

## A SHORT NOTE ON THE CRYSTALLINE ELECTRIC FIELDS IN HYDRATED $\text{Co}^{2+}$ SALTS

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**ABSTRACT** The paper gives a preliminary account of the theory of the susceptibility and anisotropy of hydrated  $\text{Co}^{2+}$  salts using Abragam and Pryce's Hamiltonian. It is seen that the experimental anisotropies and susceptibilities can be well fitted with theory on the assumption that the anisotropic crystalline electric field changes quite appreciably from salt to salt and with temperature.

The magnetic susceptibility of  $\text{Co}^{2+}$  salts have been investigated by Schlapp and Penney (1932) on the basis of Van Vleck's (1932) theory of crystalline electric fields. This investigation, however, assumes a single  $\text{Co}^{2+}$  ion in the unit cell of the salts and deals with only two extreme cases of the magnitude of the asymmetric part of the electric field as compared to the spin-orbit coupling. Uryu (1956) has recently attempted to explain the experimental principal susceptibilities of  $\text{Co}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystal (Jackson 1924, Bose 1948) using the method of Abragam and Pryce (1951). The main drawback of this attempt is that it takes into consideration only the three lowest Kramer's doublets, and contains a serious mistake in the fundamental assumptions regarding the energy levels.

On the basis of the limited X-ray structural data (Hofmann, 1931) and paramagnetic resonance data (Bleaney and Ingram, 1951) on the  $\text{Co}^{2+}$  Tutton salts, we have assumed an approximate tetragonal symmetry of the ( $\text{Co}^{2+}, 6\text{H}_2\text{O}$ ) octahedron of which there are two ions in the unit cell, with the tetragonal axes inclined at  $\sim 34^\circ$  to the  $\chi_1$  magnetic axis of the crystal, and following Abragam and Pryce's method have developed a general expression for the susceptibilities of the  $\text{Co}^{2+}$  ion in the crystals which is a complicated function of  $\Delta$ , the tetragonal fields splitting parameter,  $\alpha$  and  $\alpha'$ , the effective Lande splitting factors in the crystals and  $\zeta$  the spin-orbit coupling coefficient.

We find that in order to fit the experimental principal susceptibilities and anisotropies (Jackson, 1924; Bose, 1948), it is enough to take  $\alpha$ ,  $\alpha'$  to be more or less the same in each of the different salts but  $\Delta$  is quite different. Moreover, for a given salt  $\Delta$  is found to vary appreciably with temperature in the entire range studied

(Table I). Similar variations in  $\Delta$  have been observed by us in  $\text{Ti}^{2+}$  caesium alum (Bose *et al.*, 1959) and to a smaller extent in  $\text{Cu}^{2+}$  (Bose *et al.*, 1957),  $\text{Ni}^{2+}$  (Bose *et al.*, 1958),  $\text{Cr}^{3+}$  (Dutta Roy, 1956) and  $\text{V}^{3+}$  (Dutta Roy *et al.*, 1959) salts and are ascribed to the changes in structure from salt to salt and due to thermal expansion of the lattice. It is interesting to note that  $\zeta$  is the same for all the salts and has the same value as for the free ion, indicating that the covalent overlap of  $3d$ -orbitals of the  $\text{Co}^{2+}$  ion and the  $s$ - and  $p$ - orbitals of the surrounding water oxygens is negligible (Owen, 1955). The values of  $\Delta$ ,  $\alpha$ ,  $\alpha'$  are found to be different from those obtained by Abragam and Pryce (1951). Owing to very short relaxation times in the  $\text{Co}^{2+}$  salts, the paramagnetic resonance values for  $g_{\parallel}$  and  $g_{\perp}$  could be obtained only at  $\sim 20^{\circ}\text{K}$  (Bleaney and Ingram) with which the theoretical values are in reasonable agreement.

We give below (Table I) the parameters for the different salts taken to give the best fits of the theoretical square of the moments  $P_{\parallel}^2$  and  $P_{\perp}^2$  along and perpendicular respectively to the tetragonal axis of the  $\text{Co}^{2+}$  ion at different temperatures with the experimental values (Table II). In view of fairly large uncertainties in the existing experimental data, it is not very useful to refine the theoretical parameters

The details will be published elsewhere shortly.

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TABLE I

Salts	$\alpha$	$\alpha'$	$\Delta$ $\text{cm}^{-1}$		$g$ -values at $20^{\circ}\text{K}$					
			Temp $^{\circ}\text{K}$ .	at different Tempera- tures	Experimental		Theoretical			
					$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	$g_{\perp}$		
$\text{Co}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.08	1.53	290	1030	6.45	3.00	6.2	2.9		
			77.2	1230					(for $\Delta = 1250$	
			14.5	1265					$\text{cm}^{-1}$ )	
$\text{Co}(\text{NH}_4\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$	1.095	1.46	296.7K	864	No resonance value					
			185.8	740						
			86.8	720						
$\text{Co}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.245	1.28	300	280	6.56	2.96	6.60	2.71		
			200	300					(for $\Delta = 720$	
			100	320					$\text{cm}^{-1}$ )	

TABLE II

$\text{Co}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$			$\text{Co}(\text{NH}_4\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$			$\text{Co}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$		
T°K.	$P_{  }^2$	$P_{\perp}^2$	T°K.	$P_{  }^2$	$P_{\perp}^2$	T°K.	$P_{  }^2$	$P_{\perp}^2$
290	29.22 (29.19)	18.78 (18.75)	296.7	29.40 (29.66)	19.40 (19.59)	300	29.31 (29.49)	21.88 (22.08)
77.2	34.44 (34.33)	11.19 (10.88)	185.8	30.39 (29.58)	18.24 (17.56)	200	30.79 (30.14)	20.11 (19.42)
14.5	30.12 (29.80)	7.05 (6.65)	86.8	28.81 (28.09)	14.32 (13.65)	100	29.31 (29.23)	15.56 (15.19)

The values in the parenthesis indicate the experimental results.

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