

Table 1. Variation of  $e^2K/\sigma Tk^2$  with  $\epsilon_F/kT$  for metals

$\epsilon_F/kT$	$e^2K/\sigma Tk^2$	
	Dominant acoustic mode scattering	Dominant ionized impurity scattering
0.0	2.172	46.89
0.1	2.184	46.86
0.2	2.196	46.74
0.3	2.211	46.68
0.4	2.226	46.56
0.5	2.241	46.50
0.6	2.256	46.38
0.7	2.271	46.26
0.8	2.286	46.17
0.9	2.304	46.08
1.0	2.319	45.96
1.5	2.409	45.36
2.0	2.499	44.73
2.5	2.589	44.16
3.0	2.673	43.53
3.5	2.751	43.05
4.0	2.820	42.51
4.5	2.883	42.19
5.0	2.934	41.86
5.5	2.988	41.66
6.0	3.018	41.28
6.5	3.054	41.09
7.0	3.081	40.89
7.5	3.105	40.71
8.0	3.126	40.62
8.5	3.144	40.47
9.0	3.159	40.41
9.5	3.171	40.38
10.0	3.180	40.23

For a non-degenerate semiconductor having Maxwellian velocity distribution of electron (or hole velocities), equation (5) may be shown to reduce to

$$\frac{K_c}{\sigma T} = \frac{k^2}{2e^2} (5-n) \quad (10)$$

where

$$v \propto v^n$$

and  $K_c$  represents the contribution to thermal conductivity by the charge carriers.

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#### Magnetic properties of $\text{LiCoPO}_4$ and $\text{LiNiPO}_4$ \*

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THE lithium orthophosphates of divalent nickel and cobalt are isostructural with minerals lithiophilite ( $\text{LiMnPO}_4$ ) and triphylite ( $\text{LiFePO}_4$ ). All four are members of the olivine family.

Polycrystalline  $\text{LiNiPO}_4$  and  $\text{LiCoPO}_4$  were prepared from lithium carbonate and the orthophosphates of ammonium, nickel and cobalt. The mixtures were reacted in air at  $800^\circ\text{C}$ . Lattice parameters were determined by X-ray diffraction;<sup>(1)</sup> for  $\text{LiCoPO}_4$   $a:b:c = 10.20:5.92:4.70$  Å, and for  $\text{LiNiPO}_4$  the orthorhombic cell dimensions are 10.03, 5.85 and 4.68 Å. The space group is *Pnma* with the transition-metal ions occupying mirror plane sites at  $\pm(x, \frac{1}{4}, z)$  and  $\pm(\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$ , where  $x \sim +0.28$  and  $z \sim -0.02$ .

Magnetic susceptibility data taken with a vibrating-sample magnetometer are shown in Fig. 1; no field dependence was observed. In the paramagnetic region,  $\text{LiCoPO}_4$  follows a Curie-Weiss law, with  $\mu_{\text{eff}} = 5.7 \pm 0.1 \mu_B$  and  $\theta = 90 \pm 3^\circ\text{K}$ . The effective moment is larger than those observed in  $\text{Co}_2\text{SiO}_4(5.1 \mu_B)$  and  $\text{CoCaSiO}_4(4.8 \mu_B)$ . In cobalt calcium orthosilicate,  $\text{Co}^{2+}$  ions occupy the inversion sites, and in  $\text{Co}_3\text{SiO}_4$ , both positions. The mirror symmetry site is the larger of the two octahedra, and a larger moment is expected since

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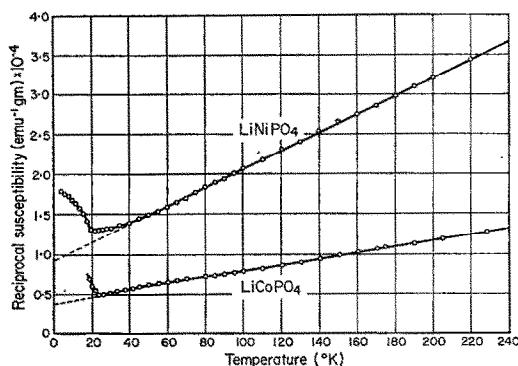


FIG. 1. Reciprocal magnetic susceptibility of polycrystalline LiCoPO<sub>4</sub> and LiNiPO<sub>4</sub>.

there is less orbital quenching. Similar effects are noted in other transition metal olivines. The Curie-Weiss law coefficients for LiNiPO<sub>4</sub> are 3.35  $\mu_B$  and 79°K. In both compounds the susceptibility reaches a maximum at  $23 \pm 2$ °K, indicative of a paramagnetic-antiferromagnetic phase transition.

To establish the magnetic order, neutron diffraction patterns were taken above and below the transition temperature. All the magnetic reflections could be indexed on the chemical unit cell so that only four spin directions need be determined. The best agreement was obtained with collinear arrangements in which the spins at  $(x, \frac{1}{4}, z)$  and  $(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$  are parallel to one another and antiparallel to those at  $(1-x, \frac{3}{4}, 1-z)$  and  $(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z)$ . This is the same configuration observed in LiMnPO<sub>4</sub><sup>(2)</sup> but the spin directions differ. In LiCoPO<sub>4</sub> the spins lie along  $b$ , which is also the preferred direction in Co<sub>2</sub>SiO<sub>4</sub>. The

moments are collinear to  $a$  in LiMnPO<sub>4</sub> and probably to  $c$  in LiNiPO<sub>4</sub>, where the magnetic intensities are very weak. The magnetic structure of LiCoPO<sub>4</sub> is illustrated in Fig. 2. Antiferro-

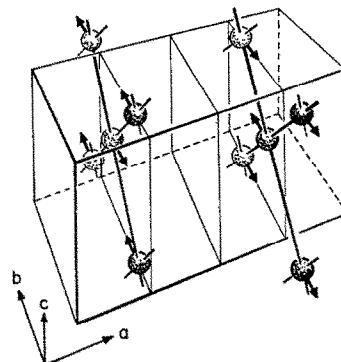


FIG. 2. Magnetic structure of LiCoPO<sub>4</sub>. Antiferromagnetic LiNiPO<sub>4</sub> and LiMnPO<sub>4</sub> adopt similar arrangements with different spin directions.

magnetic Co-O-Co superexchange interactions couple the spins closely in planes parallel to (100). Only long-range forces operate between neighboring planes.

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