of lithiophorite, $(Al,Li)MnO_2(OH)_2$. *Acta Crystallogr.* **5**, 676-680.

________ (1955): The crystal structure of chalcophanite, $ZnMn_3O_7{\cdot}3H_2O$. *Acta Crystallogr.* **8**, 165-172.

Received June 14, 1993, revised manuscript accepted October 2, 1993.