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Magnetic behaviour of pollucite-related phases

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The magnetic susceptibilities of powdered samples of $Cs_2CuGe_5O_{12}$, $Cs_2FeGe_5O_{12}$, $Cs_5NiSi_5O_{12}$, $Rb_2CoGe_5O_{12}$ and $CsFeGe_2O_6$ have been measured as a function of temperature. For the first four, the data show the transition metal ion to be in a distorted tetrahedral environment, in agreement with the expected pollucite-like structures. The data for $CsFeGe_2O_6$ are also consistent with this interpretation, but the results are less certain. An unusual feature of these materials is the substitution of a range of divalent transition metal ions into the aluminosilicate framework.

1. Introduction

Pollucite, $CsAlSi_2O_6$ is a framework silicate which is of interest for several nuclear materials applications [1, 2]. The unit cell of pollucite is cubic with the space group Ia3d [3–5]. The crystal structure comprises a three-dimensional aluminosilicate framework built of four- and six-membered rings of corner-sharing (Si, Al)O_4 tetrahedra. Cs ions occupy 12-coordinate distorted sites within this framework. Recently, we have reported a new family of silicate phases (α), with formulae $Cs_2MSi_5O_{12}$(M = Be, Mg, Fe, Co, Ni, Zn, Cd) and $Rb_2MSi_5O_{12}$(M = Mg, Fe, (Co, Zn)), and which have the pollucite structure [6, 7]. These may be regarded as derived from pollucite by the replacement mechanism

$$2Al^{3+} \rightarrow M^{2+} + Si^{4+}$$

In addition, a related family of germanate phases, labelled β phases has been synthesized [8]: $A_2MGe_5O_{12}$ (A = Rb, Cs and M = Be, Mg, Co, Zn). These phases are structurally similar to pollucite but have a different cubic space group, $I\bar{4}3d$ and are best regarded as derived from the $KBSi_2O_6$ structure [9].

Several of the α and β phases form one or more of the γ and δ polymorphs, which are also cubic, or the ε, ζ and η polymorphs which are of lower symmetry than cubic. From the similarity of their powder patterns of those of the parent α and β phases, it is very likely that these polymorphs have structures which are distorted variants of the pollucite structure.

An unusual feature of this large family of phases containing a range of divalent transition metal ions is that the transition metal ion is distributed into tetrahedral sites in the silicate framework. However, the crystal structure determinations [6–8] were incomplete because the M, Si (or Ge) atoms appeared to be disordered over one set of crystallographically equivalent sites. Instead of determining the individual site symmetries, bond lengths, etc., for M and Si (or Ge), an averaged structure was obtained which indicated distorted tetrahedral coordination for these atoms. The present report describes magnetic susceptibility measurements on a selection of α and β phases and has the objective of confirming the oxidation state and coordination number of the transition metal ion.

2. Theory

The analysis of magnetic susceptibility data for solid compounds containing paramagnetic transition-metal ions requires a little discussion of the kind of results which might be expected. The basic theory with which we work is due to Van Vleck [10]. A free transition-metal ion has a well-defined but highly degenerated ground state. When the ion occupies a site in a crystal lattice some of the degeneracy is lifted and the ground state is separated from excited states by energies of the order of 10 000 cm^{-1}. The degeneracy of the ground state may be further lifted by spin-orbit coupling, although the splittings are much smaller than those produced by the crystal field. In addition, under the influence of an applied magnetic field, the degeneracy of the ground state may be further lifted although by an even smaller amount (first-order Zeeman effect). Mixing of excited states into the ground state also occurs (second-order Zeeman effect).

The magnetic susceptibility depends on the magnetic moment and thus on the angular momenta corresponding to the states. It also depends on the occupancy of the states which varies with temperature according to the Boltzmann Law. When splittings caused by the crystal field, spin-orbit coupling and the magnetic field are large, the ground state is separated from excited states by large energies and tends to be the only state occupied at ordinary temperatures. With A states, for which the degeneracy is one, this is particularly true and ions with A ground states in the crystal field have temperature-independent magnetic moments. For E states in the crystal field, with a degeneracy of two, this is also often the case. With T states, on the other hand, which have a degeneracy of

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TABLE I Ground states of some transition metal ions, both as free ions and in octahedral and tetrahedral environments

d-electrons	Free ion	Octa.	Tetr.	Mn	Fe	Co	Ni	Cu
1	^2D	$^2T_{2g}$	^2E	VI				
2	^3F	$^3T_{1g}$	$^3A_2$	V				
3	^4F	$^4A_{2g}$	$^4T_1$	IV	V			
4	^5D	^5E_g (hs)	$^5T_2$	III	IV			
5	^6S	$^6A_{1g}$(hs)	$^6A_1$	II	III			
6	^5D	$^5T_{2g}$(hs)	^5E		II	III		
7	^4F	$^4T_{1g}$(hs)	$^4A_2$			II		
8	^3F	$^3A_{2g}$	$^3T_1$				II	
9	^2D	^2E_g	$^2T_2$					II

three, the influence of spin-orbit coupling and an applied field, yield excited states which are close in energy to the ground state. Consequently, these excited states are partially occupied at ordinary temperatures and the magnetic moments vary with temperature. Thus, the magnetic moments of ions having T crystal field ground states will vary with temperature.

These guidelines [10, 11] are used to interpret the results for the individual phases studied here. The ground states of some transition-metal ions in different environments is shown in Table I.

3. Experimental procedure

The magnetic susceptibilities of the compounds were determined by the Gouy method between 80 and 313 K using a Newport Instruments Gouy Balance. The magnetic field was calibrated using tris-1, 2-diaminoethane nickel thiosulphate as a standard [9]. The temperature scale was calibrated using copper (II) sulphate pentahydrate. Measurements of the susceptibility of the phases was always made at several field strengths to check for possible ferromagnetic behaviour.

Measurements were made on the following phases: $Cs_2M(II)Ge_5O_{12}$ (M = Cu, Fe); $Cs_2Ni(II)Si_5O_{12}$, $CsFe(III)Ge_2O_6$ and $Rb_2CoGe_5O_{12}$. These were prepared as described previously [6–8, 20] and analysed by X-ray powder diffraction. The two phases with Ni(α-phase) and Co(β-phase) were reported previously [7, 8]. The other three are new [20] and belong to the family of β-phases.

4. Results

The experimental susceptibility data, χ_M^{corr}, corrected for the diamagnetism of the other atoms apart from the transition metal atoms are shown in Table II. These were used to construct Cruie-Weiss law ($\chi_M^{corr} = C/(T + \theta)$) plots of inverse molar susceptibility against temperature (T), Fig. 1. The plots are all linear and were used to extract the Curie–Weiss constants, C and θ, given in Table III. The magnetic moment, μ_{eff}, was calculated from [11]

$$\mu_{eff} = (N\beta^2/3k)^{-1/2}(\chi_M^{corr} xT)^{1/2}$$

where k is the Boltzmann constant and β the Bohr magneton (BM), and plotted against temperature, Fig. 2.

5. Discussion

5.1. $Rb_2CoGe_5O_{12}$: a β-phase

Fig. 2 shows that the magnetic moment, μ_{eff}, is effectively independent of temperature and satisfies the equation

$$\mu_{eff} = 4.64 \pm 0.05 + (2.1 \pm 2.1) \times 10^{-4} T$$

Any variation of the moment with temperature is within the experimental error in the measurements. This suggests an A or E ground state with tetrahedral coordination of the cobalt ion as indicated in Table I. The blue colour of the sample could be interpreted as due to Co^{2+} and therefore to the ground state being $^4A_2$. Second-order Zeeman splitting should produce a small temperature-independent paramagnetism. The data are consistent with a small contribution from this source which depends on the energy difference between the ground state and excited ^4T states, that is, $10Dq$ and is given by $8N\beta^2/10Dq = 2.088/10Dq$ with Dq in cm^{-1}. The data are not sufficiently accurate to be able to make an estimate of $10Dq$. Other evidence concerning the environment of the cobalt ion can be adduced by considering the effective magnetic moment (4.64 B.M.). This is different from the spin-only value (3.87 B.M.), calculated from $\mu_{spin\ only} = g[S(S + 1)]^{0.5}$ where g is the g-value and S is the spin quantum number, because of the mixing in of the $^4T_1$ state,

TABLE II Magnetic susceptibility data. Variation with temperature of the mean molar susceptibility, $\bar{\chi}_M^{corr}$, (c.g.s. units × 10^{+6}) corrected for the diamagnetic susceptibility of the alkali metal, silicon or germanium and oxygen

$Rb_2CoGe_5O_{12}$		$Cs_2NiSi_5O_{12}$		$Cs_2CuGe_5O_{12}$		$Cs_2FeGe_5O_{12}$		$CsFeGe_2O_6$	
T(K)	$\bar{\chi}_M^{corr}$	T(K)	$\bar{\chi}_M^{corr}$	T(K)	$\bar{\chi}_M^{corr}$	T(K)	$\bar{\chi}_M^{corr}$	T(K)	$\bar{\chi}_M^{corr}$
93	29 014	88	15 969	88	3 313	88	36 262	78	29 562
113	23 932	103	14 043	103	2 907	103	29 703	93	26 311
133	20 588	123	12 338	123	2 553	123	25 607	113	22 746
153	18 012	143	10 897	143	2 279	143	22 494	133	20 101
183	15 153	163	9 648	163	2 058	163	19 863	153	17 771
183	15 090	183	8 698	183	1 875	183	17 881	173	16 184
213	12 859	193	8 231	193	1 745	203	16 226	193	14 747
243	11 156	203	7 688	203	1 704	223	14 827	213	13 612
273	9 497	213	7 516	213	1 655	243	13 582	233	12 592
292	9 487	223	7 078	223	1 594	273	12 191	253	11 729
313	9 115	233	6 911	233	1 547	292	11 578	273	11 063
		243	6 558	243	1 494	313	10 840	293	10 363
		253	6 379	273	1 374			313	9 753
		275	5 974	290	1 300				
		295	5 589	313	1257				
		313	5 276						

TABLE III Constants in the Curie–Weiss equation $\chi_M^{corr} = C/(T + \theta)$

M	C (c.g.s.)	θ(K)
Co(II)	2.80 ± 0.04	4 ± 4
Ni(II)	1.72 ± 0.02	17 ± 3
Cu(II)	0.45 ± 0.01	53 ± 5
Fe(III)?	3.44 ± 0.01	39 ± 1
Fe(II)	3.55 ± 0.01	15 ± 1

giving an orbital contribution to the ground state. This results in the moment being bigger than the spin-only value by a factor $(1\text{-}4\lambda/10Dq)$, where λ is the spin-orbit coupling constant. It is larger because λ is negative for d^n systems with $n > 5$. We can estimate a value for $\lambda/10Dq$ as 0.049 ± 0.003. The free ion value of λ, $\lambda_0 = 178\,\text{cm}^{-1}$. This places an upper limit on $10Dq$ of $3600\,\text{cm}^{-1}$, which is reasonable for an ion in a tetrahedral environment considering the position of O^{2-} in the spectrochemical series.

The evidence presented here indicates that the cobalt is present as Co^{2+} in a tetrahedral site; no comment can be made about any distortions of the environment.

5.2. $Cs_2NiSi_5O_{12}$: an α-phase

Fig. 2 shows clearly that μ_{eff} varies with temperature from 3.35 B.M. at 88 K to 3.57 B.M. at 333 K. This is consistent with a T ground state (presumably $^3T_1$) and consequently with a tetrahedral site.

A closer consideration of the states of the nickel ion can lead to more detailed evidence about the site symmetry. The ground state of the free Ni^{2+} ion is ^3F and the first excited triplet state is ^3P. The ground state in a tetrahedral crystal field splits into three states $^3T_1$, $^3T_2$ and $^3A_2$ the first of which is the ground state. Its energy is determined by interaction with the excited ^3P state and is measured by a parameter A [12, 13] (A = 1.5 indicates little interaction, while smaller values indicate increasing interaction). A distortion of the tetrahedral site will cause further splitting of the ground state which can be measured by the parameter Δ. Spin-orbit coupling causes further splitting. The value of the spin-orbit coupling constant in the crystal field is usually reduced below its free-ion value ($-178\,\text{cm}^{-1}$) due to the nephelauxetic effect. Delocalization of the electrons on to the oxide ions reduces the effective orbital angular momentum on the Ni^{2+} ion, the effect of which is measured by the orbital reduction parameter, k. Values of $k < 1$ indicate delocalization. The experimental data may be fitted [12] with the parameters $A = 1.5$, $\lambda = -140\,\text{cm}^{-1}$, $\Delta = 1400\,\text{cm}^{-1}$ and $k = 0.8$. Of particular importance is the value of Δ which indicates a considerable distortion of the tetrahedral site, and the value of k which indicates considerable delocalization. To summarize, then, the magnetic evidence suggests that the Ni^{2+} ion is in a considerably distorted tetrahedral environment.

5.3. $Cs_2CuGe_5O_{12}$: a β-phase

The data indicate that the effective magnetic moment varies markedly with temperature and that at room temperature has a value near that expected for the spin-only moment for a d^9 ion such as Cu^{2+} (1.73 B.M.). The Cu^{2+} free ion has a ^2D ground state which splits in a tetrahedral crystal field, yielding a $^2T_2$ ground state which is expected to give an effective magnetic moment which would vary with temperature. A detailed analysis of the data [14–19] suggest that the tetrahedral site is considerably distorted. We can conclude that the copper ion is in the 2+ oxidation state and is in a distorted tetrahedral site.

5.4. $CsFeGe_2O_6$: a β-phase

Fig. 2 shows that the effective magnetic moment varies with temperature from 4.29 B.M. at 78 K to 4.97 B.M. at 333 K. In this phase the iron is ostensibly in the 3+ oxidation state, a d^5 system which will have a free-ion ground state, ^6S. The position of O^{2-} in the spectrochemical series precludes the possibility of low spin configurations so that the ground state expected in a tetrahedral environment is $^6A_1$ or $^6A_{1g}$ in an octahedral site. There can be no orbital contribution to the magnetic moment so that we would expect a temperature independent moment, $\mu_{\text{eff}} = 5.92$ B.M. The observed moment is lower than this and is temperature dependent. A possible interpretation of the data [18] is to suppose that some of the iron is oxidized to the 4+ oxidation state. An analysis of the data shows that the amount of Fe(III) would have to be relatively small; they are consistent with there being 85% Fe(IV) which has a $^5T_2$ ground state in a tetrahedral site and a spin-only moment of 4.90 B.M. The analysis also indicates that the site is distorted. An assumption that the iron is present as Fe(V) is not in agreement with the experimental data. The presence of Fe(II) in a

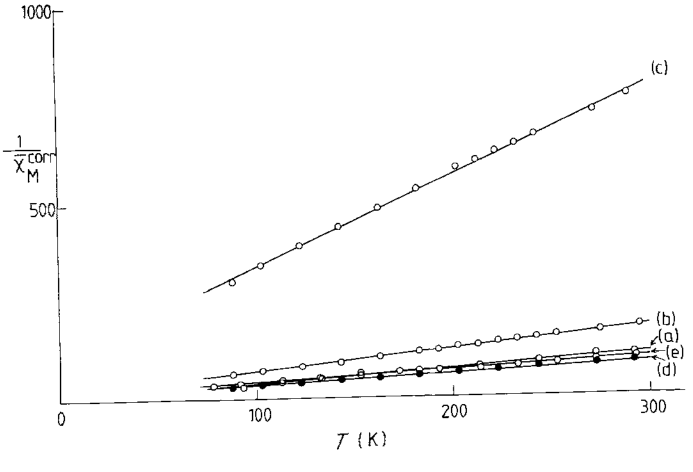

Figure 1 Variation of the inverse of the molar susceptibility corrected for the diamagnetism of all the atoms except that of the transition metal, $1/\chi_M^{corr}$ against temperature (K) for the following compounds: (a) $Rb_2CoGe_5O_{12}$; (b) $Cs_2NiSi_5O_{12}$; (c) $Cs_2CuGe_5O_{12}$; (d) $CsFeGe_2O_6$; (e) $Cs_2FeGe_5O_{12}$.

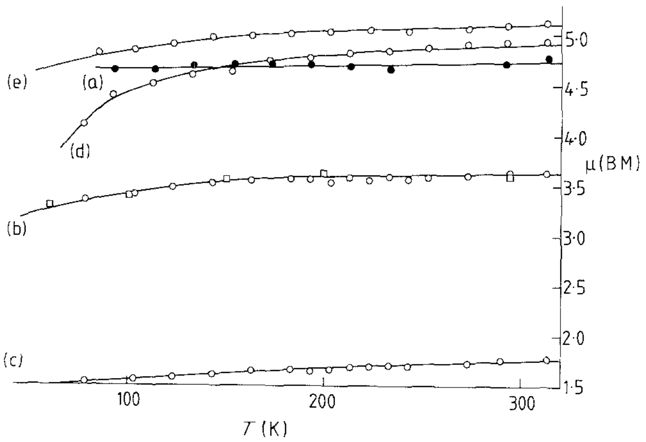

Figure 2 Variation of the effective magnetic moment, $\mu_{\rm eff}$, against temperature (K) for the following compounds: (a) $Rb_2CoGe_5O_{12}$; (b) $Cs_2NiSi_5O_{12}$, (□) $\mu_{\rm eff}$ calculated with $A = 1.5$, $\lambda = -140\,{\rm cm}^{-1}$, $\Delta = 1400\,{\rm cm}^{-1}$ and $k = 0.8$; see text; (c) $Cs_2CuGe_5O_{12}$; (d) $CsFeGe_2O_6$; (e) $Cs_2FeGe_5O_{12}$.

tetrahderal site is ruled out because it would have a ^5E ground state and would be expected to give a temperature-independent moment. There remains the possibility of Fe(II) in an octahedral site although the conditions of the synthesis probably preclude this. We can conclude that the iron is not present as Fe^{3+} in a tetrahedral site but could be present largely as Fe^{4+} with some cation vacancies.

5.5. $Cs_2FeGe_5O_{12}$: a β-phase

Fig. 2 shows that the magnetic moment falls from 5.23 B.M. at 313 K to 4.96 B.M. at 83 K. The value of the moment is greater than the spin-only value (4.98 B.M.). A d^6 ion Fe^{2+} in a tetrahedral site has a ^5E ground state but mixing in components of the excited $^5T_2$ state would be expected to introduce some angular momentum into the ground state and give a moment greater than the spin-only value. This does not account for the temperature dependence of the moment. Certain distortions of the site will split the ^5E state and would be expected to introduce a temperature dependence into the moment, although we cannot quantify this assertion at present. We can, however, assert that the magnetic evidence is not inconsistent with an Fe^{2+} in a distorted tetrahedral site.

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