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Crystal structure of a pink muscovite from Archer's Post, Kenya: implications for reverse pleochroism in dioctahedral micas

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Abstract

The crystal structure of a reverse pleochroic muscovite containing both Fe^{3+} and Mn^{3+} has been determined by standard single-crystal X-ray methods. The mica has a $2M_1$ polytype, space group $C\,2/c$. Cell constants are $a = 5.1988$Å *esd* 0.0021, $b = 9.0266$Å *esd* 0.0019, $c = 20.1058$Å *esd* 0.0044, $\beta = 95.782°$ *esd* 0.039, $V = 938.72$Å *esd* 0.48. Average bond lengths in tetrahedral sites are 1.646Å and 1.639Å, comparable to bond lengths in Si–Al tetrahedra of other analyzed muscovites, but also compatible with minor site occupancy by Fe^{3+}. Mean bond strengths and electron densities for the sites are also compatible with but do not require minor amounts of tetrahedral Fe^{3+}. A pleochroic mechanism related to tetrahedral Fe^{3+}, therefore, cannot be ruled out. Thermal vibration ellipsoids of atoms in the octahedral layer, however, are oriented with long axes perpendicular to the layer, which suggests the possibility that reverse pleochroism is due instead to an unusual configuration of d-orbitals for octahedrally-coordinated Fe^{3+} or Mn^{3+}.

Introduction

The pink muscovite from Archer's Post, Kenya, was first chemically analyzed and described by Richardson (1975), hereafter referred to as "paper I." The chemical analysis from that study is reproduced in Table 1. Mössbauer and optical absorption spectroscopy were used to relate optical properties of the mica to its crystal chemistry. The Archer's Post muscovite is reversely pleochroic; that is, it absorbs polarized light more efficiently when that light is vibrating in a plane perpendicular to the basal cleavage [E ⊥ (001)] than when it is parallel to it [E ∥ (001)]. Trioctahedral micas are occasionally reversely pleochroic, but the Archer's Post muscovite is still the only reported example of reverse pleochroism in a dioctahedral mica.[1]

Spectra recorded in paper I were ambiguous but generally supported the conclusion that reverse pleochroism is the result of charge transfer between a tetrahedrally-coordinated Fe^{3+} ion and an O^{2-} ligand that bridges to the layer of octahedrally-coordinated cations. Absorption is enhanced when the electric vector of the polarized light beam is coupled with the vibronic mode of the Fe^{3+}–O^{2-} bond, which is roughly parallel to [001]. This mechanism was first suggested for trioctahedral micas (Faye and Hogarth, 1969; Hogarth *et al.*, 1970), and it was reasonable to expect it to apply to dioctahedral micas as well.

Shortly after paper I appeared, however, Annersten and Hålenius (1976) published a critique which questions the likelihood of Fe^{3+} in tetrahedral coordination. They compared spectra in paper I with their own and with one recorded for a ferrian muscovite by Goodman (1976) and concluded that Fe^{3+} is almost certainly in octahedral coordination in the Archer's Post muscovite. This conclusion poses a dilemma, expressed by Richardson (1976): either "(1) Annersten and Hålenius are correct, and Faye and Hogarth's explanation does not apply to reverse pleochroic dioctahedral micas or (2) Faye and Hogarth's mechanism applies to reverse pleochroic muscovite, and Annersten and Hålenius are wrong." The work that is the subject of this paper

[1] Paper I reports that a rose muscovite from Pilar, N. M. (Schaller and Henderson, 1926) is also reversely pleochroic. Gresens and Stensrud (1977), however, have pointed out that this statement was the result of a misreading of Schaller and Henderson's paper.

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-3	7	761	747
-1	1	490	432
-1	3	283	299
-1	6	208	-261
-1	7	164	-190

H = -6

K	L	FO	FC
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-6	3	271	238
-6	7	126	-157
-6	8	422	430
-6	10	820	723
-6	11	210	262
-4	1	303	-314
-4	4	174	190
-4	5	467	428
-4	6	799	722
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0	16	405	-446
0	18	696	-668
2	-13	137	184
2	-12	210	-251
2	-7	117	158
2	-2	107	-187
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4	-5	116	154
6	-5	122	-133

H = -5

K	L	FO	FC
-9	1	237	-187
-9	2	368	-395
-9	3	844	736
-9	5	532	475
-7	1	324	332
-7	2	186	-205
-7	6	114	-105
-7	7	561	504
-7	15	356	408
-5	1	240	186
-5	3	199	199
-5	4	198	-200
-5	6	401	398
-5	7	324	-340
-5	9	315	-326
-5	10	101	-104
-5	11	364	-321
-5	12	96	-110
-5	13	477	-464
-5	14	485	419
-5	16	387	-298
-5	18	140	-125
-3	1	601	553
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-3	3	951	-892
-3	4	274	-35
-3	5	1033	-966
-3	11	1507	-1444
-3	13	305	-316
-3	15	228	303
-3	17	127	-211
-3	18	128	140
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-1	4	167	231
-1	6	475	-458
-1	7	494	-492
-1	8	110	147
-1	9	154	-172
-1	11	374	-403
-1	13	136	-239
-1	14	464	-451
-1	15	521	-487
-1	16	248	252
-1	18	100	116
-1	22	158	-173
7	-11	203	240
9	-3	710	-603

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K	L	FO	FC
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-10	4	317	466
-10	8	149	264
-8	2	265	-349
-8	7	126	290
-8	9	104	83
-8	11	101	-108
-8	13	126	-156
-8	14	300	-331
-8	16	383	-283
-6	1	402	-378
-6	2	602	542
-6	3	231	210
-6	4	383	-390
-6	5	120	79
-6	6	691	-647
-6	8	464	-440
-6	10	180	202
-6	12	622	-628
-6	14	831	-780
-6	15	138	-181
-6	16	271	-303
-6	18	247	277
-4	2	419	-405
-4	3	172	-174
-4	4	569	-566
-4	5	418	379
-4	6	175	177
-4	7	138	-192
-4	8	217	-217
-4	9	138	-165
-4	10	238	-246
-4	12	138	-156
-4	13	300	333
-4	14	353	332
-4	15	302	-318
-4	16	541	-529
-4	18	395	-300
-4	23	163	-201
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-2	2	560	529
-2	3	256	-231
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-2	7	697	-694
-2	9	172	-194
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4	-2	116	155
6	-17	116	-178
6	-5	79	-114
8	-13	135	-147
8	-12	109	112
8	-2	542	-385

H = -3

K	L	FO	FC
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-11	4	122	181
-11	7	167	-218
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-9	4	152	-194
-9	5	191	200
-9	6	193	189
-9	8	188	274
-9	9	838	-845
-9	11	172	241
-9	14	148	270
-9	17	507	-442
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-7	19	122	-174
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-1	13	130	151
-1	14	427	-416
-1	15	280	-279
-1	17	222	184
-1	18	188	218
-1	24	318	263
-1	25	208	260
7	-19	146	182
9	-15	700	599
9	-12	203	-201
9	-1	139	207

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-10	2	124	-153
-10	6	132	-339
-10	10	128	195
-8	3	166	244
-8	4	99	183
-8	6	152	236
-8	7	111	148
-8	9	209	173
-8	10	179	236
-8	14	176	215
-8	15	411	385
-6	1	672	-619
-6	2	1604	1377
-6	3	121	152
-6	4	1149	1039
-6	5	241	215
-6	6	81	137
-6	8	297	333
-6	9	242	-268
-6	10	1511	1389
-6	11	276	302
-6	14	199	-228
-6	17	228	-225
-6	24	437	355
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-4	2	100	126
-4	3	433	-417
-4	4	634	-611
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-4	12	193	233
-4	13	433	444
-4	14	869	833
-4	15	487	-465
-4	18	109	181
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-4	23	164	-161
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-2	9	252	-245
-2	10	518	-497
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-2	19	210	222
-2	21	138	177
-2	25	204	152
-2	26	138	-126
0	-24	174	166
0	2	1378	-1329
0	4	833	-780
0	6	1112	-1106
0	8	434	-435
0	10	1516	-1508
0	12	614	-621
0	14	333	385
0	22	185	175
4	-20	100	-102
4	-14	121	162
8	-17	101	149
8	-13	321	-283

H = -1

K	L	FO	FC
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-9	4	121	-147
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-9	8	256	324
-9	9	93	-125
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-9	13	712	735
-9	15	160	252
-9	16	198	222
-9	18	328	-293
-9	19	412	386
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-7	3	649	597
-7	4	105	-160
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-5	19	139	-173
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-3	16	155	-191
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-1	5	248	253
-1	6	734	-726
-1	7	375	-373
-1	8	118	123
-1	9	82	-107
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-1	19	129	-208	2	21	268	-272	10	0	162	-229	5	14	164	227	2	4	224	-219	12	1	199	-214	7	11	720	-653
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3	-21	100	-88	4	1	365	-320	10	8	131	175	7	1	325	322	2	11	836	820	K	L	FO	FC	9	6	187	-212
3	-2	50	86	4	2	466	426	10	9	104	-108	7	2	217	222	2	13	843	-756	1	0	90	-109	9	7	778	-632
5	-15	89	131	4	3	359	341	10	10	416	389	7	3	908	-747	2	14	158	-200	1	1	230	-231	9	8	377	306
7	-19	115	-161	4	4	593	-586	10	12	813	654	7	4	703	-594	2	16	283	-303	1	2	621	-670	9	13	270	-327
7	-15	104	-116	4	6	404	-387	10	14	165	-197	7	5	714	631	2	17	410	409	1	3	610	597	11	4	166	201
9	-18	279	-265	4	7	260	-277	12	-5	153	-184	7	6	126	147	2	20	132	101	1	4	834	845	11	5	104	-95
9	-14	158	158	4	8	124	-159	12	0	669	638	7	8	293	284	2	21	437	-379	1	5	116	-163				
11	-8	169	-204	4	10	308	-345	12	1	481	-367	7	9	347	-338	2	22	198	-248	1	6	92	-110		H =	4	
				4	11	432	436	12	6	238	269	7	10	142	-184	2	23	220	305	1	7	65	-75	K	L	FO	FC
	H =	0		4	12	1069	-1057	12	9	332	-343	7	12	134	-165	4	0	502	525	1	8	253	-273	-8	-5	365	428
K	L	FO	FC	4	13	623	-62?					7	13	983	824	4	1	176	229	1	9	274	305	-4	-19	105	-99
-12	2	146	196	4	14	371	375		H =	1		7	14	304	307	4	2	675	665	1	11	760	714	0	-4	100	135
-8	18	116	-176	4	17	370	356	K	L	FO	FC	7	17	146	227	4	3	400	412	1	12	460	471	0	0	1665	1547
-6	12	110	110	4	18	361	-327	-11	-2	99	176	7	21	227	292	4	5	462	-451	1	14	336	-345	0	2	1234	1237
-6	18	97	55	4	21	272	-272	-3	-4	57	75	9	0	533	515	4	6	642	677	1	15	296	277	0	4	114	151
-6	19	166	194	4	23	256	270	1	0	356	-380	9	1	746	621	4	8	259	266	1	17	249	267	0	6	238	270
-4	5	68	101	4	24	364	-311	1	1	290	-315	9	3	1135	923	4	10	355	340	1	19	125	206	0	8	1601	1530
-4	15	82	-97	5	6	37	-175	1	2	202	-225	9	4	332	-306	4	11	95	152	1	20	117	184	0	10	111	185
-4	19	74	42	5	10	49	-51	1	3	110	144	9	5	169	207	4	13	405	-405	2	2	44	-431	0	12	87	-140
-4	20	78	-89	6	0	2329	-1995	1	4	796	818	9	6	103	-133	4	16	200	220	3	0	171	-248	0	16	697	698
-4	22	261	231	6	1	495	431	1	5	810	-788	9	8	639	500	4	18	147	193	3	1	535	564	2	0	535	507
-4	26	127	-143	6	2	530	-482	1	6	462	-449	9	9	1372	1038	4	21	121	-178	3	5	304	284	2	2	424	416
-2	-8	48	50	6	3	84	127	1	11	104	-138	9	10	314	-330	4	22	433	422	3	6	161	185	2	3	531	532
-2	6	44	-49	6	5	124	-142	1	12	391	390	9	11	510	403	4	24	166	191	3	7	1172	1128	2	4	635	603
-2	11	67	-82	6	6	424	-384	1	13	419	-407	9	12	239	-233	5	15	77	-67	3	8	185	-242	2	5	492	-516
-2	14	64	-98	6	7	221	-233	1	14	418	-406	9	13	225	-280	6	0	984	-900	3	9	607	-577	2	6	194	233
0	2	383	319	6	8	991	-868	1	17	323	-334	9	16	255	241	6	1	361	306	3	11	196	-203	2	7	123	154
0	4	356	-423	6	9	525	506	1	21	342	-340	9	17	729	595	6	3	182	214	3	12	184	198	2	10	104	-176
0	6	1016	1015	6	10	529	520	3	0	270	-268	11	1	166	149	6	4	1072	949	3	13	838	777	2	11	286	238
0	8	470	507	6	11	123	-155	3	1	1343	-1249	11	2	249	-234	6	5	78	-122	3	15	1159	1036	2	19	247	299
0	10	1448	-1509	6	13	290	-270	3	3	910	-893	11	3	320	284	6	6	380	395	3	16	254	-244	2	20	375	330
0	12	255	261	6	14	724	-656	3	5	1200	-1129	11	4	538	438	6	7	254	-232	3	17	131	-149	2	21	233	-258
0	14	625	629	6	16	1054	-953	3	7	341	-325	11	6	137	-163	6	8	517	-443	3	19	460	410	4	0	555	-584
0	16	1189	1037	6	17	335	305	3	8	130	-161	11	7	163	224	6	9	351	330	3	21	783	630	4	1	115	-145
0	18	165	236	6	20	315	-321	3	9	1563	-1507					6	10	1164	1053	3	23	175	251	4	3	388	383
0	20	638	539	6	22	815	-607	3	10	176	216		H =	2		6	12	999	948	5	2	813	797	4	4	404	-389
0	22	859	704	6	24	219	-254	3	11	683	-662	K	L	FO	FC	6	14	393	371	5	3	136	205	4	6	234	-279
0	24	579	465	8	-21	200	-202	3	13	443	486	-2	-22	117	-167	6	15	206	-227	5	4	985	-906	4	7	115	-146
0	28	116	123	8	-9	84	113	3	15	431	422	0	0	824	788	6	17	178	203	5	5	55	-74	4	9	91	-80
2	0	226	204	8	-8	71	-82	3	16	81	-107	0	2	704	704	6	18	508	469	5	7	101	-173	4	10	268	285
2	1	198	219	8	0	300	-279	3	17	1230	-1049	0	4	352	-391	6	20	193	278	5	8	423	415	4	11	421	388
2	2	334	309	8	2	422	-385	3	23	675	-573	0	6	978	-1006	8	3	356	-344	5	9	93	132	4	12	644	-591
2	3	588	597	8	3	378	-359	3	25	959	-729	0	8	769	749	8	4	166	191	5	11	243	285	4	13	262	-313
2	4	665	662	8	4	123	-162	5	0	243	273	0	10	1226	-1233	8	5	254	263	5	12	510	-496	4	14	140	-169
2	5	921	-909	8	5	361	366	5	1	296	-273	0	12	1758	-1716	8	6	136	141	5	14	426	382	4	15	130	-211
2	7	257	265	8	6	139	-184	5	3	479	-419	0	14	552	-550	8	8	477	411	5	15	325	309	4	17	151	151
2	9	113	146	8	11	309	-264	5	4	646	-583	0	16	386	402	8	10	288	293	5	17	134	201	4	20	416	-348
2	10	230	233	8	13	559	498	5	5	468	-473	0	18	934	-819	8	11	385	-365	5	19	136	210	6	0	731	-725
2	12	281	287	8	14	203	-234	5	6	555	531	0	20	227	-281	8	12	278	238	6	8	79	716	6	2	1121	-1043
2	13	547	-578	8	15	170	-195	5	7	396	-391	0	22	203	224	10	0	586	-475	7	1	94	121	6	3	224	256

FL REQUIRED TO LOAD 56700
FL REQUIRED TO RUN 124500
INITIAL TRANSFER TO DISTN - 2337

BLOCK ASSIGNMENTS.

BLOCK	ADDRESS	LENGTH	FILE
DISTN	100	30672	LGO
ADDEP	30772	62	LGO
CONANG	31054	32	LGO
DERDIS	31106	244	LGO
DERPAR	31352	104	LGO
DET3X3	31456	23	LGO
DISLIS	31521	532	LGO
DLDV	32233	43	LGO
DPHI	32276	20	LGO
MATMUL	32316	56	LGO
MATRAN	32374	32	LGO
MATTST	32426	36	LGO
NEISR	32464	457	LGO
X2XXX	33143	111	LGO
DECOD	33254	101	LGO
TRANSL	33355	133	LGO
ARCCOS	33510	54	LGO
INTTBL	33564	6	LGO
MTY	33572	6	LGO
/STP,END/	33620	1	
/FCL,C,/	33601	26	
/QLINLMT/	33627	1	
/QJOBSFL/	33630	2	
/QASAFLG/	33632	1	
/,QCOMP,/	33633	1	
/QS,IO,/	33634	171	
FTN4LIB	34025	1	FTN4LIB
ATAN,	34026	60	FTN4LIB
CIO=	34106	13	FTN4LIB
COMIO=	34121	60	FTN4LIB
ENDJ=	34201	2	FTN4LIB
FECMSK=	34203	41	FTN4LIB
FLTIN=	34244	156	FTN4LIB
FLTOUT=	34422	314	FTN4LIB
FMTAP=	34736	406	FTN4LIB
FORSYS=	35344	662	FTN4LIB
/QOVERL:/	36226	1	
FORUTL=	36227	16	FTN4LIB
F,OPEN	36245	120	FTN4LIB
F,RDYI	36365	31	FTN4LIB
F,READB	36416	346	FTN4LIB
F,READF	36764	170	FTN4LIB
F,REW	37154	41	FTN4LIB
F,WEOF	37215	52	FTN4LIB

6	4	211	-242
6	7	421	-382
6	8	1415	-1162
6	9	275	284
6	10	471	-444
6	12	168	243
6	13	103	-150
6	15	120	-137
6	16	716	-675
8	0	502	-401
8	3	233	-285
8	4	188	-206
8	6	193	-271
8	9	111	176
8	11	263	-294
10	2	232	-227
10	3	103	-119
10	4	208	257

H = 5

K	L	FO	FC
-9	-6	118	197
-7	-3	104	106
-1	-2	103	114
1	1	514	-537
1	2	556	-559
1	4	346	330
1	5	300	-331
1	6	107	146
1	7	531	-487
1	8	84	-146
1	9	467	-470
1	10	195	-253
1	12	454	482
1	16	129	-175
3	0	198	-133
3	1	182	-268
3	3	617	-629
3	5	727	-729
3	7	192	205
3	9	570	-526
3	11	978	-895
3	13	447	-446
3	15	355	368
3	17	528	-485
5	0	146	-174
5	2	387	382
5	3	146	-227
5	4	136	-199
5	5	115	-165
5	9	556	-526
5	10	321	362
5	12	226	-299
7	1	724	663
7	2	349	347
7	3	280	-282
7	4	287	-275
7	7	463	405
7	8	172	212
9	2	131	194

H = 6

K	L	FO	FC
-2	-16	151	191
0	0	617	-579
0	2	402	330
0	6	1366	-1244
0	8	227	264
0	12	777	-755
2	3	429	421
2	6	100	130
2	10	454	-435
2	11	434	424
4	2	299	372
4	3	414	379
4	10	369	406
6	4	208	282
6	6	759	756

H = 7

K	L	FO	FC
1	2	459	-415
1	3	319	308
3	0	159	-57
3	1	848	704

```
07.47.04. SMRL104.      7.822 CP SECONDS EXECUTION TIME
07.47.04. SMRL104.     35.233 CHARGING UNITS USED
07.47.04. SMRL104.   LINK    RETURNED       1 BLD, BS= 00128,FS=000012B
07.47.04. SMRL104.   FINALIB RETURNED       1 BLD, BS= 01000,FS=000100B
07.47.04. SMRL104. ENTERDS,TAPE7=/HELLANDB/SMR/MUSCOV,10955.
07.47.05. SMRL104.  ERASED SMR MUSCOV 10955
07.47.05. SMRL104.   TAPE7   UNLOADED       1 BLD, BS= 00408,FS=0000018
07.47.05. SMRL104.   TAPE7              127 WORDS STORED IN CACHE.
07.47.05. SMRL104.   CACHE22 RETURNED       6 BLD, BS= 00408,FS=1204668
07.47.05. SMRL104. STOTAPE,TAPE7=/HELLANDB/SMR/MUSCOV,10955.
07.47.06. SMRL104.   FLS=0218  FLL=0146K  LCM BUFFERS=0316K  TOTAL LCM=0465K
07.47.06. SMRL104.   FLS=0236  FLL=0146K  LCM BUFFERS=0316K  TOTAL LCM=0507K
07.47.06. SMRL104.   7600 STOTAPE VERSION 2.6
07.47.06. SMRL104.   TAPE7   UNLOADED       2 BLD, BS= 00028,FS=0000018
07.47.06. SMRL104. STOTAPE,TAPE8=/HELLANDB/SMR/MUSDIS,10955.
07.47.06. SMRL104.   TAPE8   UNLOADED       1 BLD, BS= 00408,FS=0000018
07.47.06. SMRL104.   TAPEPAC DISK 1
07.47.06. SMRL104.   TAPEPAC UNLOADED       1 BLD, BS= 00028,FS=0000018
07.52.57. SMRL104.   STAGING COMPLETE   07.52.57.       33 CUS.
07.52.57. SMRL104.   TAPEPAC RETURNED       1 BLD, BS= 00028,FS=0000018
07.52.58. SMRL104.   TAPE7 = 125 WORDS, 1 RECORDS, 0 FILES TRANSFERRED, VERSION = 9, DATE = 10 FEB 81
07.52.58. SMRL104.   TAPE8 = 230 WORDS, 1 RECORDS, 0 FILES TRANSFERRED, VERSION = 3, DATE = 10 FEB 81
07.52.58. SMRL104.   ********************************
07.52.58. SMRL104.   PRU WRITTEN      = 4
07.52.58. SMRL104.   ACTIVE PRU       = 5523              21 PERCENT
07.52.58. SMRL104.   INACTIVE PRU     = 3590              14 PERCENT
07.52.58. SMRL104.   AVAILABLE PRU    = 16807             65 PERCENT
07.52.58. SMRL104.   ********************************
07.52.58. SMRL104.   AT44,60  001310R 0000RP  000023W 0000WP
07.52.58. SMRL104.   STATION RETURNED       1 BLD, BS= 00028,FS=0000018
07.52.58. SMRL104. COPY,INPUT,IR,TAPE5/RR.
07.52.58. SMRL104.   FLS=020K  FLL=0146K  LCM BUFFERS=0254K  TOTAL LCM=0442K
07.52.58. SMRL104.       FROM INPUT              0W        1R        0F        0L
07.52.58. SMRL104.   TOTAL TO TAPE5              0W        1R        0F        0L
07.52.58. SMRL104.   COPY COMPLETE.
07.52.58. SMRL104.   OUTPUT  QUEUED PR      2 BLD, BS= 00208,FS=0000218
07.52.58. SMRL104.. *J BJ0744J   801573E 10FE681RZ N 000117          RICHARDSON
07.52.58. SMRL104.. ..............................
07.52.58. SMRL104.. SECTORS TRANSFERRED        583
07.52.58. SMRL104.. MAX DISK SECTORS           560
07.52.58. SMRL104.. CP SECONDS               7.922
07.52.58. SMRL104.. SYSTEM SECONDS           0.198
07.52.58. SMRL104.. OLD BLOCKS                  22
07.52.58. SMRL104.. LCM BUFFER LOADS            29
07.52.58. SMRL104.. ITO CUS                     10
07.52.58. SMRL104.. KWORDS XFERRED             100
07.52.58. SMRL104.. CIO CALLS                  370
07.52.58. SMRL104.. STAGING CUS                 67
07.52.58. SMRL104.. ..............................
07.52.58. SMRL104.. TOTAL JOB CUS              117
07.52.58. SMRL104.. COST + OVERHEAD   $       6.02
07.52.58. SMRL104.. ..............................

07.56.47. SMRL104.  OUTPUT  QUEUED PR 139 HO
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