[4]C. L. Allyn, T. Gustafsson, and E. W. Plummer, to be published.

[5]P. M. Williams, P. Butcher, J. Wood, and K. Jacobi, Phys. Rev. B 14, 3215 (1976).

[6]G. Broden and T. N. Rhodin, Solid State Commun. 18, 105 (1976).

[7]S. P. Weeks, E. W. Plummer, and T. Gustafsson, in Proceedings of the Conference on Photoemission from Surfaces, Noordwijk, Netherlands, September, 1976 (to be published).

[8]D. E. Eastman and J. E. Demuth, Jpn. J. Appl. Phys., Suppl. 2, Pt. 2, 827 (1974).

[9]J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. 31, 540 (1973).

[10]M. A. Van Hove and S. Y. Tong, J. Vac. Sci. Technol.

12, 230 (1975).

[11]J. W. Davenport, Phys. Rev. Lett. 36, 945 (1976).

[12]K. Jacobi, M. Scheffler, K. Kambe, and F. Forstmann, to be published.

[13]J. Hermanson, Solid State Commun. 22, 9 (1977).

[14]C. H. Li, A. R. Lubinsky, and S. Y. Tong, to be published.

[15]S. Y. Tong and M. A. Van Hove, Solid State Commun. 19, 543 (1976).

[16]J. B. Pendry, Phys. Rev. Lett. 27, 856 (1971).

[17]J. W. Gadzuk, Phys. Rev. B 10, 5030 (1974).

[18]A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974).

[19]G. E. Becker and H. D. Hagstrum, Surf. Sci. 30, 505 (1972).

[20]E. W. Plummer and T. Gustafsson, to be published.

Superhyperfine Splitting and the Dynamic Jahn-Teller Effect for the Ferrous Ion in KMgF₃

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Superhyperfine structure for the ferrous ion in KMgF₃ has been observed. A Jahn-Teller energy of 108 cm^{-1} is determined from the magnitude of the g factor as an upper limit, ignoring covalent contributions. The temperature dependence of the width of the normal electronic Zeeman transitions indicates an excited level at 94 cm^{-1} above the ground state. This energy-level separation agrees with the calculated position of the lowest spin-orbit–split excited state reduced by the dynamic Jahn-Teller effect.

The superhyperfine (SHF) spectrum has been observed for the ferrous ion as a dilute substitutional impurity in KMgF₃. The interaction of the electron spin of the ferrous ion with the nuclear magnetic fields of the six nearest-neighbor fluorine nuclear spins $(I = \frac{1}{2})$ leads to a splitting of the electronic Zeeman transition. Although it is possible to use the SHF spectra to obtain information concerning the interaction of the electron and its nearest neighbors, we will emphasize in the following the application of the SHF spectra to provide insight into the possibility of a dynamic Jahn-Teller effect (DJTE).[1] The narrowness of the SHF lines facilitates this approach. The electronic ground state of the ferrous ion is a triplet in an octahedral crystal field. Spin transitions between all the members of the Zeeman-split triplet result in two distinctive features in the EPR spectra. Firstly, there is a spin transition between the $m_s = 0$ and $m_s = \pm 1$ Zeeman-split ($\Delta m = \pm 1$) triplet. This transition is broad due to its sensitivity to linear strains in the lattice. There is a second transition (normally forbidden in a strictly cubic environment) between the $m_s = \pm 1$ members of the Zeeman-split triplet ($\Delta m = 2$) which occurs at approximately half the magnetic field of the "$\Delta m = 1$" transition. This transition

is typically narrower than the $\Delta m = 1$ since it is not sensitive to all linear lattice distortions but only to those with orthorhombic symmetry. These two features of the ferrous EPR spectra have been considered in detail for a MgO host lattice[2] where no superhyperfine structure is observed. The SHF spectrum in Fig. 1 shows this so-called $\Delta m = 2$ half-field line and is only observed in specimens with low impurity concentrations[3] (Fe²⁺ < 30 ppm). Higher impurity concentrations increase the strain broadening to the point that SHF structure is no longer discernible.

The SHF spectrum for the ferrous ion displays the characteristic splitting and anisotropy due to the interaction of the electron with six nearest-neighbor nuclear spins. The SHF splitting for the ferrous ion in KMgF₃ show in Fig. 1 exhibits a seven-line splitting of the electronic Zeeman transition which is due to the interaction of the electron with the six equivalent octahedrally coordinated fluorine nuclei $(I = \frac{1}{2})$ when the field is along the [111] direction. The relative intensity of the SHF lines agrees with the ratio expected for six nearest-neighbor fluorine atoms. The spectra for various other magnetic-field directions are also consistent with the interpretation that the spectra are due to SHF interaction with
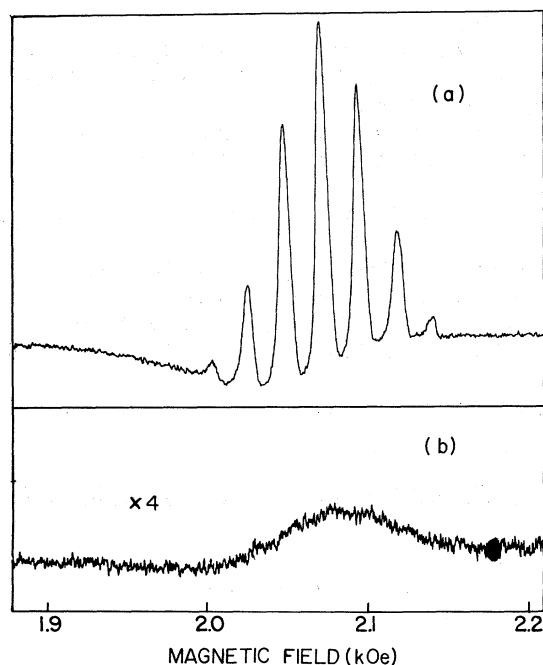
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FIG. 1. The derivative spectra for the $\Delta m = 2$ electronic transition. (a) The superhyperfine structure is observed at 4.2°K when the field is along the [111] direction. (b) At higher temperatures (18°K) the details of the superhyperfine structure disappear and only a smaller broadened feature remains. The measurements are made with a 20-GHz spectrometer.
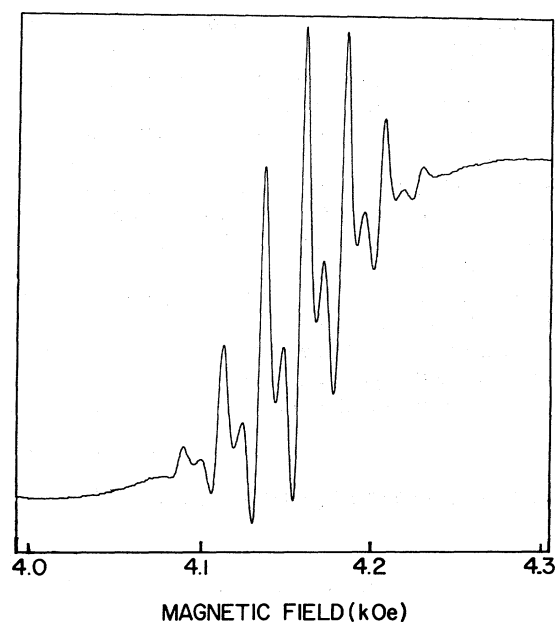

FIG. 2. The superhyperfine structure for the double quantum transition appearing at the center of the $\Delta m = 1$ strain-broadened line. Between the seven-line SHF spectrum ($\vec{H} \parallel [111]$) is a six-line "forbidden transition" spectrum. The double quantum transition intensity is enhanced by using higher power levels. The temperature is 4.2°K and the measurement frequency is 20 GHz.

the fluorine nuclear spin. There are details of the spectra which are as yet unexplained, such as the shape of the lines which deviate significantly from what is expected for a simple Lorentzian or Gaussian absorption derivative. These lines may contain unresolved contributions due to so-called "forbidden transitions" which are resolved in the double quantum spectrum discussed below. There is also a low-level undulation of the background level which appears to be due to ferrous ions in more strongly strained sites. The effective g factor for these sites is larger than the SHF value, indicating a zero-magnetic-field splitting from a lattice strain distribution which is not centered at zero strain. The ions contributing to the SHF spectra are expected to be at very low-strain sites while the smaller background comes from a more highly strained region in the crystal. The SHF spectrum rapidly broadens as the temperature increases, and any distinctive features disappear above 17°K [Fig. 1(b)].

At low power levels the only SHF spectrum observed is for the $\Delta m = 2$ transition, but as the

power level is increased a second set of superhyperfine lines appears at the center of the $\Delta m = 1$ transition (Fig. 2). A feature similar to this has been observed for various transition-metal ions (Ni^{2+}, Co^{+1}, and Fe^{2+}) in MgO[4] and has been shown to be due to a double quantum transition between the $m_s = +1$ and $m_s = -1$ levels. The appearance of the SHF spectra at this position for a $KMgF_3$ host is direct evidence that this is also a double quantum transition. As seen in Fig. 2, not only does the seven-line spectrum of the normal SHF structure appear, but also a six-line spectrum resulting from so-called forbidden transitions. These double quantum features and the interpretation of the SHF structure in terms of neighboring fluorine interactions will be considered elsewhere, and we will now return to our discussion of the relevance of the SHF structure to the DJTE.

The change in the crystal-field parameters due to DJTE has been formulated by Ham[5] as reduction parameters. This approach has been successfully applied by Ham, Schwarz, and O'Brien[1] to the ferrous ion in MgO. For the ferrous ion in $KMgF_3$, the narrow-line superhyperfine spectrum provides a more accurate empirical deter-

mination of the g factor (3.440 ± 0.005) than was previously possible from strain-broadened features. The SHF spectrum is quite sensitive to the local geometry and motion, which in turn should reflect the effect of any dynamic Jahn-Teller parameters. In this investigation no significant static Jahn-Teller distortion is detected even at low temperatures $(2.5°K)$ where the g factor is observed to be isotropic to 1 part in 2000.

The magnitude of the g factor for $MgO:Fe^{2+}$ is found to be significantly lower than the computed crystal-field value $(3.428$ vs $\sim 3.5)$. This difference has been attributed to reduction of the spin-orbit interaction by the DJTE. Previous reports of the g factor for the ferrous ion in $KMgF_3$ (which failed to see SHF interactions—possibly a result of the strain broadening due to a higher impurity concentration) have indicated an even more substantially reduced g factor,[6] and an analogy made with the results in MgO has suggested an even stronger DJTE in $KMgF_3$ than in MgO. The g factor determined in this investigation using crystals which exhibit SHF structure is not in agreement with these previous observations but, in fact, yields a magnitude closer to the crystal-field value $(3.44$ vs $\sim 3.5)$ than in MgO. The difference in the values obtained in this investigation and the theoretical crystal-field value could be due to both covalency and the DJTE. In the following we will ignore covalency to determine an upper bound on the magnitude of the DJTE. If we analyze the g-factor shift using the results of Ham, Schwarz, and O'Brien,[5] we obtain an upper bound on the Jahn-Teller energy (E_{JT}) of 108 cm^{-1}, indicating a weaker Jahn-Teller effect in $KMgF_3$ than in MgO. The Jahn-Teller energy is derived using a range of local-mode frequencies of $300-400$ cm^{-1} and assuming coupling only to the T_{2g} distortions. This latter assumption results from features observed in acoustic relaxation measurements on the same samples and will be treated in detail elsewhere. The same conclusion has been reached by Regnard, Chappert, and Ribeyron[7] from Mössbauer measurements.

The lowest excited states of the ferrous ion are split from the triplet ground state by spin-orbit interactions. Crystal-field theory predicts a separation of ~ 190 cm^{-1} but the actual magnitude of the spin-orbit splitting can be reduced by the DJTE. This spin-orbit splitting can be obtained theoretically from the calculations of Ham, Schwarz, and O'Brien using the JT energy previously derived from the measured g factor. A reduced spin-orbit separation of 97 to 126 cm^{-1}
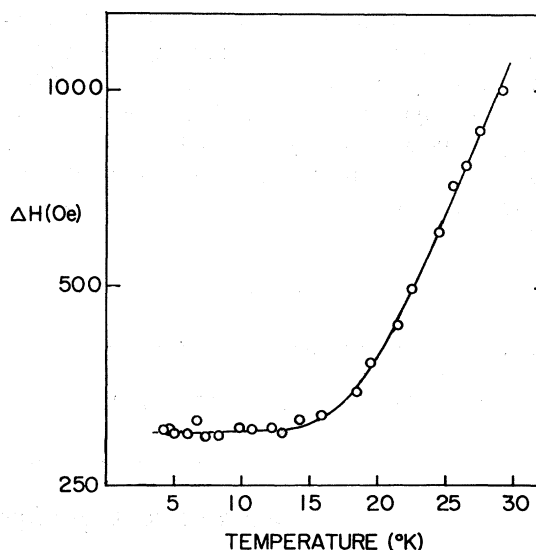

FIG. 3. The width (ΔH) of the $\Delta m = 1$ transition as a function of temperature. The curve corresponds to an expression containing an inhomogenous-broadening term and an Orbach term $\Delta H = \Delta H_0 + \Delta H \exp(-s/kT)$, where $\Delta H_0 = 300$ G and $s = 94$ cm^{-1}.

results from this calculation using the local-mode frequencies indicated previously. A feature of the EPR spectra which suggests an energy level in this region is the temperature dependence of the width of the $\Delta m = 1$ transition. As seen in Fig. 3, at low temperature the width of the $\Delta m = 1$ peak is constant and may be broadened due to strains resulting from lattice imperfections. The width increases above about $16°$ and can be fitted by an Orbach process (indirect transitions) with an energy of 94 cm^{-1}. This value is slightly less than the DJTE-reduced values derived above, although the small difference may well be rationalized by the introduction of some covalency, which would further reduce the theoretical values. The energy level determined from measurement of the $\Delta m = 1$ width appears to be the first excited state of the ferrous ion 94 cm^{-1} above the ground state. This value contradicts conclusions determined from infrared absorption measurements where features have been seen at this energy but, because of an unusual concentration dependence[8] or magnetic-field behavior, have been ruled out as an electronic state.[9] Our result does agree more closely with some earlier infrared measurements.[10]

The ferrous ion in $KMgF_3$ exhibits behavior similar to the ferrous ion in MgO in many respects, although the DJTE is slightly reduced. The g is closer to the crystal-field value in $KMgF_3$ as de-

termined from the SHF spectra. The first excited state is observed at 94 cm^{-1} which agrees with the calculated position due to spin-orbit splitting reduced by a dynamic Jahn-Teller effect.

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[1]F. Ham, W. Schwarz, and M. O'Brien, Phys. Rev. 185, 548 (1969).

[2]D. McMahon, Phys. Rev. 134, A128 (1964).

[3]Grown in the Crystal Growth Facility, Oklahoma State University.

[4]J. Orton, P. Auzins, and J. Wertz, Phys. Rev. Lett. 4, 128 (1960).

[5]F. Ham, Phys. Rev. 138, A1727 (1965).

[6]J. Vallin and W. Piper, Solid State Commun. 9, 823 (1971).

[7]J. Regnard, J. Chappert, and A. Ribeyron, Solid State Commun. 15, 1539 (1974).

[8]T. Ray, J. Regnard, J. Laurant, and A. Ribeyron, Solid State Commun. 3, 1959 (1973).

[9]A. Hjortsberg, B. Nygren, and J. Vallin, Solid State Commun. 16, 105 (1975).

[10]R. Frankel, C. Abeledo, and A. Misetich, Solid State Commun. 12, 1147 (1973).

Quasiatomic Auger Spectra in Narrow-Band Metals

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In this Letter it is shown that quasiatomiclike Auger spectra in narrow-band metals are a direct result of electron correlation effects. It is shown that if the "on-site" Coulomb interaction is much larger than the one-electron–band width, the Auger spectrum consists of an intense narrow atomiclike peak together with a weak broad bandlike peak at higher kinetic energy. On the other hand, if the Coulomb interaction is small the Auger spectrum will resemble the convolution of the band density of states convoluted with itself.

Some time ago it was proposed by Lander[1] that valence-band density-of-states information could be obtained from Auger spectra involving valence-band electrons. Using a one-electron–like picture and neglecting matrix-elements effects, Lander argued that the Auger line shape should be the valence-band density of states convoluted with itself. In numerous investigations, however, atomiclike Auger spectra have been found with hardly any visible band-structure effects. These atomiclike Auger spectra are common for narrow d bands whereas the spectra in which band-structure effects are found usually involve broad s-p bands. In recent investigations[2,3] of some $3d$-series metals (Cu, Zn, Ga, Ge, As, and Se) it has been shown that all of the essential features of the $L_{23}M_{45}M_{45}$ Auger spectra can be explained in terms of an atomic model. The relative intensities of the final-state two-hole terms are in good agreement with atomic calculations, the term splittings are close to those calculated for the free atom, and even the satellite structure in Cu and Zn as well as the anomalous intensity ratio of the $L_2M_{45}M_{45}$ to the $L_3M_{45}M_{45}$ spectra are

explained very well by use of an atomic model and a Coster-Kronig transition preceding the Auger transition.[4] The only substantial difference between the Auger spectrum in the metal and that in the free atom is a shift of the spectrum. This shift is due to extra atomic relaxation or polarization effects which effectively reduce the Coulomb interaction between the two holes in the final state. This polarization reduction of the two-hole Coulomb interaction is expected because of the highly polarizable medium in which the doubly ionized "atom" is situated.

This quasiatomiclike behavior is at first glance unexpected and has, to our knowledge, not been explained. Feibelmann, McGuire, and Pandey[5] have shown that matrix-element effects are important for the L_{23} VV Auger lines of Si. However this cannot explain the atomiclike spectra of the $3d$ and $4d$ metals because here the individual final-state terms are clearly seen with widths much less than the bandwidth.

In this Letter I give a simple physical picture based on well-known electron correlation effects and an exactly solvable model which describes