Interference Effects in Neutron Scattering from Magnetic Clusters

A. Furrer
Institut für Reaktortechnik, Eidgenössische Technische Hochschule Zürich, CH-5303 Würenlingen, Switzerland

and

H. U. Güdel
Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern, Switzerland
(Received 8 June 1977)

Inelastic neutron scattering experiments have been performed on binuclear Cr^{3+} clusters and trinuclear Fe^{3+} clusters embedded in molecular complexes. The intensities of transitions within the exchange-split ground state observed at various transfers exhibit an oscillatory behavior due to interference effects which are a direct picture of the metal-metal distances in the cluster. From these measurements, precise magnetic-form-factor data of Cr^{3+} and Fe^{3+} have been obtained.

Recently inelastic neutron scattering has been introduced for studying exchange interactions in isolated clusters of magnetic ions.[1,2] In contrast to the classical methods (measurements of the bulk properties, magnetic resonance experiments), the neutron scattering technique yields direct information about the exchange interactions since the energies of transitions between the exchange-split ground-state levels can be directly determined. Neutron scattering is also superior to optical techniques, because optical spectroscopic data cannot, in most cases, be collected over a wide temperature range because of broadening and partial quenching of the emission at higher temperatures; moreover, the wave-vector dependence of the intensities in the neutron experiment yields direct information about the form factor of the unpaired electrons and about the geometrical configuration of the magnetic ions in the cluster. The latter gives rise to a characteristic interference term in the neutron cross-section formula.

In this Letter, we present the observation of interference effects in neutron scattering from polynuclear clusters of transition metals embedded in molecular complexes in which the interacting magnetic ions are effectively in S states, i.e., the ligand fields are sufficiently strong to quench the orbital angular momentum. Under these circumstances the neutron cross-section formula can easily be derived,[3] and no assumptions have to be made concerning the wave-vector dependence of the scattering. Thus the magnetic form factor can be determined directly from experiment, in contrast to neutron diffraction and inelastic neutron scattering from spin waves in magnetically ordered systems in which experiments the evaluation of the form factor is based on assumptions concerning both the magnetic structure and the ordered magnetic moment, and cooperative phenomena often create uncertainties in the interpretation of spin-wave data. These disadvantages do not exist in inelastic neutron scattering experiments performed on magnetic clusters in which well-defined transitions between the exchange-split ground-state levels are observed. As a consequence, rather precise form factor data can be obtained up to $\lambda^{-1}\sin\theta = 0.4$, which is demonstrated in the present work.

Experiments were performed on polycrystalline samples of deuterated acid rhodo chromium chloride, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5\cdot H_2O$, and deuterated α-metavoltine, $K_{10}[Fe_3O(SO_4)_6(H_2O)_3]_2\cdot 12H_2O$, which contain binuclear Cr^{3+} clusters and trinuclear Fe^{3+} clusters, respectively. Details of the sample preparation are given elsewhere.[2,4,5] In these classical inorganic materials, each cluster is effectively shielded from its neighbors, and magnetic interactions between clusters can be neglected. From x-ray work it is known that the Cr-Cr distance in acid rhodo chromium chloride is 3.85 Å,[6] and the Fe^{3+} ions in α metavoltine are arranged in an equilateral triangle with a Fe-Fe distance of 3.33 Å.[7] In both complexes, the coupling of the transition-metal ions is antiferromagnetic and can be well described by a Heisenberg Hamiltonian

$$\mathcal{H} = -2J\sum_{i,j}\vec{S}_i\cdot\vec{S}_j. \qquad (1)$$

$\mathcal{H}$ commutes with the total spin $\vec{S}=\sum_i\vec{S}_i$ of the cluster. For a Cr^{3+} pair we have $S_1=S_2=\frac{3}{2}$; thus $\mathcal{H}$ splits the electronic ground state into four spin

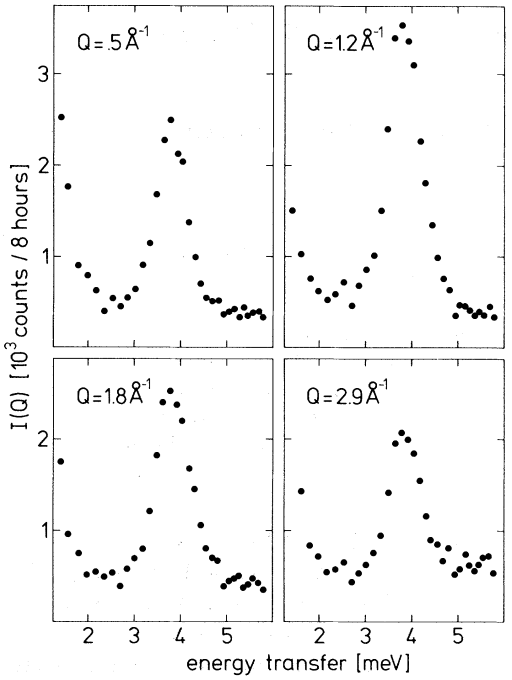

FIG. 1. Energy spectra of neutrons scattered from deuterated acid rhodo chromium chloride at 4.2 K. The spectra are transformed to a linear energy scale and corrected for analyzer and detector sensitivity.

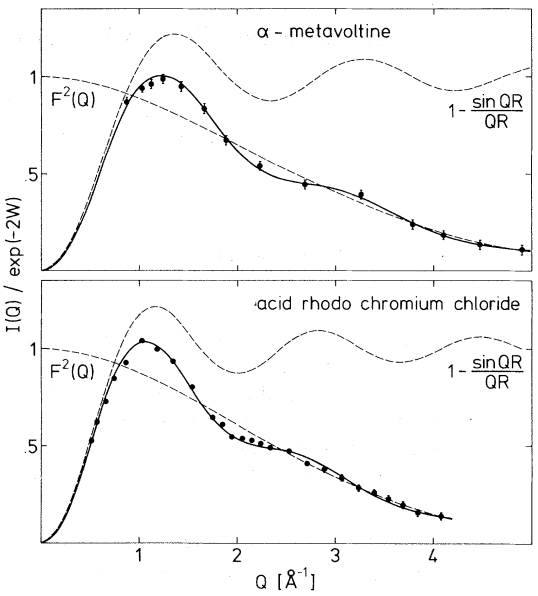

FIG. 2. Normalized peak intensities of the transition from the ground level to the first excited spin level at 4.2 K. The full lines correspond to the predictions of Eq. (5).

levels with energy eigenvalues

$$E(S) = -J[S(S+1) - \tfrac{15}{4}], \quad S = 0, 1, 2, 3. \qquad (2)$$

From luminescence spectroscopy[8] and inelastic neutron scattering experiments[2,4] on acid rhodo chromium chloride the exchange parameter was determined to be $J = -1.9$ meV. For a Fe^{3+} triad we have $S_1 = S_2 = S_3 = \frac{5}{2}$; thus, for the particular case of an equilateral triad, $\mathcal{H}$ gives rise to eight spin levels with energy eigenvalues

$$E(S) = -J[S(S+1) - \tfrac{105}{4}], \quad S = \tfrac{1}{2}, \tfrac{3}{2}, \ldots, \tfrac{15}{2}. \qquad (3)$$

From neutron spectroscopy[5] on α-metavoltine, the exchange parameter $J = -3.2$ meV was obtained.

The present inelastic neutron scattering experiments were carried out on a multiangle-reflecting crystal (MARC) spectrometer at the reactor Diorit, Würenlingen, in the neutron energy-loss configuration. The monochromator energy was kept fixed at 14.96 meV, and a pyrolytic graphite filter was used to reduce higher-order contamination. The measurements were performed at 4.2 K.

Typical energy spectra observed for acid rhodo chromium chloride are shown in Fig. 1. There is a well-resolved inelastic line whose magnetic origin has been confirmed in previous experiments[2,4] by comparing the variation of the intensities with temperature. The phonon scattering is weak and does not give rise to a peaked structure in the energy range of interest: It slightly raises the background level when the momentum transfer $\hbar\vec{Q}$ is increased (see Fig. 1). Thus the inelastic peak arising at an energy transfer of 3.8 meV can be identified as a magnetic transition from the ground level ($S = 0$) to the first excited spin level ($S = 1$). In the data analysis, the inelastic line has been approximated by a Gaussian, and the sum of instrumental background and phonon contributions has been assumed to be linearly dependent upon energy transfer. The results of the least-squares fitting procedure are shown in Fig. 2. The peak intensities markedly deviate from the usual form-factor behavior expected for scattering contributions of magnetic origin. In particular, the peak intensity rapidly increases with increasing momentum transfer $\hbar\vec{Q}$ and has a maximum at $Q = 1$ Å^{-1}. It will be shown that the oscillatory behavior of the intensities is due to interference effects which are a direct picture of the metal-metal distances in the cluster.

The energy spectra obtained for α-metavoltine have been analyzed in a similar way. The results are summarized in Fig. 2. The observed intensities correspond to the transition from the ground level ($S = \frac{1}{2}$) to the first excited spin level

($S=\frac{3}{2}$) at an energy transfer of 9.8 meV. Again the peak intensities do not exhibit the usual form-factor behavior because of interference effects.

The intensity of a transition $S \rightarrow S'$ can be calculated from the thermal-neutron cross-section formula which is given by[3]

$$I \sim \exp\left(-\frac{E(S)}{k_B T}\right)\exp(-2W)F^2(Q)\sum_{\alpha,\beta}\left(\delta_{\alpha\beta}-\frac{Q_\alpha Q_\beta}{Q^2}\right)\sum_{i,j}\exp[i\vec{Q}\cdot(\vec{R}_i-\vec{R}_j)]\sum_{M,M'}\langle SM|\hat{S}_i^{\alpha}|S'M'\rangle\langle S'M'|\hat{S}_j^{\beta}|SM\rangle, \quad (4)$$

where $\exp(-2W)$ is the Debye-Waller factor, $F(Q)$ the form factor, $\vec{R}_i$ the position vector of the ith metal ion in the cluster, $|SM\rangle$ and $|S'M'\rangle$ the eigenvectors of the Hamiltonian (1), and $\alpha, \beta = x, y, z$. The structure factor of Eq. (4) has to be averaged in $\vec{Q}$ space, since the experiments have been carried out for polycrystalline material. By performing the appropriate sum over the metal ions in the cluster, we obtain

$$I \sim \exp\left(-\frac{E(S)}{k_B T}\right)\exp(-2W)F^2(Q)\mathfrak{M}\left(1-\frac{\sin QR}{QR}\right). \quad (5)$$

Here $\mathfrak{M}$ stands symbolically for the matrix elements of Eq. (4) which have been evaluated elsewhere[4,5] by means of tensor operator methods. The last term in Eq. (5) is the interference term in which R denotes the metal-metal distance within the cluster. For irregular cluster configurations, more complicated interference terms appear.

There are three Q-dependent terms in Eq. (5). X-ray data on acid rhodo chromium chloride[6] and α-metavoltine[7] give detailed information on both the metal-metal distance in the cluster and the thermal parameters of the metal ions, so that the interference term, as well as the Debye-Waller factor, is known. The latter, however, varies by less than 10% in the range of momentum transfers $\hbar Q$ covered in the present experiments. Thus the form factor $F(Q)$ can be directly determined from the observed peak intensities without any assumptions. This is demonstrated in Fig. 2 where the full line through the experimental data corresponds to the best description of Eq. (5) based on a smoothed form-factor curve.

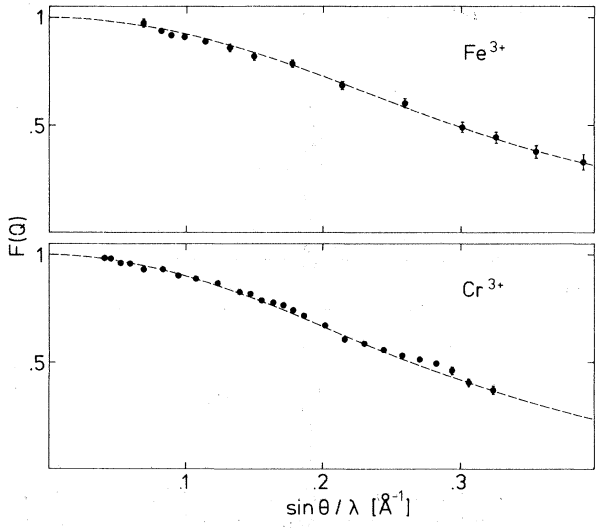

FIG. 3. Magnetic form factors for Cr^{3+} in acid rhodo chromium chloride and for Fe^{3+} in α-metavoltine. The broken lines correspond to the calculated form factors of Ref. 9.

In Fig. 3 we give the form factors of Cr^{3+} and Fe^{3+} as derived from the present experiments. Our results are in good agreement with the calculated form factors.[9] As far as we are aware, no experimental form-factor data of Cr^{3+} have been published so far. By means of the present method the form factor can be determined rather precisely even at large $\sin\theta/\lambda$ values where the accuracy in neutron diffraction is normally limited to (30–50)% due to instrumental resolution and overlap of different elastic lines. These difficulties did not arise in the present experiments as can be seen from Fig. 1; moreover, the instrumental resolution of the MARC spectrometer is independent of the momentum transfer $\hbar Q$ for nondispersive excitations.

As a byproduct of the present experiments we have been able to determine the exchange splitting at 4.2 K more accurately than in previous experiments.[2,4,5] In acid rhodo chromium chloride, the $S=0$ and $S=1$ ground-state levels are separated by 3.822 ± 0.012 meV; and in α metavoltine, the separation between the $S=\frac{1}{2}$ and $S=\frac{3}{2}$ ground-state levels is 9.84 ± 0.09 meV.

[1]W. J. L. Buyers, E. C. Svensson, and T. M. Holden, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976*, edited by R. Moon, CONF-760601 (National Technical Information Service, Springfield, Va., 1976), p. 771.

[2]A. Furrer and H. U. Güdel, J. Phys. C 10, L191 (1977).

[3]W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, Oxford, 1971), p. 109.

[4]H. U. Güdel and A. Furrer, Mol. Phys. 33, 1335 (1977).

[5]A. Furrer and H. U. Güdel, to be published.
[6]J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. 12, 2928 (1973).
[7]J. Thich, thesis, Rutgers University, New Jersey, 1975 (unpublished).
[8]J. Ferguson, H. U. Güdel, and M. Puza, Aust. J. Chem. 26, 513 (1973).
[9]R. E. Watson and A. J. Freeman, Acta Crystallogr. 14, 27 (1961).

Observation of Thermally Induced Potential in a Superconductor

Charles M. Falco
Argonne National Laboratory, Argonne, Illinois 60439
(Received 20 June 1977)

Potential differences have been measured between a normal probe and a superconducting probe attached to a superconductor held in a temperature gradient. These observations suggest that a thermoelectrically generated quasiparticle current is flowing in the superconductor and allow evaluation of the thermal transport coefficient for the quasiparticles.

The first measurement of a thermoelectric transport coefficient in a superconductor was reported by Meissner in 1927.[1] It was found that a circuit consisting of two metals gave rise to no thermoelectromotive force when both metals were superconducting. This, and many subsequent experiments,[2] have shown that with the exception of flux flow[3] and certain electrostatic phenomena[4] all conventional thermoelectric effects vanish in the superconducting state. However, as Ginzburg[5] first noted, there exists in a superconductor the possibility of a simultaneous flow of a normal current of density $\vec{j}_n = L_T(-\nabla T)$ and a supercurrent $\vec{j}_s = -\vec{j}_n$. This prediction of a "superconducting fountain effect" was qualitatively verified by Clarke and Freake[6]; however, they were unable to obtain quantitative information on the transport coefficient L_T. More recently[7] calculations based on the two-fluid model have predicted that this flow of normal current in a superconductor gives rise to a nonquantized contribution to the magnetic flux in a loop made up of two different superconductors. Experimental data[8-10] indicate the existence of such a magnetic flux with a value of as much as five orders of magnitude[10] larger than predicted by theory. This discrepancy, coupled with the opportunity to study quasiparticle transport and relaxation processes in a nonequilibrium superconductor, prompted us to make measurements of the pair and quasiparticle electrochemical potentials in a superconductor held in a temperature gradient. It has been predicted[11] that in nonequilibrium situations in which the electron and hole branches of the quasiparticle excitation spectrum are unequally populated, the quasiparticles in a superconductor may be described by a different electrochemical potential from that which describes the pairs. This Letter reports our initial results showing the first experimental evidence for a pair-quasiparticle electrochemical potential difference in a superconductor in a temperature gradient.

A normal-metal tunnel junction and superconducting metal probe were placed in a nonequilibrium region of a thin-film superconductor. It has been shown[12] that this allows a direct measurement of the quasiparticle and pair electrochemical potentials to be made. A strip of 99.999%-purity Sn in the form of a "T" (Fig. 1) of width d ~2 mm, length ~2 cm, and thickness ~2000–4000 Å was evaporated onto a 1-mm-thick sapphire substrate and oxidized. A small rectangle (~2.5

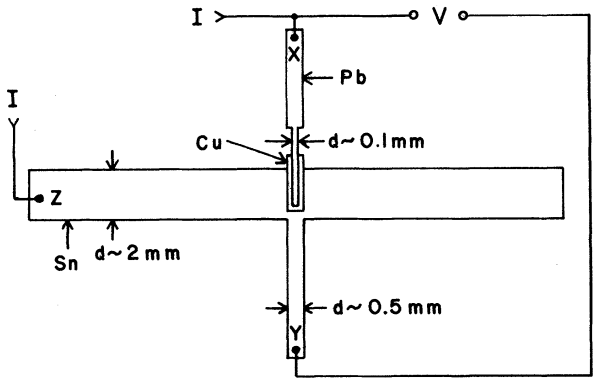

FIG. 1. Sample configuration. The Sn film is deposited on a sapphire substrate and oxidized, followed by the Cu electrode and Pb strip. 0.08-mm-diam Nb wires connected to a superconducting quantum interference device voltmeter allow the potential difference between points X and Y to be measured.