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Spontaneous Magnetic Order Induced by an Intratriplet Mode in the Dimerized Singlet–Ground-State System $Cs_3Cr_2I_9$

Bruno Leuenberger and Hans U. Güdel
Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland

and

Peter Fischer
Labor für Neutronenstreuung, Eidgenössische Technische Hochschule Zürich, CH-5303 Würenlingen, Switzerland

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$Cs_3Cr_2I_9$ represents a novel class of antiferromagnetic dimerized singlet–ground-state systems. Neutron scattering shows a transition to magnetic order below 7 K. The soft mode was identified as an intratriplet mode rather than a singlet-triplet exciton mode by relation of the magnetic order to the spin dynamics. A reduced magnetic moment of the Cr^{3+} ions is ordered ferromagnetically within the dimers even though the corresponding interaction is antiferromagnetic.

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Singlet–ground-state magnetism has attracted a great deal of scientific interest. Much effort has been devoted to the question under what conditions a singlet–ground-state system orders magnetically and whether there is a softening of an associated mode as the transition temperature is approached from the disordered phase.[1] Studies of soft modes in relation to the spontaneous ordering are of ultimate interest because they enable us to relate the exciton dynamics to the static magnetic structure. They can thus significantly improve our understanding of phase transitions. It has been argued that the true soft mode in singlet-triplet systems is probably not the singlet-triplet mode, but rather a zero-frequency intratriplet mode.[2–4] Most studies so far on singlet–ground-state systems were done with rare-earth compounds, in which anisotropy effects are important and the singlet-doublet or singlet-triplet situation arises from the interplay of crystal-field and spin-orbit interactions.[1] They are therefore not ideal systems in the sense that the relevant states are pseudo singlet and triplet states. In addition, they suffer from the disadvantage that the exchange is not restricted to nearest neighbors in the lattice. This is in contrast to the family of insulating compounds $Cs_3Cr_2X_9$ (X=Cl, Br, I), in which the singlet-triplet situation arises from an isotropic intradimer interaction, and only nearest-neighbor exchange has to be considered. These dimerized singlet–ground-state systems therefore provide a novel class of magnetic materials with interesting properties.[5,6] In this Letter we present the first observation of spontaneous magnetic order in the dimer compound $Cs_3Cr_2I_9$. This ordering shows a number of unique features. The dimerization of the system enables us to deduce the nature of the soft mode from the structure of the ordered phase. This is in contrast to single-ion systems, in which the exciton mode has to be studied carefully near the transition temperature in order to determine if the mode becomes soft or stays hard.[4] These studies are limited by the energy resolution of the neutron spectrometer.

The structure of $Cs_3Cr_2X_9$ (X=Cl, Br) is hexagonal, $P6_3/mmc$, with two dimers $Cr_2X_9{}^{3-}$ per unit cell, which form two sublattices. The Cr-Cr separation is 3.4 Å within a dimer and 8 Å between nearest-neighbor dimers.[7] The schematic structure is shown in Fig. 1, with the three relevant interactions. Each Cr^{3+} is in a spin-only ground state with $S=\frac{3}{2}$ ($^4A_2$). The antiferromagnetic intradimer exchange (J) produces the singlet-triplet situation. The two energetically higher dimer levels, quintet and septet, are neglected in the present study, because they are not populated at low temperatures. The interdimer interactions J_p and J_c lead to an energy dispersion of the singlet-triplet excitation. The dispersion has been studied for

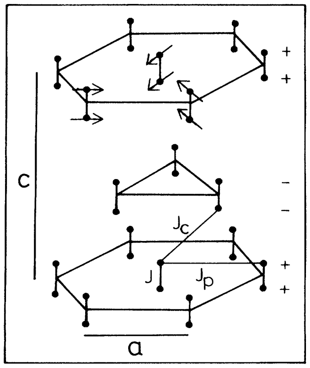

FIG. 1. Schematic structure of $Cs_3Cr_2I_9$ showing only the Cr^{3+} ions. The three interactions J, J_p, and J_c are included. The hexagonal lattice parameters at room temperature are $a=8.04$ Å and $c=20.2$ Å. The triangular magnetic structure is indicated by arrows and plus/minus signs.

$Cs_3Cr_2Br_9$ by inelastic neutron scattering and the following parameters were derived: $J = -1.03$ meV (intradimer), $J_p = -0.054$ meV (interdimer, intrasublattice), and $J_c = -0.039$ meV (interdimer, intersublattice). All the three interactions are antiferromagnetic for $Cs_3Cr_2Br_9$ as they are for $Cs_3Cr_2Cl_9$, which has also been studied.[8] The exchange parameters of both compounds can be rationalized by a simple molecular orbital model, which predicts a reduced intradimer exchange and an enlarged interdimer interaction for the iodide.[8] The Hamiltonian is of the Heisenberg type and thus completely isotropic. It considers only interactions between nearest-neighboring dimers:

$$H = -\tfrac{1}{4}J \sum_i (\mathbf{K}_i \cdot \mathbf{K}_i - \mathbf{L}_i \cdot \mathbf{L}_i) - \tfrac{1}{4}J_p \sum_{ij} (\mathbf{K}_i \cdot \mathbf{K}_j + \mathbf{L}_i \cdot \mathbf{L}_j) - \tfrac{1}{4}J_c \sum_{ij'} (\mathbf{K}_i \cdot \mathbf{K}_{j'} - \mathbf{L}_i \cdot \mathbf{L}_{j'}), \tag{1}$$

with

$$\mathbf{K}_i = \mathbf{S}_{i1} + \mathbf{S}_{i2}, \quad \mathbf{L}_i = \mathbf{S}_{i1} - \mathbf{S}_{i2}. \tag{2}$$

$\mathbf{S}_{i1}$ and $\mathbf{S}_{i2}$ are the spin operators of the Cr^{3+} ions of dimer i. $\mathbf{K}_i$ is the dimer spin operator, while $\mathbf{L}_i$ is a so-called pseudo dimer spin operator. i,j and i,j' sum over dimers on the same and different sublattices, respectively. The first term in Eq. (1) separates the singlet and triplet dimer levels by J. $\mathbf{K}$ has no matrix elements between the singlet and triplet states, but it has nonzero matrix elements within the triplet state. $\mathbf{L}$, on the other hand, has matrix elements only between the singlet and triplet states. $\mathbf{L}$ is therefore responsible for the singlet-triplet excitations, while $\mathbf{K}$ drives only intratriplet excitations, which have zero frequency within the Hamiltonian (1).

The magnetic ordering of such a system depends on whether $\mathbf{K}$ or $\mathbf{L}$ is the ordered quantity. By use of Eqs. (1) and (2) and the antiferromagnetic nature of J, J_p, and J_c we are able qualitatively to predict and to discuss the corresponding magnetic structures, which we will call K and L order, respectively. $\mathbf{L}$ is the ordered quantity if the singlet-triplet exciton mode becomes soft at the transition temperature. As a consequence the ordering of the Cr^{3+} spins within the dimers is antiferromagnetic. The dimer pseudo spins are ordered antiferromagnetically within the same sublattice, but ferromagnetically between the sublattices. This is a result of the different signs of the term $\mathbf{L}_i \cdot \mathbf{L}_j$ in Eq. (1) for the corresponding interactions J_p and J_c. On the other hand, if the K order is realized by an intratriplet mode as soft mode, then a reduced magnetic moment of the Cr^{3+} ions within a dimer is ordered ferromagnetically, while the ordering of the dimer spins is antiferromagnetic within and between the sublattices. We thus have the remarkable prediction that an antiferromagnetic intradimer interaction (J) produces a ferromagnetic order of the Cr^{3+} spins within the dimer. The ordering of these Cr^{3+} spins is not complete, however. K has an expectation value of 1 in the ordered phase. Accordingly, the spin of the Cr^{3+} ions is only $\frac{1}{2}$, compared with its maximum value of $\frac{3}{2}$. In the following paragraph we will show that the magnetic order of $Cs_3Cr_2I_9$ is successfully interpreted and discussed within this simple framework.

Powder samples of $Cs_3Cr_2I_9$ were prepared as described in Ref. 7. $Cs_3Cr_2I_9$ exists in two modifications, one of which is isostructural with $Cs_3Cr_2Br_9$ and belongs to the space group $P6_3/mmc$.[7] A powder sample containing mainly this modification was used for the measurements. The second modification shows no magnetic ordering down to 1.5 K and its existence does not interfere with the results discussed in this Letter. The extremely air-sensitive powder sample was sealed in a vanadium cylinder and mounted in a helium cryostat. The neutron scattering experiments were performed on the two-axis spectrometer DMC, which is equipped with a multidetector. Magnetic susceptibility measurements were performed with a sample of $Cs_3Cr_2I_9$ of the $P6_3/mmc$ modification by use of the moving-sample technique.

Figure 2 shows the magnetic susceptibility of $Cs_3Cr_2I_9$. The sharp peak around 8 K is related to magnetic order. The data above 10 K were analyzed within the random-phase approximation and lead to $J = -0.8$ meV and $J_p + J_c = -0.15$ meV. The susceptibility therefore shows that the interaction parameters are indeed antiferromagnetic, as expected.[8] Figure 3 shows the diffraction patterns at 4.2 and 12 K in the region of small scattering angles. Two magnetic Bragg peaks are clearly visible in the 4.2-K spectrum. They

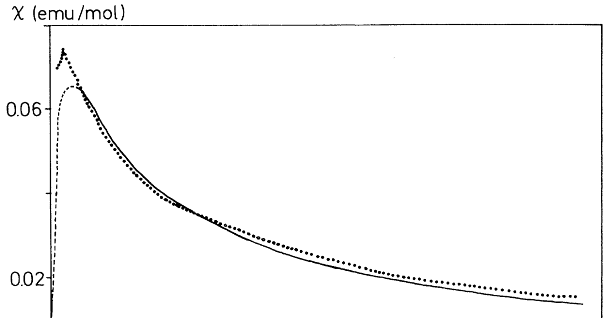

FIG. 2. Magnetic susceptibility of a powder sample of $Cs_3Cr_2I_9$. The full line represents the least-squares fit to the data above 10 K.

are absent in the 12-K pattern. A few additional, but significantly weaker, magnetic peaks could also be identified. They are included in Fig. 4. From the positions of the magnetic peaks we derive a magnetic unit cell which is enlarged in the *a* direction of the hexagonal lattice by approximately $\sqrt{3}$ compared to the nuclear cell. In the *c* direction the magnetic cell coincides with the nuclear cell. There is a small deviation (3%–4%) of the observed magnetic peak positions from those calculated for a $(\sqrt{3}a,\sqrt{3}a,c)$ unit cell. We attribute this to a small incommensurability of the magnetic and nuclear structures which is not relevant to the present discussion. The two strong magnetic peaks are thus assigned to the $(\frac{1}{3}\,\frac{1}{3}\,0)$ and $(\frac{1}{3}\,\frac{1}{3}\,1)$ reflections. The same relationship between nuclear and magnetic unit cells is found in many hexagonal antiferromagnets with a triangular spin structure.[9] The intensity of the magnetic Bragg peaks is given by the neutron cross section:

$$\left(\frac{d\sigma}{d\Omega}\right)_t \sim F(\boldsymbol{\kappa})^2\tfrac{1}{2}[1 \pm \cos(\boldsymbol{\kappa}\cdot\mathbf{R})][\mathbf{P}_t^2-(\mathbf{P}_t\cdot\boldsymbol{\kappa})^2/\kappa^2]\sum_\tau \delta(\boldsymbol{\tau}-\boldsymbol{\kappa}), \qquad (3)$$

with

$$\mathbf{P}_t=\sum_d \langle \mathbf{t}_d\rangle \exp(i\boldsymbol{\kappa}\cdot\mathbf{d}). \qquad (4)$$

t represents one of the two dimer operators **K** or **L**, $F(\boldsymbol{\kappa})$ is the magnetic form factor of Cr^{3+}, $\boldsymbol{\kappa}$ is the scattering vector, $\boldsymbol{\tau}$ is a reciprocal magnetic lattice vector, and **d** is the position vector of a dimer in the magnetic unit cell. $\mathbf{P}_t$ contains all the information about the magnetic structure. **R** is the Cr-Cr separation within a dimer. $1 \pm \cos(\boldsymbol{\kappa}\cdot\mathbf{R})$ is a modulation factor arising from the localized dimer mode. The plus sign is appropriate for $\mathbf{t}=\mathbf{K}$, while the minus sign should be used for $\mathbf{t}=\mathbf{L}$. Calculated and observed relative intensities for the *L* and *K* order are compared in Fig. 4. A triangular spin structure in the basal plane was found to lead to the best agreement between observed and calculated intensities, and the values in Fig. 4 were calculated with this structure. There is no doubt from this comparison that the realized magnetic order is the *K* order. The intense $(\frac{1}{3}\,\frac{1}{3}\,0)$ peak would be absent in the *L* order because of the dimer factor $1 \pm \cos(\boldsymbol{\kappa}\cdot\mathbf{R})$ in Eq. (3). The $(\frac{1}{3}\,\frac{1}{3}\,2)$ reflection should be dominant for the *L* order, but experimentally it is very weak, in perfect agreement with the *K* order. We are forced to conclude by this clear-cut result that the magnetic order in $Cs_3Cr_2I_9$ is induced by an intratriplet mode rather than a singlet-triplet exciton mode. It is important to note that our main argument in this assignment is not the detailed structure of $\mathbf{P}_t$ [Eq. (4)], i.e., the triangular spin structure in the basal plane, but rather the dimer modulation factor in Eq. (3), which is independent of the detailed magnetic structure. From a comparison of the magnetic intensities with nuclear

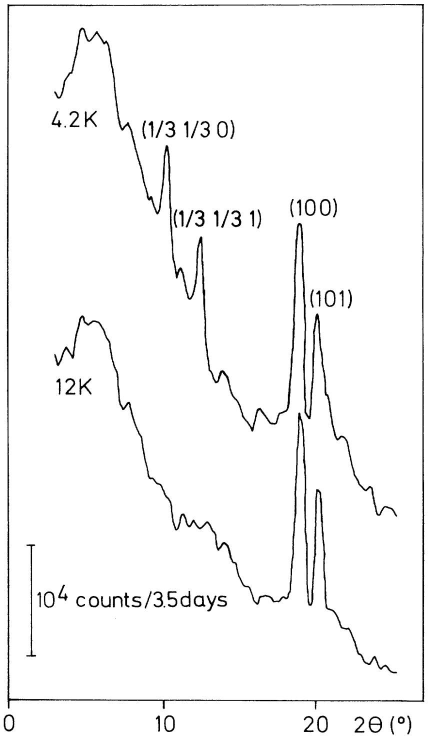

FIG. 3. Neutron diffraction patterns of $Cs_3Cr_2I_9$ in the region of small 2Θ values. The wavelength was 2.322 Å. The nuclear (100) reflection is contaminated with a nuclear Bragg peak from the second modification of $Cs_3Cr_2I_9$ (Ref. 7).

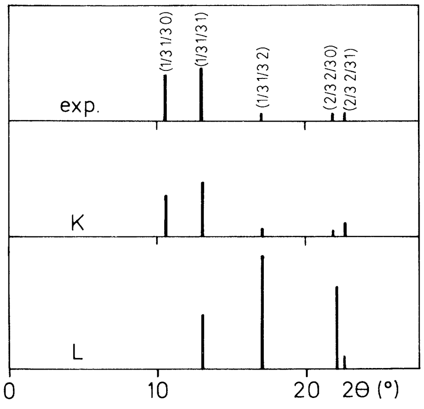

FIG. 4. Observed and calculated (for *K* and *L* order) magnetic neutron diffraction patterns.

Bragg peaks at 1.5 K we estimate an ordered dimer moment of $K = 0.91$. This corresponds to an ordered moment S of the Cr^{3+} ions of 0.45. Within the estimated experimental error there is no significant reduction of the ordered moments compared to the theoretical values of $K = 1$ and $S = \frac{1}{2}$, respectively. This provides further strong support for our interpretation.

To conclude, we have elucidated the nature of the soft mode associated with the magnetic ordering in $Cs_3Cr_2I_9$ from the properties of the magnetic structure. A reduced magnetic moment of the Cr^{3+} ions within a dimer is ordered ferromagnetically, even though the corresponding interaction is antiferromagnetic. This at-first-sight puzzling conclusion is a direct result of the K order of the system. As far as the dimer is concerned the magnetic ordering of this compound is therefore accompanied by a transition from an antiferromagnetic to a ferromagnetic alignment of the magnetic Cr^{3+} moments. If the compound is treated as consisting of individual Cr^{3+} ions, then one would conclude that the ordered magnetic moment $S = 0.45$ is drastically reduced compared with the value of the free ion, for which $S = \frac{3}{2}$. The origin of this reduction lies in the antiferromagnetic dimerization, which produces a magnetic system with alternating strong and weak interactions. The compound should therefore be considered as consisting of interacting Cr^{3+} dimers, rather than individual Cr^{3+} ions.

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