Temperature-Dependent Sinusoidal Magnetic Order in the Superconductor $HoMo_6Se_8$

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A magnetic phase transition (T_M =0.53 K) to a long-period (~ 10^2-Å) magnetic state has been observed via neutron scattering in the superconductor (T_c =5.6 K) $HoMo_6Se_8$. The characteristic wave vector q_c is *strongly temperature dependent* even though no higher-order satellites are observed. With use of a Ginzburg-Landau model it is found that the temperature dependence of q_c can be explained as due to a renormalization of the superconducting order parameter caused by the coupling to the local magnetization density.

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Ternary rare-earth superconductors which display a propensity for ferromagnetism have received considerable experimental as well as theoretical attention recently.[1] In the two compounds which have been studied previously in detail,[2,3] $ErRh_4B_4$ and $HoMo_6S_8$, the competition between these two cooperative phenomena was found to result in the development of a long-wavelength sinusoidal component to the magnetization at intermediate temperatures, followed at lower temperatures by a first-order transition to a normal conducting state with pure ferromagnetism. Although the detailed behavior of the two materials is different, the characteristic wave vector q_c in the modulated state was essentially temperature independent. In the present note we wish to report the discovery of a new "ferromagnetic" superconductor, $HoMo_6Se_8$. The wave vector q_c in the sinusoidal state is found to be strongly temperature dependent, with the full available holmium moment developing in this phase. Thus there is no genuine ($q=0$) ferromagnetic component (in zero applied field) at any temperature, and the superconductivity persists to low temperatures. We use a Ginzburg-Landau model to calculate the change in q_c associated with the temperature-dependent variation of the local (isotropic) magnetization density $m(q)$. We find that the London penetration depth has a marked dependence on m^2, which is responsible for the observed temperature variation of q_c.

The sample is a polycrystalline material[4] with a superconducting transition of 5.6 K as measured by ac susceptibility techniques. No sign of reentrant behavior (in zero field) was observed down to 40 mK. The neutron scattering experiments were carried out at the National Bureau of Standards research reactor. Field-dependent diffraction and inelastic scattering data were collected above the magnetic phase transition with use of conventional triple-axis spectrometers. Details of these measurements will be reported elsewhere: For present purposes we simply remark that the crystal-field magnetic ground state of the Ho^{3+} yields $\mu_z = 6\mu_B$/(formula unit) with the trigonal axis as the preferred direction. To study the low-temperature magnetic state the sample was mounted in a pumped ^3He cryostat. Conventional diffraction data were collected with a filtered incident neturon beam of wavelength 2.43 Å on a triple-axis spectrometer set for elastic scattering. Our best data, however, were obtained on the small-angle neutron spectrometer. This instrument employs a two-dimensional position-sensitive detector to collect data about the incident beam, and is ideally suited to study such long-wavelength magnetic states. Figure 1(a) shows the observed intensity as a function of wave vector $|\vec{q}|$ above and below the magnetic transition. These data have been radially averaged since in the absence of a magnetic field the intensity distribution of scattering is symmetric about the incident beam. A single resolution-limited Bragg peak is observed at $q_c = 0.062$ Å^{-1}, demonstrating that a tranvsersely polarized sinusoidal magnetic state has developed with a spatial periodicity (at low temperatures) of $2\pi/q_c = 101$ Å. No higher-order satellites (to within 1% of the primary modulation) were detected at any temperature. In addition we found no evidence for a ferromagnetic component to the magnetization.

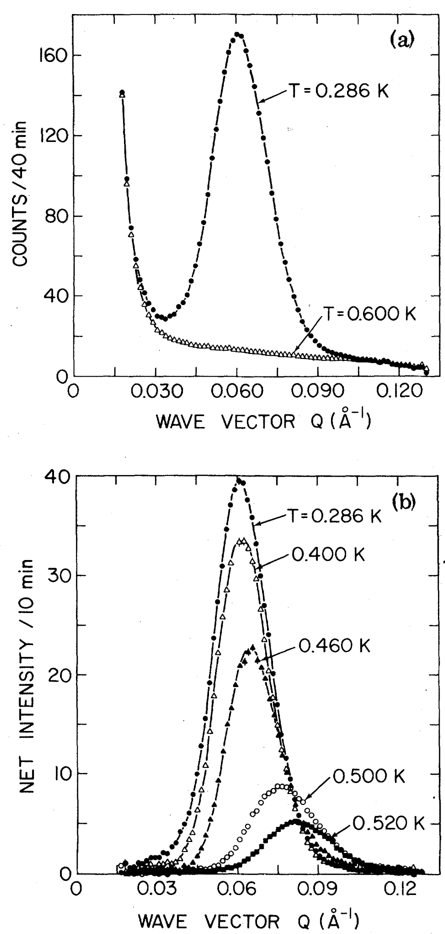

FIG. 1. (a) Observed intensity as a function of wave vector above and below the magnetic transition, indicating the development of a long-wavelength (101-Å) sinusoidal magnetic state in the superconducting phase. (b) Temperature dependence of the scattering at several temperatures. Note that the position of the peak shifts to larger q with increasing temperature.

With increasing temperature the magnetic intensity decreases and the characteristic wave vector increases as shown in Fig. 1(b). These data have been fitted by a Gaussian peak, and the results for the integrated intensity {proportional to $[m(q_c)]^2$} and q_c are shown in Fig. 2. The open circles represent temperatures for which the width of the scattering was substantially larger than instrumental resolution, so that these points are presumed to be above T_M. The width of the scatterining in fact increases very rapidly above T_M, and for $T > 0.56$ K there is no peak in the scattering at finite q. One interesting point to note is that these data were all taken on a warming cycle. All experimental indications are that the same curves are obtained on cooling, but the equilibrium times on cooling are much longer. For example, on warming from low temperatures to above T_M the system equilibrates in about 1 min, whereas for the reverse process the system takes over 50 h to (presumably) fully equilibrate. The slow response apparently originates primarily from q_c shifting to lower values, rather than from the strength of the scattering changing. We were not able to observe any intrinsic width

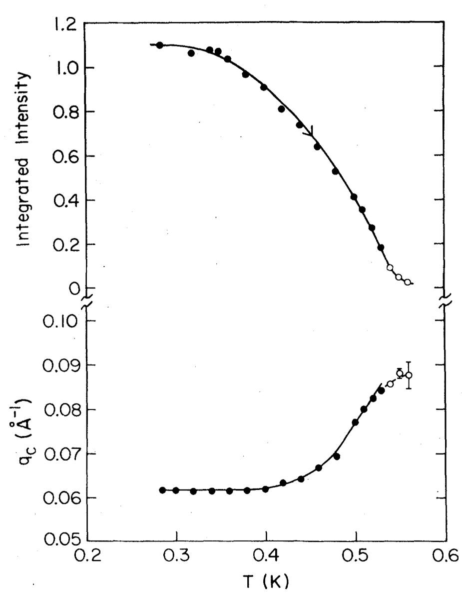

FIG. 2. Temperature dependence of the integrated intensity (which is proportional to the square of the ordered magnetic moment at q_c) and the characteristic wave vector q_c. The solid curve for q_c is given by the theory [Eq. (7)].

to the scattering during cooling.

There are four basic states which have been proposed as possibilities for these ferromagnetic superconductors: (i) the spontaneous vortex[5,6] lattice, (ii) the laminar state,[7] (iii) the linearly polarized state,[5] and (iv) the spiral state.[5,8,9] For (i) q_c has the opposite temperature dependence to that observed, while the laminar model was proposed to explain the behavior of $ErRh_4B_4$, where the ferromagnetic component of the magnetization coexists with the sinusoidal state. We do not believe that such a model is appropriate for $HoMo_6Se_8$. This then leaves the spiral state or the linearly polarized state. We emphasize that our diffraction data are consistent with either model; it is not possible to determine directly which state is realized experimentally from powder data alone. Energetically the linearly polarized state is stabilized if sufficient magnetic anisotropy is present, but how much anisotropy is sufficient for the present system of interest is not known. In the numerical calculations of Greenside, Blount, and Varma[5] the linearly polarized state has qualitatively the correct temperature dependence (due to the M^4 term in the free energy), but higher-order satellite peaks should be observed.[10] We present a simple analytical calculation, based on an assumed spiral state, which shows that the development of a local magnetization weakens the superconducting state (increasing the London penetration depth λ), thereby producing a decrease in q_c. We expect similar arguments to hold for the case of linear polarization.

In the case of a spiral state we can calculate the temperature dependence of q_c by the following method. First we note that spiral ordering increases the magnetic free energy by the gradient term

$$F_M = \tfrac{1}{2}C_1\, q^2 m^2, \tag{1}$$

where C_1 is a materials constant. The diamagnetic energy is

$$F_d = 2\pi\, m^2/(1+q^2\lambda^2) \approx 2\pi\, m^2/q^2\lambda^2, \tag{2}$$

where we assume that the periodicity of the spiral is large compared to the interspin spacing but small compared to the penetration depth λ. For simplicity we neglect the nonlocal correction[8] to λ. Minimization with respect to q^2 then gives

$$q_c^{\,4} = (1/C_1)4\pi/\lambda^2. \tag{3}$$

We now use the Ginzburg-Landau (GL) model to find the suppression of $|\psi|$, the superconducting order parameter, by $\boldsymbol{m}$. This in turn will increase λ and hence decrease q_c. The use of the GL model may be justified by the small electron mean free path in these systems. In any case it provides a phenomenology for describing the expected reduction of the superconducting response that results from the presence of the magnetic spiral state. In terms of $|\psi|^2$, F_d can be written as

$$F_d = \tfrac{1}{2}C_2(m^2/q_c^{\,2})|\psi|^2, \tag{4}$$

where we have used $C_2|\psi|^2 = 4\pi/\lambda^2$, with C_2 a constant of the superconductor. For $T \ll T_c$ the intrinsic condensation free energy is

$$F_{GL} = -\tfrac{1}{2}a|\psi|^2 + \tfrac{1}{4}b|\psi|^4 \tag{5}$$

with a and b both taken to be constant in this low-temperature regime. Minimization of Eqs. (4) and (5) with respect to $|\psi|^2$ and substitution into Eq. (3) gives the desired result

$$q_c^{\,4} = \frac{C_2}{C_1}\frac{a}{b}\left(1 - \frac{C_2}{a}\frac{m^2}{q_c^{\,2}}\right) = q_0^{\,4}\left(1 - C_3\frac{m^2}{q_c^{\,2}}\right) \tag{6}$$

with $C_3 \equiv C_2/a$. q_0 is the spiral wave vector for $m=0$.

Depending on the value of C_3, Eq. (6) can yield a marked temperature dependence to q_c. To leading order we can let $q_c = q_0$ in the last term in Eq. (6) to obtain

$$q_c = q_0(1 - \tfrac{1}{4}C_3\, m^2/q_0^{\,2}). \tag{7}$$

The solid curve in Fig. 2 is given by Eq. (7), which, however, takes it outside its range of validity. More generally we can transform Eq. (6) to the dimensionless form $y - y^3 = x$ by introducing the variables $y = (q_c/q_0)^2$ and $x = C_3 m^2/q_0^{\,2}$. As the temperature decreases below T_M, x increases, reducing y below its initial value of 1.0 as shown in Fig. 3. At $y = 1/\sqrt{3} = 0.577$, $x = 2/3\sqrt{3} = 0.385$. The system will be unable to follow a further increase in x and the coexistence of the spiral state with superconductivity will be destroyed in a first-order transition. The dashed curve thus indicates that smaller values of y are not in a physically realizable regime in the model. For $HoMo_6Se_8$, y falls below this critical value as m^2 becomes large as shown by the dotted curve (with $C_3 = 0.0053$ and $q_0 = 0.085$ Å^{-1}). Thus the good agreement with the linearized theory shown in Fig. 2 is fortuitous at large m; the full theory is able to account for the observations only up to $m^2 \sim \tfrac{1}{2}$. At larger m^2 the theory pre-

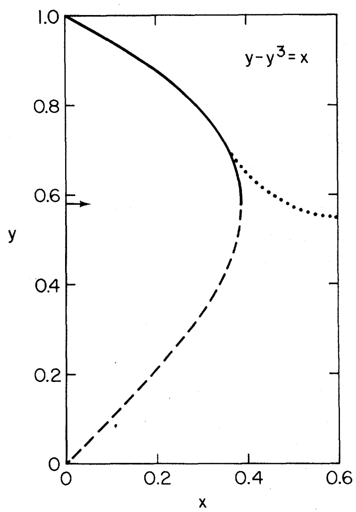

FIG. 3. Predicted dependence of $y=(q_c/q_0)^2$ on $x=C_3(m/q_0)^2$, where q_0 is the wave vector at the transition [see Eq. (6)]. The dashed curve indicates that this region is physically inaccessible. The dotted curve shows the experimental results for $HoMo_6Se_8$.

dicts that the variation in q_c becomes more rapid, eventually becoming unstable, whereas the observations indicate that q_c saturates (if equilibrium actually has been achieved). Thus the theory may need to be refined in the regime where the amplitudes are large.

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